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About this Journal

KONA Powder and Particle Journal is a refereed scientific journal that publishes articles in the field of powder and particle science and technology annually since 1983. This journal is distributed free of charge to the members of scientific communities and universities and research libraries throughout the world by the Hosokawa Powder Technology Foundation (www.kona.or.jp/) established by Mr. Masuo Hosokawa in 1991.

The Chinese character "粉" in the cover is pronounced as "KONA" in Japanese, and means "Powder", which was hand-written by Mr. Eiichi Hosokawa, the founder of the Hosokawa Micron Corporation (www.hosokawamicron. co.jp/en/global.html).

About the Cover

Intermetallic compounds are homogeneously ordered, solidstate compounds of two or more metallic elements. They have distinctive electronic structures which are completely different from those of mixed metals. This characteristic leads to unique electrical, thermal, magnetic, semiconducting, and chemical properties, which in the end, opens the door to a wide range of applications. Their highly ordered atomic structure, even at the surface, is favorable for solidstate catalysis. Studies related to the catalytic application of intermetallic compounds are usually focused on the binary systems. Recently, ternary metallic element systems in Heusler Alloys demonstrate promising features for catalysis because of their novel fundamental catalytic properties. Review of this topic is discussed on pp. 110-121.



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Publication Office

Hosokawa Powder Technology Foundation (www.kona.or.jp) (in the headquarters building of Hosokawa Micron Corporation) 1-9, Shodaitajika, Hirakata-shi, Osaka 573-1132, Japan E-mail: contact_zainq@hmc.hosokawa.com

Printing Office: Nakanishi Printing Co., Ltd., Japan

Publication Date: 10 January 2021



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Reviewer Appreciation

Kikuo Okuyama, Editor-in-Chief

Hiroshima University, Japan



I would like to express my sincere gratitude to the reviewers for their hard work for the KONA Powder and Particle Journal. Thanks to the generous contributions of the volunteer reviewers as well as the interest of researchers in our journal, the number of submission to this journal is increasing after the registration on the major international journal platforms and its level is further improving. Thanks to their strong support and effort, I am pleased to inform that 2019 Impact Factor (JCR) of the KONA Powder and Particle Journal is increased to 2.326, with the CiteScore 2019 of 4.2. Because of the limited space of this annual journal, the number of papers published here is regrettably rather restricted. Therefore only the papers of good quality will be selected for the journal and further improved and refined by the reviewing process.

The editorial team of the KONA Journal would like to take this opportunity to gratefully acknowledge the reviewers here and deeply appreciate their valuable time and professional contributions to the KONA Journal. We apologize to any reviewers who may have been inadvertently omitted from this list. We are sincerely grateful to all who have been of any assistance to the publication of this journal.

BOURGEOIS, Florent COPPENS, Marc-Olivier GRADOŃ, Leon HICKEY, Anthony KAGE, Hiroyuki KANO, Junya KWADE, Arno

Likuo Okujoma

October 2020

MAKINO, Hisao MATSUYAMA, Tatsushi MOUDGIL, Brij OTANI, Yoshio PURI, Virendra RASTEIRO, Maria da Graça SAITO, Fumio

SAKKA, Yoshio TANAKA, Toshitsugu TOKORO, Chiharu YAMAMOTO, Hiromitsu YOKOYAMA, Toyokazu

Editor's Preface

Brij M. Moudgil Chairman of American Editorial Board University of Florida, USA



As Chair of the American Editorial Board, I am pleased to introduce the KONA Powder & Particle Journal No. 38. In continuation of the past tradition, this issue presents high quality review articles and original research papers. The journal is reaching out to an ever-expanding cadre of researchers as illustrated by the diversity of disciplines represented by the authors of the articles. KONA continues to serve academic and industry researchers from physical sciences to engineering and beyond. Furthermore, increased recognition of KONA as a high quality journal is a testimonial that recent changes in the review process, format and accessibility are moving in the right direction.

Powder technology continues to be recognized as an important business with tremendous global opportunity. Technological advances in the field are demanding more complex particle design and powder properties. An example would be advanced sensor technologies that require multifunctional particle platforms with high precision to meet lower and lower detection limits with high reliability. If designing such particles is a challenge, it is even a bigger challenge to manufacture them on large scale. Most often large-scale production of precision particles remains an empirical exercise. Hopefully, advances in simulation and modelling, which is fast approaching practical scale systems, would lead to new scale-up paradigms.

With diversification of the disciplinary base of particle and powder researchers, it is critical for KONA to reach out to young researchers with different professional backgrounds, and also to publish more state-of-the-art review articles – a hallmark tradition of KONA over the several decades. In this regard, KONA may invite academic and industry researchers, especially those who are at the forefront of scientific and technological advances, to publish comprehensive review articles in the journal. These articles will further reinforce KONA's position as a reliable source for powder and particle related information. Additionally, KONA may also invite young researchers who are within a few years of receiving their advanced degrees to publish overview articles closely related to their particle and powder related research endeavors.

While many institutions of higher learning were already offering select degree programs and courses online, the sudden emergence of the pandemic compelled delivery of almost all courses online, practically overnight. As challenging as it has been for instructors to suddenly shift to the online mode, it is equally if not more challenging for the students to be thrust into this new learning environment. That said, it is not all doom and gloom! This unique situation certainly provides an opportunity to rejuvenate and redesign the course materials in a way that is meaningful to the students without losing the rigor of learning the subject matter. Simply repackaging the old material into digital delivery mode will not do. We can expect that education's new business model will drive the online delivery mode for most courses, with in-person learning confined to only a handful of courses.

However, serious challenges exist with online learning platforms, accessibility being a critical one. Many university students, even in developed countries, lack the internet bandwidth and other resources which their peers may





have. Another serious challenge is almost assured disruptions due to future pandemics and climate change-related disasters. Mitigating such risks requires the design of flexible curriculum for completing coursework and degree programs on the academic front.

As there is a paradigm shift in knowledge creation and delivery from traditionally strong powder and particle research centers and institutes to individuals and smaller group efforts, acquisition of deep understanding of complex systems may be at risk. However, this challenge may be overcome to an extent with the availability of more powerful and robust search engines and other IT mediated modalities. Such resources can hopefully enhance the existing curriculum and enable development of new teaching modes to train the next generation of powder and particle technology professionals.

Overall, I believe that harnessing the application of AI/ML and advanced computational tools has the potential of revitalizing both the instruction and application of particle and powder technology.

I invite you to explore and enjoy this issue of KONA. Let us continue to work together and make KONA ever more relevant and reliable as a source of particle and powder technology knowledge and know-how.

Bizi M. Montgil

Brij M. Moudgil Chair, American Editorial Board September 23, 2020

From Quasi-static to Intermediate Regimes in Shear Cell Devices: Theory and Characterisation[†]

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Abstract

The design of new technology for processing and manufacturing particulate products requires understanding granular rheology over a broad range of conditions. Powders display a complex behaviour due to their ability to rearrange under stress, and as a result, granular flow is generally classified into three flow regimes, namely a quasi-static regime dominated by frictional contacts, an inertial regime dominated by collisional and kinematic stresses and an intermediate regime where the three sources of stress are important to establish a stress-strain rate relationship. Characterisation of the flowability is generally restricted to the flow initiation in quasi-static regime, even if, transition into inertial conditions is very common in practical applications involving the control of dense flows, such as powder handling, particle formation processes or additive manufacturing. This work presents a critical review of available techniques to characterise the departure from the quasi-static regime into an intermediate flow. We revise the application of shear cells and present different strategies to modify classic devices with external actuation, such as aeration, to operate at higher inertial numbers. We pay particular attention to innovative designs using aerated Couette flow configurations, highlight the complexity in the standardisation and the challenges in advancing towards a universal model.

Keywords: granular rheology, aeration, Couette flow, shear cell, flowability, characterisation

1. Introduction

A universal description of granular rheology is both a fundamental and industrial challenge. Complex granular flows are a feature of natural phenomena such as landlines, rock slumping and sand dunes as well as in industrial processes such as granulation, milling and fluidisation. Powders, particulates and gravels are often the scaffolds where complex biological, physical or chemical processes take place, and underpin disciplines spanning from geomechanics (Wheeler and Sivakumar, 1995) to volcanology (Petford, 2003), including the study of dense flows such as soil (Pastor et al., 2009) and sediments (Baumgarten and Kamrin, 2019). Powders constitute a large proportion of raw materials, intermediates, products and waste in the primary and the process industry, and the energy, environmental and manufacturing sectors. Pigments, ceramics, petrochemicals, plastics, bulk and fine chemicals or fast-moving consumer goods are only some examples.

Although powders have been studied for a century, our

understanding of granular flow is far from that of simple fluids or solids. Individual particle interactions lead to a collective behaviour that makes powders restructure under stress. If compressed, they respond as an elastic solid; but when diluted, they behave like a fluid (Jaeger et al., 1996). Solid-like behaviour steams from the formation of a network of contacts, the so-called force chains, that transmit the stress. In addition to these frictional contacts, particle interactions are altered by a broad range of forces from electrostatics and van der Walls to liquid and solid bridges (Hartmann and Palzer, 2011). The dissipation and storage of energy in the force chains allow a bed of particles to remain static and fail only under the application of a given stress. But as the flow becomes more rapid, force chains reorganise and break. When the deformation (strain rate) is faster than the ability for the force chains to recombine, they can no longer transmit and absorb stress, and the material restructures creating a fluid-like relation between the applied stress and strain rate (Campbell, 2006). As a powder dilates, the free space between individual grains increases and the transport of momentum becomes dominated by instantaneous collisions of nearby particles. For sufficiently diluted cases, the flow displays a gas-like behaviour where collisions are rare, and the motion of each grain is uncorrelated from its neighbours.

The changes in the stress-strain rate relation are related



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Received 6 July 2020; Accepted 21 August 2020 J-STAGE Advance published online 26 September 2020

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to how grains reorganise and how the local force network responds to structural properties such as particle concentration, size and shape. Understanding the transition between different flow behaviours is crucial to develop new technologies because solid operations span a wide range of particle concentration, consolidation stress and shear rate. The design of a powder processing plant involves flows spanning from dilute inertial systems, such as in pneumatic transport, to slow frictional flows in storage, packaging, tabletting, or agglomeration devices like roller compaction (Wu et al., 2010) or twin-screw granulation (Dhenge et al., 2013). Operations such agglomeration in high shear mixers (Knight et al., 2001) or fluidised bed granulators are designed to work under dense conditions and display local transitions between solid and liquid-like behaviour (Mort, 2009). In many cases, this happens in an uncontrolled way through the agglomeration and deposition of cohesive powders in multiphase reactors, heat exchangers (Diaz-Bejarano et al., 2017) or spray dryers (Francia et al., 2015).

No universal framework unifies the description of granular rheology, and therefore, industry relies heavily on empirical characterisation to classify the flowability of powders. The earliest attempts used scores based on flow tests such as the Carr (Carr, 1965), and Hausner (Hausner, 1967) ratios, or more recently the Taylor composite index (Taylor et al., 2000). The use of properties such as unconfined yield strength or tensile strength is also common, but the flowability function, FF, defined as the ratio of the major principal stress to the unconfined yield stress in the powder, is perhaps the most utilised metric to characterise powder flow (Hassanpour et al., 2019). The characterisation is typically limited to identify a flow threshold, that is, the stress required to initiate flow, and it rarely extends into studying the dynamic flow properties. The work of GDR Midi (Midi, 2004) describes in detail the characteristics of granular flows in six typical experimental configurations. Those where the stress is imposed, such as heaps, drums, annular flows and inclined planes display a hysteresis in the yield stress. A given stress is required to establish a dense flow, but much smaller stresses are needed to maintain it. The yield point itself depends not only the particle properties but also on the stress history of the sample. All typical flow configurations (Fig. 1) show a complex flow pattern where dense areas governed by enduring frictional contacts interplay with other more dilute ones driven by instantaneous particle collisions. Ultimately, all develop complex velocity distributions varying from a localised shear band in the confined systems to linear and exponential decays in free surface flows. Given that the behaviour of a powder varies drastically from one to another, it is required to carry our several static and dynamic tests to properly evaluate the flowability as close as possible to the desired design conditions (Krantz et al., 2009).

Most available tests focused on the flow initiation and



Fig. 1 Typical configurations to study granular flow: (a) Couette (b) rotating drums and flows in (c) chutes e.g. parallel planes, inclined, vertical (d) and heaps.

suffer from two limitations: transportability and universality. The discrepancies observed across different devices (Koynov et al., 2015) are a reflection of an overly simplified description of the system and inconsistencies in the experimental procedures. The effect of the stress history of a sample is well-known (Swize et al., 2019), but without a common way to condition the powder, it is challenging to draw any direct comparison between different tests and samples. The measurements are also not universal. The most established techniques are shear cells limited to a quasi-static flow (Schwedes, 2003). It is a consequence of the practical difficulty in studying inertial systems and the historical need to inform the design of silos. Although it is key to understand a dense granular flow (Sundaresan, 2001), the characterisation of dynamic properties is still far from the same level of detail.

Recent works have summarised the scope of the techniques available today to study the flowability of powders (Ogata, 2019), and the challenges involved in developing reliable dynamic tests for the study of caking and cohesive materials (Ghadiri et al., 2020). They discuss in detail the effects of properties such as size and shape, cohesion and how the interstitial fluid and the applied stress affect the flowability. Here, we will focus on the latter and specifically discuss the characterisation of the transition between two extreme flow regimes, namely solid-like and fluid-like flow, in a shear device. We provide an overview of the design and application of classic units and discuss the strategies to develop similar tests in modified devices that can cover a broader range of shear and consolidation stresses. The manuscript is organised as follows: Section 2 introduces the granular flow regimes and presents a brief overview of the mathematical modelling of granular flows. A brief review of the characterisation of the flow threshold,



including a summary of shear cells is given in **Section 3**. The strategies to re-design the conventional shear devices to experimentally capture the transition from solid-like to fluid-like behaviour using an external actuation are discussed in **Section 4**, followed by conclusions and suggestions for future work.

2. Rheology of granular flows

2.1 Flow regimes

The flow behaviour of granular material depends on the applied stress, particle concentration and the effects of the interstitial fluid. If the concentration is high or close to the maximum packing, the material exhibits solid-like behaviour where stresses are transferred with frictional contacts between grains and slip layers move relative to each other along the applied shear. In this regime, namely frictional or "quasi-static" regime (Fig. 2a), the contacts between grains have a long duration, and deformation of the grain layers occurs very slowly (Campbell, 2002). Due to a highly dense concentration of particles, there is no much free space for the interstitial fluid, and its effects are usually neglected. In the quasi-static regime, flow is often studied by using soil mechanics principles or more specifically, plasticity models detailed in the next section. On the contrary, when the applied stress or the external energy transfer is sufficiently high, the particles have enough inertia to leave their layers and flow more independently. This flow regime is referred to as "rapid flow" or "inertial" regime. Here the transport processes are considered governed by binary instantaneous particle-particle collisions and random motions (Fig. 2a). With an analogy with the kinetic theory of monatomic gases, the concepts of the socalled granular thermal energy or "granular temperature" and the random fluctuating kinetic energy of particles are introduced in the framework of continuum modelling. The main formal differences between inertial granular flows and molecular gases are the finite size of particles and the non-equilibrium behaviour. The particle-particle collisions are dissipative; therefore, the fluctuating kinetic energy of the particles is dissipated to thermodynamic heat. The applied shear generates fluctuating kinetic energy through collisional and kinematic stresses (Fig. 2b). For a collisional stress, any collision between particles moving at their mean velocity in a simple shear will enhance random motion and lead to a velocity fluctuation quantified in the granular temperature. However, for a kinematic stress, the motion of a particle parallel to a velocity gradient generates a random velocity along its path (Fig. 2bii) and a source of anisotropy in the fluctuating kinetic energy.

For inertial granular flows with low and moderate solid concentrations, the interstices between the particles are



Fig. 2 Granular rheology. Sources of (a) stresses (kinematic, collisional and frictional) in a quasi-static, an intermediate and an inertial flow regime for varying inertial number *I*, normal stress σ , shear rate $\dot{\gamma}$ and solid fraction ε_s (b) generation of fluctuating kinetic energy in kinematic and collisional mechanisms.

far larger than in the quasi-static regime. These spaces are filled with fluid, and the granular material is then described as a multiphase flow, referred to as a gas-solid suspension, where the fluid-particle interactions become significant on the momentum transfer between phases. Many advanced formalisms, however, focus on a collision-dominated regime and disregard the effect of interstitial fluid. Other effects typical of real-life scenarios like shape, polydispersity or interparticle forces are often excluded from a continuum formulation. In the extreme of a very dilute (kinematic) gas-solid suspension, particle-particle collisions never happen, and the solid phase momentum simply diffuses as the particles travel through the medium (Tsao and Koch, 1995). Their motion is mainly driven by the carrier fluid and the interstitial fluid contributes to the particle stresses with a covariance between particle and fluid fluctuations (Koch, 1990). Gas-solid suspensions are not within the scope of this review, and comprehensive discussions are available elsewhere (Fan and Zhu, 2005).

In between these two extreme regimes, there exists an intermediate regime with a characteristic particle contact time larger than the instantaneous collision time but lower than an enduring contact. It lies between the quasi-static state dominated by frictional forces and the inertial state dominated by collisional stresses, and therefore, affected by both. This work concerns with the experimental characterisation of such a system. From a phenomenological modelling view, the transition between regimes can be characterised by the inertial number, *I*, given by Jop et al. (2006), as a scaled shear rate quantifying the interplay of the consolidation and the shear stress acting on a particle:

$$I = \frac{\dot{\gamma} d}{\sqrt{\sigma / \rho}} \tag{1}$$

$$I = \frac{t_{\sigma}}{t_{\gamma}} = \frac{\sqrt{\sigma / \rho} / d}{1 / \dot{\gamma}}$$
(2)

I can be interpreted as the ratio between the time scale associated with the consolidation and the time scale of the strain as given in Eq. (2). As discussed in GDR Midi (Midi, 2004), the shear or deformation time scale, t_{y} , can be though to represent the time needed to create a deformation by moving the top layer applying a shear stress, τ . The confinement scale, t_{σ} , represents the time needed to reorganise this structure pushing the top layer to its lower position and creating a packed system. Fig. 3 illustrates the concept shearing a granular layer. If the confinement is very quick compared to the deformation, the system will remain structured at a high concentration. On the contrary, if σ is not high enough to preserve the confinement, the system dilates. In the limit of $I \rightarrow 0$ a powder remains in a quasi-static state and the system behaviour is independent of the shear rate and purely controlled by a constant ratio between the shear and the normal stresses, $\tau \sigma$, denoted by different authors as apparent viscosity, μ_a or η_a , or the bulk, $\mu_{\rm b}$, or effective, $\mu_{\rm eff}$, friction coefficient or angle of



Fig. 3 Depiction of the inertial number *I* as the ratio of the deformation and compression timescales, t_y and t_{σ} .

internal friction. In practical terms, even in a quasi-static flow t_{σ} cannot tend to zero, and in reality, the grains experience rearrangements and slow displacements that result in intermittent dynamics. When the inertial number, *I*, increases, the particle inertia starts to play a significant role in the transport of momentum, and the system behaviour becomes dependent on the shear rate.

2.2 Overview of mathematical modelling

This work does not intend to review the modelling of granular flows. Here we present a brief overview of the phenomenological, theoretical and computational approaches used to described granular flows in the context of shear-cell devices. We refer the interested readers to Capriz et al. (2008) and Rao and Nott (2008) for a boarder discussion and comprehensive reviews on kinetic theories, plasticity, continuum and discrete modelling of granular flow and the relevant references.

A continuum description is the preferred way to describe granular flow in industrial processes handling billions of particles. For quasi-static flows, the theory of plasticity is often used to develop continuum models. Specifically, the plasticity theory determines the normal, σ , and shear stresses, τ , as a function of the strain rates (changes in the distance of adjacent particles with time in the neighbourhood of a point). In a slow regime, the frictional stresses are independent of the strain rate, and under a normal stress, granular material will shear only when the shear stress, τ , exceeds a critical value. The failure behaviour is simply described by a yielding law such as a Mohr-Coulomb criterion but yielding laws do not provide information on how particles flow or blocks of particles deform. To overcome this limitation, plastic potential theories are complemented with the critical state theory using yield and potential functions. Chen and Mizuno (1990) proposed a pathway to relate the applied stress to the deformation and Vun et al. (2010) listed the procedure to follow: (i) define a yield function, (ii) apply a plastic potential function to relate the rate of strain tensor to stress and (iii) set up a flow rule that links the yield function to the plastic function. The proposed quasi-static models feature different vield functions. For example, Srivastava and Sundaresan (2003) used the extended von Mises function, while Christakis et al. (2006) developed a viscoplastic model based on the Drucker-Prager plasticity function. The extended von Mises yielding law-based models was criticized (Dartevelle, 2004) for not accounting for energy dissipation and predict infinite dilatancy, but these physical inconsistencies are removed with a 3-D "compressible" formulation (Gray and Stiles, 1988). The limitations of these functions are discussed by Andreotti et al. (2013).

Rapid granular flows have been investigated by experimental studies and statistical mechanical methods. The



well-known experimental study of Bagnold (1954) where spherical spheres were sheared in a coaxial cylinder rheometer, is the pioneering work on the constitutive behaviour of inertial granular flows. This heuristic study showed that the solid stresses, σ and τ , were a function of the square of the applied shear rate, $\dot{\gamma}$, at high rotating velocities. From the view of the theoretical modelling, the Kinetic Theory of Granular Flow (KTGF), an extension of the classical kinetic theory of gases to dense and inelastic granular flows, has been developed for forty years (Garzó and Dufty, 1999; Lun et al., 1984; Yang et al., 2016). In the KTGF approach, the granular material is modelled as a continuum medium, and the transport equations for solid concentration, momentum and granular temperature are derived. The square relation between the solid stress and the shear rate has been theoretically confirmed by KTGF models. Early comparisons of with annular-shear-cell test measurements were first reported by Lun et al. (1984) and later on several other studies (Hanes and Inman, 1985; Hsiau and Jang, 1998; Orlando and Shen, 2012). However, these experimental configurations provide information on the bulk behaviour of the granular material and not the motion of individual grains. Further comparisons of KTGF predictions with local granular measurements include the work of Wildman et al. (2008) where positron emission particle tracking (PEPT) was used to measure solid concentration and mean velocity profiles inside a three-dimensional annular shear cell.

Besides a continuum formulation, granular material can be studied by computational approaches such as Discrete Element Modelling (DEM) where individual particles are tracked via a Lagrangian approach solving Newton's equations of motion and describing particle-particle collisions with a soft sphere model (Guo and Curtis, 2015). These simulations are classified as highly resolved because they can provide flow properties at particle-scale such as velocities, contact number and forces. Due to the high demand for computational resources, the method is applicable for academic studies and small-scale laboratory experiments. DEM simulations capture the persistence of a Bagnold regime (da Cruz et al., 2005) in homogeneous shearing of particles in fully periodic domains with Lees-Edwards boundary conditions, and are used to investigate boundary effects on confined geometries such as Couette flows (Vescovi et al., 2014).

The intermediate regime was first experimentally identified in inclined plane chutes (Pouliquen, 1999) and later in a Couette shear cell (Tardos et al., 1998), where the shear stress τ was found to depend on the strain rate to a power of between 0 and 2 that is a function of the solid concentration. While continuum models are available for quasi-static and inertial granular flows, the closures for the intermediate regime are still under debate. Johnson and Jackson (1987) proposed a semi-empirical model that super-imposed collisional and frictional stresses modelled with a critical state and an algebraic function of solid concentration. A similar "additive" approach was applied by (Savage, 1998) with using von Mises yield criterion. From a more empirical point of view, Jop et al. (2006) unified these two extreme regimes with a simple visco-plastic constitutive law without any fitting parameter and validated their model with experiments of a granular pile flowing between rough sidewalls. The model is called the $\mu(I)$ model. It is based on the Coulomb criterion and a bulk friction coefficient function of the inertial number, I, Eq. 1. Similarly, da Cruz et al. (2005) performed DEM simulations of plane shearing with frictional, inelastic disks and found that small values of I correspond to the quasi-static regime of soil mechanics, while large values correspond to the collisional regime of the KTGF.

There have been different ways to incorporate the frictional contribution of a dense flow into the KTFG (Wu et al., 2020). For example, Chialvo et al. (2012) carried out homogeneous shear DEM simulations of frictional and frictionless particles in the quasi-static and inertial regimes, and proposed corrections to the model of Garzó and Dufty (1999) to bridge these regimes using the $\mu(I)$ rheology model. Similarly, Vescovi et al. (2014) performed DEM of wall-bounded plane shearing of particles and used the expression for the correlation length developed by Berzi (2014) to modify the model of Garzó and Dufty (1999). Jenkins (2006) proposed a phenomenological correction to the rate of collisional dissipation in the KTGF model that describes the decrease in dissipation of fluctuations during enduring contacts. There are several studies that attempt to expand the $\mu(I)$ models to a non-local rheology, for example, using additional transport equations to describe a weight function between fluid and solid-like parts of the stress tensor (Aranson and Tsimring, 2001; 2002), or proposing new closures for $\mu_{\rm b}$ dependent on coordination number and the evolution of a fabric anisotropy tensor (Sun and Sundaresan, 2011). An application of non-local $\mu(I)$ rheology in quasi 2-D shear cell experiments has also been given by Tang et al. (2018).

3. Quasi-static characterisation: shear cells

Shear cells are experimental devices designed to evaluate the flowability of a powder finding the relation between applied normal stress, σ , and the shear stress, τ , required for a static powder bed to fail. The operate performing shear tests by applying two orthogonal stresses on a sample and measuring its response. The first stress is denoted by the normal or consolidation stress, σ (see **Fig. 4a**). σ is often aligned with the gravity acceleration and includes the weight of the powder. The second stress is orthogonal to the first one, and denoted by the shear stress, τ . It





Fig. 4 (a) A granular layer under shear, τ , and consolidation, σ , stress. (b) Yield locus line, $\tau = \mu \sigma + C$; μ : angle of internal friction; *C*: cohesive strength; UYS, MPS: unconfined yield stress and major principle stress.

is increased gradually until the sample reaches its yield point and starts flowing. Shear tests include two steps, a so-called pre-shearing test followed by the application of four to six different shear stresses. The objective of the pre-shearing test is to create a reproducible structure in the powder by applying a reference consolidation stress. The sample is consolidated at high normal stress, $\sigma_{\rm pr}$, and then it is sheared until it fails and the recorded shear stress, τ_{pr} , reaches a constant value, denoted steady-state conditions. The pre-shearing normal and shear stresses $(\sigma_{\rm pr}, \tau_{\rm pr})$ set a reference point for the study (blue point - Fig. 4b). At this point, if the shear stress is removed, the displacement ceases, but the sample reorganises into the same structure and so it exhibits the same response when it is sheared further. After the preparation stage, several experiments are conducted varying σ and τ , denoted "shear tests" or "shear points" (red - Fig. 4b). The sample is sheared to the failure point with a decrease in the consolidation stress ($\sigma < \sigma_{nr}$). For each value of σ , the shear stress corresponding to the bed failure, τ , is recorded and reported in a (τ , σ) diagram to build the yield locus line: $\tau = \mu \sigma + C$ where μ is the angle of internal friction and C is the cohesive strength. The locus line describes the yield stress in quasi-static granular flow, it takes the form of a Coulomb behaviour where the yield stress is independent of the shear rate. It should be noted that the state of stress achieved in the sample after the pre-shearing is particular to each device, which introduces a degree of specificity to the method.

The angle of internal friction, μ , is reported as the slope of the yield locus line connecting all (τ,σ) pairs. In other words, the ratio between the shear and normal stresses τ/σ

required for a sample consolidated at $(\sigma_{\text{DT}}, \tau_{\text{DT}})$ to yield. Mohr circles are used to derive other important parameters. The principal stresses are defined as the base of the stress tensor that creates no shear stress in the system and therefore, minor and major, MPS, principal stresses can be obtained as the intersection of a Mohr circle with the axis $\tau = 0$. A Mohr circle tangent to any point in the yield locus line is a representation of the conditions for critical failure at that combination of σ and τ . The principal stresses that describe the structure of the powder sample are obtained from the Mohr circle that contains the reference $(\sigma_{\rm DT}, \tau_{\rm DT})$ and is tangent to the yield locus. The unconfined yield stress, UYS, is defined as the normal stress required for the powder to yield under no shear. It is obtained from the Mohr circle that contains the origin (a sample sustaining no stress) and the yield locus line. There are other definitions of the locus line stemming from shear tests. The bulk (or effective) $\mu_{\rm b}$ friction factor defined from a bulk yield locus line ($\tau = \mu_{\rm b}$ σ) that contains the origin and is tangent to the Mohr circle of the pre-sheared sample. The relation between the shear and the normal stress in the pre-shearing point is given by $\tau = \mu_{ss} \sigma$ with μ_{ss} the steady-state angle of internal friction. The flowability function, FF, is reported as the ratio of MPS to UYS.

Shear cells, or testers, can be classified into two categories: direct and indirect testers. In a direct tester the geometry of the device imposes a sheared region on the sample, whereas in an indirect tester, the sheared zone in the powder develops independently according to the stress applied. Many indirect testers such as the uniaxial, bi-axial and tri-axial testers were developed for specific applications and are generally not commercially available (Feise and Schwedes, 1995; Jenike, 1970; Schwedes, 1996). This work will focus on describing succinctly direct units, particularly examples of commercially available translational and recent rotational devices. More comprehensive details of the design and the historical development of shear cells can be found in the literature (Schwedes, 2003).

3.1 Jenike type translational testers

The working principle of translational shear testers is creating shear by sliding one section of the sample. Jenike provided one of the first translational devices used to study flowability (Jenike, 1970) and design silos, leading to an ASTM standard (Carson and Wilms, 2006). It consists in a container, or cup, with a stationary base and an upper ring subject to shearing. The cup is filled with a powder sample, and the lid is used to compact it by applying a constant vertical force (**Fig. 5a**). A horizontal force is applied to the top ring until the bed fails and starts to slide. **Fig. 5b** depicts the typical evolution of the shear stress, τ , in the pre-shearing and shearing steps. In a Jenike test, the steady-state flow condition is met when one observes a no





Fig. 5 Translational testers. (a) Cross-section of a sliding device (b) Qualitative illustration of the evolution of the shear stress during the experimental procedure.

changes in $\tau_{\rm pr}$ under the pre-shearing normal stress, $\sigma_{\rm pr}$. In a successive step, τ is set to zero removing the force and is σ is reduced. The sample is sheared gain, and the value of τ at the failure point is recorded as the first shearing point. Additional tests using new samples are required to obtain each point of the yield locus (Fig. 5b). The simplicity of the test made it widely accessible to industry as a way to rank powders and study the effects of environmental conditions, composition, moisture, size and shape. However, this simple configuration comes with a significant limitation. The cell has a short shearing path, limited by the maximum displacement, and for that reason, it does not allow for a continuous test. A new sample is needed to measure each shear point, which leads to a time-consuming process with a substantial intervention of the operator, and thus prone to error.

Several works tried to overcome this limitation introducing a "constant volume methodology" (Duffy and Puri, 1999; Ladipo and Puri, 1997; Schulze, 2008; Tsunakawa and Aoki, 1982) whereby the Jenike tester is modified to operate continuously. After the steady-state flow is achieved at the prehearing test, σ is gradually reduced at a small speed releasing the load on the lid. The corresponding evolution of the shear stress, τ , is recorded to construct the yield locus line. The main advantage is the ability to perform a single continuous test measuring the evolution of the sample from the point (σ_{pr} , τ_{pr}) to the point *C* using one sample (green line - **Fig. 4b**). The early versions of the constant volume translational testers were subject of criticism (Schwedes, 2003) because of their complex configuration. It has been suggested that this methodology tends to underestimate the unconfined yield stress, nevertheless, to the best of our knowledge, no detailed direct comparatives confirm such a feature.

More recently, Shimada et al. (2018a; 2018b) developed a new device to evaluate flowability using a constantvolume shear tester. The methodology aims at providing continuous measurement of shear stress from a high consolidation point under no shear (σ_{cvt} ,0), through the steady-state flow reference state ($\sigma_{\rm pr}, \tau_{\rm pr}$) until the point at zero normal stress (C,0). The line from the point $(\sigma_{cvt}, 0)$ to the point (σ_{pr}, τ_{pr}) (purple line, **Fig. 4b**) is referred to as the "consolidation yield locus". The configuration of the tester is depicted in Fig. 6. The upper section of the cell can be filled with a varying height of powder, allowing one to conduct tests at a constant and controlled void fraction. Once the powder is loaded in the cell, a vertical servo motor lowers the piston compressing the sample to the desired stress (σ_{cvt} ,0). When the value is reached, the vertical motion stops at a fixed position for 2 min to relieve the excess stress. Afterwards, the horizontal servo motor applies a shearing force on the lower section until the shear stress reaches a constant value, τ_{nr} , registering the transition from $(\sigma_{\rm cvt}, 0)$ to $(\sigma_{\rm pr}, \tau_{\rm pr})$ directly (purple line - **Fig. 4b**). Next, the consolidation stress, σ , is reduced to zero by gradually lowering the vertical translation stage, reducing the shear stress from τ_{nr} to C (green line - **Fig. 4b**). The set up allows having a three-dimensional relationship between τ , σ and particle concentration ε_s . It is comparable to historical testers and obtains the yield locus line in a single test of one sample. However, it is still restricted to the length of the shearing path. While these testers are not widely available, the reports involve the use of fine powders and the possibility to use small consolidation stresses.



Fig. 6 Constant volume tester. Reprinted from Shimada et al. (2018a) under the terms of the CC-BY-NC-ND 4.0 license. Copyright: (2018) The Authors, published by Elsevier B.V.

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3.2 Rotational shear testers

Rotational testers overcome the restriction of a short shearing path employing a rotational force on two possible geometries: a circular path (Fig. 7a) or an annular path (Fig. 7b). In both, shearing is induced by rotation and the normal force is applied on the top. To shear the bulk powder, the lid and the base must rotate relative to each other. In most devices, this is achieved applying a torque, T, on the base while the lid is fixed, such as in the Schulze shear cell (Schulze, 1994). The reverse configuration, a fixed base and a rotating lid are used in testers like the FT4 (Freeman, 2007) and the Brookfield PTF (Berry et al., 2014). The surfaces of the base and the lid are roughened or equipped with blades to avoid sliding between the powder and the wall. The experimental procedure of rotational testers follows the same sequence: a pre-shearing step that conditions the sample, and a shearing test for every pair of normal and shear stresses to build the yield locus line. A rotational unit can apply an unlimited shearing path, and in this way perform multiple measurements on a single sample. It is easier to automate and therefore, reduces human error.

Many types of rotational testers can be found in literature, e.g. (Berry and Bradley, 2007; Bishop et al., 1971; Carr and Walker, 1968; Orband and Geldart, 1997; Schwedes, 1996). All operate under the same principles, and vary in their geometry, size, the range and the level of automation in the application of stress, and critically, in the sample preparation and the pre-shearing stage. Here, we will focus on describing three commercially available rotational testers: the Schulze shear cell, the Freeman FT4 shear tester and the Brookfield PTF, as representative examples of the design and the scope of the application of ring (Schulze and Brookfield) and torsional (FT4) units.

Fig. 8 describes qualitatively the experimental procedure. The Schulze shear cell (Schulze, 2008) is one of the first automated rotational shear devices. It features a rotating ring with a base that contains the sample, covered with a fixed annular lid where the normal force is applied. The inner surface of the ring and the lower side of the lid are roughened. Shearing is induced by rotating the bottom ring



Fig. 7 Diagram of (a) torsional, (b) annular (ring) shear tester.

at angular velocity, ω , maintaining the lid stationary. To apply a normal force and rotation independently, the design includes additional elements, such as tie rods and a crossbeam used to stop the lid from moving. A normal force is exerted on the top and transmitted to the sample as the normal stress, σ . An upwards force counters the weight of the lid allowing the cell to operate under a small σ . The procedure is similar to that in Fig. 5b, but without the need to change the sample. It is faster and easier to automate. After the measurement of the first shear point (σ_1 , τ_1), the sample is reconsolidated to σ_{pr} and sheared again to τ_{pr} (Fig. 8a). The normal stress, σ , is reduced, and the sample is sheared again to register the next point of the yield locus. Fig. 8b illustrates the experimental procedure in a Freeman FT4 shear tester (Freeman, 2007; Freeman et al., 2009). An FT4 shear cell is a torsional shear cell in a reverse configuration, whereby the base is stationary, and the shear is induced by a circular rotating lid (Fig. 7). The stainless-steel lid is fitted with 18 baffles of 2 mm in height to ensure that the shearing occurs only between the grains. The base is a cylindrical glass vessel plugged with a rough plastic cover on the base. The consolidation stress is applied lowering the lid onto the sample, and it is measured at the bottom. Once the desired value, $\sigma_{\rm pr}$, is reached, the cell is rotated at very low speed, and the torque is recorded continuously. The procedure is the same, but the pre-shearing is different. The consolidated sample at $\sigma_{\rm nr}$ is sheared to the failure point in consecutive pre-shearing steps until the maximum shear stress, $\tau_{\rm nr}$, registered in each step remains constant (< 1 % difference - Blue - Fig. 8b). At this reference point, the first shearing test is performed reducing σ and registering the τ required for the bed to fail. In this step, the axial position of the lid is kept constant, and τ is computed as the peak of



Fig. 8 Examples of rotational cells. Qualitative illustration of the evolution of the shear stress during the experimental procedure to construct the yield locus in (a) Schulze ring shear cell, (b) Freeman FT4 powder shear cell, (c) Brookfield PFT.



the shear curve (Red - Fig. 8b). Shearing is repeated at a varying σ to complete the yield locus line using an intermediate pre-shearing state in between each measurement to recondition the powder to $(\sigma_{\rm pr}, \tau_{\rm pr})$. Fig. 8c describes qualitatively the test in a Brookfield Powder Flow Tester PFT. A Brookfield unit is like a Schulze tester, an annular (ring) device, but arranged in a reverse configuration with a stationary base and a rotating lid. It follows an experimental procedure similar to an FT4 with a slightly different definition of τ_{pr} (Berry et al., 2014). The cell is made of a stainless-steel annular base and a bladed lid. The consolidation stress is applied lowering the lid and measured at the top of the device. The sample if consolidated at high stress, $\sigma_{\rm pr}$, and sheared several times until reaching a steady-state (Blue - Fig. 8c). One of its particularities is that the yield locus line is constructed from low to high consolidation, starting from a measurement at the lowest stress, $\frac{1}{3}\sigma_{\rm pr}$, followed by $\frac{1}{2}\sigma_{\rm pr}$ and $\sigma_{\rm pr}$.

Shear cells are used as standard for the evaluation of the flowability of industrial powders and study their stability during storage, a key attribute of formulated powders. In many cases, materials are complex matrices of crystalline and amorphous components that are prone to cake through adhesion, sintering, deliquescence and formation liquid and solid bridges. Shear cells provide a way to study the effect of particle properties and the environment in this process. For example, Deshmukh et al. (2019) reports a recent study using a Schulze cell as an in-vitro tool for oral processing of foods, but similar devices have been used for decades. Teunou and Fitzpatrick (1999) proposed a ring unit specifically designed to study foods and investigated how environmental conditions affect the flow of flour, tea and whey powders (Teunou et al., 1999). The cell was installed in a chamber with controlled relative humidity rH and T. As expected, an increase in either of the two leads to a reduction in the flowability. The effect of consolidation and storage time was studied in a Jenike type cell (Teunou and Fitzpatrick, 2000) providing the evolution of flow functions. Fitzpatrick et al. (2007) used a similar device to study the effects of formulation and storage time in dairy powders. Opaliński et al. (2012) designed another Jenike type shear tester to study moist food powder and similar works on the study of mixtures of coal and sawdust or biomass mixtures were reported by Chen et al. (2012) and Zulfigar et al. (2006). Torsional units have also been shown flexible tools. Guo et al. (2015) and Chen et al. (2018) used the FT4 shear cell to study the flow of biomass and coal blends with and without a varying level of moisture. Crawford et al. (2016) used it to study the effect of preprocessing of biomass and Léonard and Abatzoglou (2010) to investigate lubricated and unlubricated pharmaceutical powders. The FT4 shear cell was also used by Leung et al. (2017) to investigate the flowability of pharmaceutical powders mainly driven by cohesion.

Although fundamental and comparative studies are less frequent, they can shed light into the local stress distributions and on how the particle level properties relate to the bulk behaviour. For instance, Zafar et al. (2015) used a Schulze shear cell to investigate the flowability of cohesive powders, and compared the results to characterisation techniques such as the ball indentation (Hassanpour and Ghadiri, 2007) that measures the hardness at a low consolidation, and the Sevilla Powder Tester (Castellanos et al., 2004). Louati (2016) and Louati et al. (2015; 2017), used a Schulze shear cell for a fundamental investigation of the impact of moisture and particles size on the flow of glass beads, and Hammerich et al. (2020) designed a modified ring cell to study liquid saturated sediments. Wang et al., (2016) proposed instead a new method to analyse data using the FT4 under different initial consolidation. They tested over 40 powders with four initial consolidation stress and proposed an empirical relation between the flow function and a dimensionless cohesion C^* ($C^* = C/\sigma_{pr}$) that separates the effects of initial consolidation stress and the testing device.

There are other available shear devices like the Anton Parr rheometer that uses impellers for shearing, the Peschl cell that modifies a standard ring shear cell, and other commercially available units like the Hosokawa Micron Powder Tester or GranuDrum. Many others well-known testers have been developed for specific applications in research laboratories, for example, the use of fluidised beds to measured tensile strength (Castellanos et al., 2004) or flowability (Girimonte et al., 2018), and the analysis of caking with direct or indirect measurements of unconfined yield strength in uniaxial compression testers, e.g. (Hassanpour and Ghadiri, 2007; Thakur et al., 2014).

From a more fundamental point of view, the use of visualisation techniques such as Magnetic Resonance Imaging (MRI) can reveal the transmission of stress in a quasi-static flow at a particle level. Commercial shear cells made of metal are not suitable, but novel shear testers have been designed for this specific purpose (Mueth et al., 2000). The work of Cheng et al. (2006) and Sakaie et al. (2008) reports a direct measurement of the evolution of the local packing of a slow and smooth granular shear flow in a splitbottomed geometry. They sheared MRI sensitive seeds at different rotational velocities and collected MR-images after stopping the shearing process. Börzsönyi et al. (2011) followed a similar approach to demonstrate that a shear zone develops preferentially in regions with a lower friction. They studied a U-shaped horizontal shear cell consisting of two parallel L-shaped sliders and characterised the shearing band recording the displacement of MRI-sensitive poppy seeds loaded in a sample of MRI-insensitive glass beads.

Classic or new devices and commercial and custom designs, all shear cells work under the same principle. And

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yet, different dimensions, sample volume and pre-shearing procedures lead to disparities in the measurements from different testers. The impact the history of a powder has in its response to stress is well documented (Swize et al., 2019), but the sample preparation procedures are still specific to each device. The work of Berry et al. (2014) and Salehi et al. (2017a) compares the measurements of Brookfield, Schulze and Jenike testers, and Koynov et al. (2015) reports on a comparative study of shear cells evaluating the flow of coarse (59 mm) and fine (4 mm) alumina powder. Salehi et al. (2017a) found no important disparities between testers, the largest differences being ascribed to highly compressible powders, but the observations of Berry et al. (2014) were consistent with the issues listed by Koynov et al. (2015). In their comparative work, all shear cells provided a good qualitative measurement of flowability, but they were found to be more efficient with fine, cohesive powders. In free-flowing powders, measurements could not be used in a quantitative way to rank the materials but only to identify them as free-flowing. Comparison across different cells showed that not only the consolidation stress during pre-shearing is important, but also the type of shear cell. Barletta et al. (2015) provided a similar comparative analysis in the context of biomass and identified important differences only in the wall friction coefficients. It is in line with the work of García-Triñanes et al. (2019), which finds minor differences in the measurement of tensile strength of cohesive powders in a Schulze and a Brookfield unit.

The full range of available devices to characterise the quasi-static flow of complex cohesive mixtures is described by Ghadiri et al. (2020), Ogata (2019), and Schwedes (2003). Here we provided the reader with an overview of the design of classic shear testers, their limitations and their scope for application. In the following sections, we describe how the modification of the classic designs with the use of aeration and other external sources of actuation can lead to a new type of devices that are capable of performing measurements in an intermediate regime and providing a more complete picture of the granular rheology.

4. Beyond the quasi-static regime

In the quasi-static regime, the yield locus line describes the failure of a network of enduring contacts between particles in a bed of powder. Under an applied normal stress, σ , the required shear stress $\tau = \mu \sigma + C$ is purely a function of the bulk material properties and the structure of the sample created by the consolidation at (σ_{pr}, τ_{pr}) . However, at higher shear rate, or lower consolidation stresses, the powder dilates, and as it transitions into an intermediate regime, the shear stress, τ , establishes a dependency on the shear rate, $\dot{\gamma}$. There are several ways to try to replicate and characterise this transition in a modified shear cell. In order to depart from the quasi-static regime, one must operate at a higher inertial number, *I*, (see Eq. 1) by either operating at a sufficiently high shear rate, $\dot{\gamma}$, or at a sufficiently low (constant) consolidation stress, σ .

The operation at $\dot{\gamma}$ simply by operating at a high rotational speed in indeed possible (Bagnold, 1954) but in practice this can lead to attrition of fragile particles. Ghadiri et al. (2000) discuss in detail the importance of breakage and segregation in a annular cells using catalyst powder, and Hare et al. (2011) provide an example where measurements of the attrition of pharmaceutical powders in a shear cell are coupled with computational studies in an agitated bed.

Alternatively, the inertial number, I, can be reduced operating at low consolidation stress, σ . Doing so requires the application of an energy source to the bed that can overcome the action of the gravitational acceleration that would otherwise consolidate the sample. The additional energy input can be introduced by the action of a particle-fluid force using aeration or even complete fluidisation, or through mechanical acceleration, such as agitation or vibration of the sample. The following sections provide a summary of current strategies describing a selection of shear devices that use an external actuation to operate at low consolidation stresses. Modified classic shear cells are introduced in Section 4.1, and **Sections 4.2 and 4.3** describe the design of Couette-type rheometers and the use of mechanically agitated aerated or fluidised beds.

4.1 Modified shear testers

One of the first modified shear testers was introduced by Klein et al. (2003). They developed an annular (ring) cell to shear a limestone powder ($d_p < 15 \ \mu m$) at varying normal stress and a shear velocity between 0.07 to 4,200 mm/min. The design resembles a Schulze tester with the functionality of powder aeration. A motor is fixed to the base to rotate the shear cell at the desired velocity. The base and the lid are made of a permeable material, and feature 24 thin baffles to prevent the sample from sliding during the shearing process. The vertical normal stress, σ , is applied by the lid on the top of the sample. Aeration is modulated via a mass flow controller or through the measurement of air pressure in the exhaust. A fluidisation index, FI, is defined as ratio between the pressure drop of the gas flowing through a bed of powder ΔP , and the pressure drop required to counter the weight of the bed and reach the minimum fluidisation, $\Delta P_{\rm mf} = W/A$. Or in other words, the ratio between the gas superficial velocity, u_a , and the minimum fluidisation velocity, $u_{\rm mf}$, $FI = \Delta P / \Delta P_{\rm mf} \sim u / u_{\rm mf}$. When particles are aerated by a gas velocity lower than $u_{\rm mf}$, FI < 1, the bed of powder remains static but it sustains much lower normal stress, σ , due to the reduction of its effective weight under the action of a drag and buoyancy forces. Klein et al. (2003) studied the effect of aeration in the rheology of limestone.



They observed no differences in the shear stress, τ , required for the bed to fail under a constant normal stress, σ , and a fluidisation index FI < 0.7, in an indication that the powder remains in a quasi-static regime. However, under a higher FI but still operating with a fixed bed, 0.7 < FI < 1, the shear stress, τ , was found to decrease for an increasing air velocity indicating the presence of an intermediate regime between the quasi-static and the collisional regime characteristic of a fully fluidised system at $FI \gg 1$.

Another example of a classic tester with an aeration functionality was proposed by Johanson and Barletta (2004). They modified a Schulze device, to operate under a continuous counter air flow using a base of permeable media and a modified perforated lid. Air pressure was measured at the inlet and the flow was controlled with a rotameter. They performed shear experiments on a fine silica powder ($d_p = 8 \ \mu m$) and an FCC catalyst ($d_p = 50 \ \mu m$) and with a range of aeration up to FI = 1. As expected, the unconfined yield strength of the bulk material was found to decrease with increasing aeration. The effective angle of internal friction decreased approaching full fluidisation. Other modified testers include the device developed by Barletta et al. (2007), which coupled a circular cell with the rotating plate of a Peschl shear test bench to investigate the effect of aeration in the flow of fine silica ($d_{\rm p} = 7.6 \,\mu{\rm m}$) and magnesium carbonate ($d_p = 3.5 \,\mu$ m). The design resembles that of a short FT4 rheometer, featuring a circular fixed base and a bladed rotational lid. The base is 61.8 mm in inner diameter and 15 mm in height, and it consists of a porous bottom plate that ensures a homogeneous air distribution. The experimental procedure mimics that of **Fig. 8b.** Experiments were performed at low shear rates, $\dot{\gamma}$, and normal stress, σ , and below the minimum fluidisation (FI < 1). Their results confirm the observations of Klein et al. (2003): for a fluidisation index FI < 0.7 no significant differences appear in the angle of internal friction, in an indication that even when aerated, the samples remained in the quasi-static regime.

4.2 Couette-type shear testers

Annular cells are a classic arrangement to study the rheology of Newtonian and non-Newtonian flows (Viswanath et al., 2007). **Fig. 9a** provides a generic description of the geometry. In these devices, the fluid is sheared in between two coaxial cylinders: an inner rotating one called bob and an external steady cylinder called cup. The viscosity and the shear stress are computed from the angular velocity, ω , and the torque, *T*, applied to the inner cylinder. Couette-type shear testers have been often used to study granular flows. Interested readers are referred to the overview by GDR Midi (Midi, 2004) for characteristic experimental velocity profiles. The evolution of the bulk or effective friction coefficient $\mu_{\rm b}$ in a Couette cell is given as a function of



Fig. 9 Depiction of a generic geometry of a (a) Coaxial-Cylinder rheometer applied to powders, and its use within a (b) flow and (c) aerated device. Nomenclature: R_i and R_c : inner and outer radii, *L*: bed height subject to shear; ω : rotational speed.

a dimensionless characteristic shear rate, $\hat{\dot{\gamma}}_C = \dot{\gamma}_w \sqrt{d/g}$. where $\dot{\gamma}_{w}$ is the shear rate at the wall. The use of $\dot{\gamma}_{c}$ is a particular case of the general inertial number I (see Eq. 1) that considers a hydrostatic pressure as the source of the consolidation stress. Experimental velocity profiles in Couette cells show the existence of localised shear bands on the wall of the rotating cylinder that depend on the conditions of the boundaries. In order to avoid sliding, the walls of the cylinders must be roughened mechanically or by glueing particles or sandpaper. Due to the simplicity in design and control, Couette cells are an excellent alternative to study the intermediate flow regime. The type of geometry described in Fig. 9a has been used for a long time to study powders and capture the stress-strain rate relationship (Craig et al., 1986; Hanes and Inman, 1985; Savage and Sayed, 1984). Modern devices without any actuation include the units proposed by Tardos et al. (1998) and a shorter, annular device described by Klausner et al. (2000). Every cell imposes a fixed shear rate and relies on the action



of gravitational acceleration to consolidate the sample. The earlier studies establish a dependency of the shear stress on the shear rate that simply by operating at high shear rate, $\dot{\gamma}$, increasing the rotational speed of the inner cylinder, and thus $\dot{\gamma}_{w}$. The boundaries for the transition from the quasi-static to the intermediate regime and inertial regimes are still under debate. Experimental values have been proposed by Tardos et al. (1998; 2003) for the departure of the quasi-static regime, i.e. $\hat{\dot{\gamma}}_{C} \sim 0.15 / 0.25$, and the collisional regime $\dot{\gamma}_{\rm C} \sim 3$, and later confirmed in computational studies (Vidyapati et al., 2012). In order to achieve a more general description and reach a higher range of inertial numbers, I, one can also reduce the consolidation stress, σ , linked to the powder weight. In the following sections, we describe the design of Couette cells that introduce aeration or flow in a coaxial-cylinder configuration, Section 4.2.1, and virtual cells that minimise sliding effects, Section 4.2.2.

4.2.1 Aerated coaxial-cylinder rheometers

Two alternatives have been proposed in literature in order to actuate a coaxial cylinder rheometer (**Fig. 9a**) and operate at higher inertial numbers. One can impose an axial particle flow in the annular section inserting the unit in flow device (**Fig. 9b**) or inject a counter-current stream of air to reduce the consolidation stress in an aerated or fluidised chamber (**Fig. 9c**).

Tardos et al. (1998) first used a coaxial cylinder rheometer to investigate shear stress of non-aerated and aerated powders. Its geometry and operation conditions are listed in **Table 1**. The unit featured two concentrically placed cylinders and the possibility to aerate the bed. The walls of both cylinders were covered with sandpaper to minimise sliding. Two sets of experiments with and without aeration were performed to study the effects of torque and the height of the powder bed on the stress evolution. The experiments under aeration (0 < FI < 1) investigated the distribution of stress under a varying shear rate. Fine free-flowing dry powders were tested at three rotational speeds, ω , and three bed heights, *L*. The authors proposed a model for the variation of the torque, *T*, based on the assumption of a linear hydrostatic granular pressure, as:

$$T = (\tau R)2\pi RL = \pi \rho_{\rm b} gL^2 R_{\rm i}^2 \sin(\mu) \left[1 - \frac{u_{\rm g}}{u_{\rm mf}} \right]$$
(3)

Here, $\rho_{\rm b}$ is the bulk density of the powder and the last term accounts for the effect of the superficial velocity in reducing the effective weight of the sample. Eq (3) predicts a linear dependency of the shear stress with the bed height, $\tau \sim L$, and a linear dependency between of the torque with the gas velocity, $T \sim u_g$, but a quadratic dependence of the torque with the radius of the rotating cylinder, $T \sim R_i^2$, and the height of the powder bed, $T \sim L^2$. The authors assessed the validity of Eq. (3) through experimental measurements of the stress distribution in a stationary material. Unlike Eq (3), the well-known Janssen equation describes an exponential distribution of the stress across the depth, but it would predict a linear dependency, $T \sim L$, for a powder in a quasi-static regime when the normal stress reaches an asymptotic value below a certain depth. The experimental results obtained across different particle densities, diameters, shear rates and aeration levels confirmed the prediction of Eq. (3) based on hydrostatic loads and the effect of aeration in reducing σ . These experiments were operated at low shear rates, $\dot{\gamma}$, and the results did not show any relation between T and $\dot{\gamma}$. In a further series of experiments, Tardos et al. (1998) investigated the effect of higher shear rates (or higher $\dot{\gamma}_{\rm C}$) increasing the rotational speed to 250 rpm bulk samples of non-aerated coarse glass beads. The effect of the hydrostatic load was studied placing an 8 cm high layer of powder on top of the shearing column that blocked the bed from expanding. The results using different geometries showed a weak dependency of the dimensionless torque and shear rate ascribed to the variation of the annular gap that was actually sheared. However, in the configuration with an additional layer of powder, the entire annular gap was sheared, and a linear correlation appeared between the dimensionless torque and shear rate with a slope of 0.25. This is one of the first studies capturing the departure from

Table 1	Summary of aerated	or vibrated Couette-typ	pe cells for the cha	aracterisation of	intermediate granular flow.
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Reference	Material	FI	$d_{\rm p}$ [µm]	ω [rpm]	γ̈́ [s ⁻¹]	$R_{\rm e} / R_{\rm i} / r^{*} [{ m mm}]$	<i>L</i> [mm]
r1 : Anjaneyulu et al. (1995)	Glass	>1	400–900	150	0.07/1.65	32.5/6-11	20-40
r2 : Tardos et al. (1998)	Multiple	0-1	70–530	20/250	10/120	76.2/63.5	195–285
r3 : Marchal et al. (2009)	Glass	Vibrated	530		$10^{-6} - 10^2$	20/10/11.5	30
r4 : Colafigli et al. (2009)	Silica	>1	26	2.4/16	0.12/0.76	69/50	300
r5 : Langroudi et al. (2010a)	Glass	Flow	500-1000	5/60	0.25/9	152.4/101.6	101.6-406.4
r6 : Landi et al. (2012)	Glass	>1	48	3	0.13	69/50	300
r7 : Gutam et al. (2013)	Multiple	0	830-1300		0.34-1.7	75/35-60	190
r8 : Lupo et al. (2019)	Multiple	0>1	80-266	0.5	_	25/10.5	28
r9 : Yahia et al. (2020)	Glass	0-1	50-500	8/180	2.75/22	70/10-18/12-20	70



a quasi-static flow and two distinct behaviours: quasi-static at a low shear rate and intermediate at higher shear rate.

The same linear relationship between the stresses and the height was confirmed across a broader set of experiments by Tardos et al. (2003) varying the size of the internal cylinder, and including measurements of normal stresses in the radial and axial directions with the use of piezoelectric sensors. In this work, a new constitutive equation was proposed to unify quasi-static, intermediate and inertial regimes on the basis of a 2D analysis of the Couette flow using the additive approach of the stresses of Savage (1998).

Langroudi et al. (2010a; 2010b) were the first to propose the creation of a flow system to increase the inertial number in a coaxial-cylinder chamber. Fig. 9b depicts the general concept. These units offer some flexibility. They can be operated either in a batch or under a continuous axial flow of material in the annular space. The height of powder in the shearing band can be controlled with the powder flow rate, and an additional layer can be maintained above the shearing band, denoted overburden, to control the consolidation. In the study of Langroudi et al. (2010a; 2010b), the behaviour of coarse glass beads was evaluated first without the presence of the overburden. Four bed heights, L, and four rotational speeds were tested. As described by others in aerated (Tardos et al., 1998) and fluidised devices (Anjanevulu and Khakhar, 1995), shearing caused the stratification of the flow with two distinct layers of mobile and stagnant powder. Analysis of the torque was in agreement with Tardos et al. (1998) and confirmed the linear correlation between τ and the bed height, L. The analysis confirmed the presence of two regimes, a quasi-static flow at low shear rates where τ is independent of $\dot{\gamma}$, and an intermediate at higher values where τ increases with increasing $\dot{\gamma}$. The authors assumed a power-law for the stress and shear rate relation, $\tau = \dot{\gamma}^n$, and found that the *n*-index ranges from 0.5 to 1 and increasing with higher shear rate. This work provided also important additional information by measuring the normal stress, σ , acting on the shearing surface of the material. Stress sensors were placed in both the surface of the outer and inner cylinders, and a further set of experiments was conducted with a fixed bed height at 406.6 mm, an overburden of 101.6 mm and increasing ω from 5 to 60 rpm. As expected, the normal stress σ measured at the wall increased linearly with the depth in the powder bed, and it was independent on the rotational speed, ω . Measuring both the shear stress (indirectly) and the normal stress (directly), they estimated the angle of internal friction, μ , and found that it was comparable to the one evaluated with classic shear testers at low $\dot{\gamma}$. The authors proposed a constitutive model based on the data that blends the Coulomb yield condition at zero shear with a power law at a higher shear rate, $\tau / \sigma = \tan(\mu) + b |\dot{\gamma}|^n$. In a later study, Langroudi et al. (2011) used the same device equipped with capacitance probes to study the effect of polydispersity and shape in secondary flow patterns and the powder dilation.

Langroudi et al. (2010a) also studied the effects of the bed height, L, without overburden and confirmed a linear dependency of the average τ on L with a slope proportional to $\dot{\gamma}$. However, as pointed out by Ghadiri et al. (2020), there have been conflicting experimental observations. Mehandia et al. (2012) and Gutam et al. (2013) report evidence of an exponential behaviour studying in detail the axial distribution of the stress in slow regime on a similar arrangement (Table 1) including the direct measurement of radial and axial normal stresses. In their device, aeration was used only to homogenise the bed of powder, and the samples were pre-sheared during 20-30 min to remove any history effect. In contradiction with the observation of Tardos et al. (1998; 2003), all components of the stress tensor were seen to increase exponentially with the depth in the bed. The behaviour was found to be consistent with the Janssen equation across a range of conditions, which was ascribed to the inherent anisotropy of the bed fabric. In a later work, Krishnaraj and Nott (2016) associated the abnormal quadratic dependence of the stress with depth to the formation of a secondary vortex in a Couette geometry. The authors argue that the gravitational acceleration and its interplay with the confinement are responsible of causing a deviation from the expected liquid-like behaviour in isotropic plasticity models. These models disregard the transmission of stress to a boundary as the majority of computational DEM works do by imposing Lees Edwards boundary conditions. The role of geometrical constraints, particularly the size of the annular gap, therefore, requires further investigation.

Lupo et al. (2019) conducted a similar study using an Anton Paar cell featuring a pseudo-cylindrical impeller with a grooved surface. They carried out torque measurements on aerated and non-aerated samples by immersing the impeller at various bed depths. Experiments were performed below and above the minimum fluidisation using different powders (see **Table 1**). As expected, *T* decreased with the depth of the impeller for all the cases studied and decreased with increasing gas velocity. However, the more complex geometry of the cylinder/impeller requires further analysis to be able to compute the stresses.

Couette flow configurations have also used to investigate higher levels of aeration. For example, Anjaneyulu and Khakhar (1995) introduced an adapted Coaxial-cylinder rheometer to study of the rheology of a fluidised beds following an aerated arrangement, **Fig. 9c**. A viscometer (Brookfield, Synchro-Lectricas) was used to rotate an inner cylinder. Two geometries with varying internal radius were tested using glass beads with various sizes and reaching complete fluidisation FI > 1 (**Table 1**). For each airflow, the inner rotating cylinder was immersed in the glass beads sample at different elevations *L*. The experiments showed



the formation of a dynamic layer around the rotating cylinder and a static layer at the vicinity of the wall. In line with this observation, the authors proposed a pseudo-plastic constitutive equation based to describe the granular material as a Bingham fluid. Fitting the experimental results led to estimates of the bulk shear viscosity, μ , and the yield stress, τ_{v} , where τ_{v} defined as the shear stress at a very low rotational speed ($\omega \rightarrow 0$). As expected, both μ and τ_{ν} , decreased with increasing air velocity, but while τ_{y} decreased monotonically and beyond the fluidisation conditions, μ reached nearly constant value for FI > 1. This behaviour was explained by the motion of the gas from the sheared inner region to the outer packed region. The yield stress, dominated by the outer packed bed, decrease as more gas flows through for a higher FI but the viscosity, μ , remains constant since it is governed by the shearing of the rotating inner region, which does not dilate further. Both μ and τ_{μ} were found to be independent of the particle size for the same FI. At a low aeration level, the experimental results were more scattered, and the inner cylinder radius and the immersion depth had a significant effect on μ and τ_{ν} .

Colafigli et al. (2009) developed an alternative design for high aeration levels, known as the Couette Fluidised-Bed Rheometer (CFBR). A CFBR is designed to measure the apparent viscosity in a homogenous gas-fluidised bed. It features the same type of aerated geometry, Fig. 9c. The external cylinder was made of Pyrex to allow direct observation of the fluidisation dynamics, and the inner cylinder was made of stainless steel. Colafigli et al. (2009) used nitrogen at ambient conditions as the fluidisation medium and silica powder ($d_p = 26 \ \mu m$). The height of the bed was maintained at a constant value to have the inner rotating cylinder fully immersed, and enough space was left above the bed to accommodate the expansion of the bed. The apparent viscosity was evaluated from the steady-state value of the torque assuming a laminar flow in the annular gap. The values of viscosity were computed with the assumption of a Newtonian fluid and, therefore, they provide only an estimate of an "apparent" viscosity. Nonetheless, the results indicated a clear and significant decrease in the mean apparent viscosity with increasing ω . For a fixed rotational speed, the mean apparent viscosity decreased with increasing airflow. Despite it remains unclear how to convert the registered torque, T, to bulk physical properties such as viscosity or yield stress, CFBRs offer an easy way to evaluate and compare different powders and even study the effects linked to changes in particle properties or operation conditions, e.g. temperature or pressure. For example, Landi et al. (2012) used a CFBR to investigate the flow properties of moisturised glass beads with relative humidity rH ranging from 15 % to 70 %. In this work, the rH was controlled by using pre-humidified air stream used as a carrier in the bed. Surprisingly, the minimum fluidisation velocity (0.09–0.12 m.s⁻¹) followed no apparent trend with the rH, and at a fixed rotational speed (**Table 1**) the torque, *T*, was found to decrease monotonically with superficial gas velocity, independently of the value of the *rH*.

A better understanding of the development of the flow and the force chains in a Couette device can be obtained with visualisation techniques such as magnetic resonance imaging (MRI). For example, Moucheront et al. (2010) reported an MRI investigation of granular rheology in a Couette device similar to that in Fig. 9a, where the material (Mustard seeds-MRI sensitive) was confined between two plastic cylinders and sheared by the rotation of the inner one. Multi-layer MRI velocimetry was used to evaluate the velocity profiles at different elevations. The authors were able to determine the effect of the roughness of the inner cylinder and the bottom base on the flow structure. The results demonstrate that the roughness of the bottom surface has an effect localised only to a few granular layers, but the roughness of the inner cylinder wall affects significantly the system determining the sliding velocity and the friction coefficient.

4.2.2 Aerated virtual Couette configurations

The error associated with the roughness of the boundaries and the reliable estimation of shear stress τ are some of the challenges encountered by coaxial-cylinder rheometers. New modified cells address some of these issues proposing new ways to harmonise the experimental data and the wall boundary conditions. A coaxial-cylinder rheometer can be easily modified by replacing the inner cylinder by an impeller while maintaining a Couette flow. The resulting alternative design is called virtual Couette flow. It is depicted in **Fig. 10**. It has been used in the study of granular material by several authors including Marchal et al. (2009) and Yahia et al. (2020). Both studies used the same strategy: the inner cylinder is replaced by an impeller



Fig. 10 Virtual Couette Flow: (a) Schematic, L: cell height; ω : rotational speed, R_e , R_i and r^* : external, inner and optimal radii; (b) Image of the impeller denoted virtual cell. Adapted from Yahia et al. (2020) under the terms of the CC-BY 4.0 license. Copyright: (2020) The Authors, published by Wiley Periodicals, Inc.

with a longitudinal arrangement of equidistant straight baffles aligned with the radial direction, see **Fig. 10b**. The inner element rotates at a fixed position inside the material. In doing so, the impeller creates a cylindrical geometry filled with powder under solid body rotation at the velocity of the baffles. A shearing plane is created exclusively between granules at the outer surface of the moving virtual cylinder, therefore eliminating any potential sliding effects.

Marchal et al. (2009) used a virtual Couette cell to investigate the effects of mechanical vibration on granular rheology. They first introduced the definition of an optimal radial position, r^* , (see Fig. 10a) as a way to translate the torque measurement into a transportable measurement of shear rate, $\dot{\gamma}$, and stress, τ . The optimal radial position, r^* , is an exclusive geometrical property of each Couette configuration. When reported at r^* , both τ and $\dot{\gamma}$ become independent of the dimensions of the outer and inner cylinder. The formulation of r^* was confirmed with further experimentation with Newtonian and non-Newtonian fluids by Aït-Kadi et al. (2002) where several Couette-type flow configurations were tested. This is a critical step in order to fix a standard procedure to report data. Marchal et al. (2009) employed an inner cylinder made of stainless steel. The baffle width was 5 mm and six were glued also on the external cylinder surface to avoid particles sliding. The external cylinder was mounted on a plate to apply mechanical vibration during the shearing process. Experiments were performed with and without vibration using a sample of coarse glass beads and a varying the shear rate, $\dot{\gamma}$ (Table 1). The results obtained in a non-vibrated bed found no stress-strain rate relationship, but under mechanical vibration and low values of $\dot{\gamma}$ the shear stress, τ , and the shear rate, $\dot{\gamma}$, were found to be linearly proportional describing a Newtonian behaviour.

A more advanced design including aeration, called an Aerated Bed Virtual Couette Rheometer (AB-VCR) was proposed by (Yahia et al., 2020). The AB-VCR adapts a virtual Couette geometry similar to the one presented in **Fig. 10** to the FT4 Powder Rheometer. The aerated vessel of the FT4 is a glass cylinder. The inner cylindrical element (so-called virtual cell) has 3D printed six blades made of plastic material (ABS-M30i, SYS systems 3D Printing). Yahia et al. (2020) conducted experiments with and without aeration.

Under no aeration, the shear stress, τ , was found to be independent of shear rate, $\dot{\gamma}$, indicating that the powders were in the quasi-static regime. At a fixed value of $\dot{\gamma}$, the shear stress, τ , was dependent on particle size, which was ascribed to different bulk internal friction of each size class ($\mu_{500\mu m} = 0.46 + 0.02$, $\mu_{50-80\mu m} = 0.36 + 0.01$, $\mu_{160-210\mu m} = 0.32 + 0.01$). The bulk friction coefficient measurements were compared with FT4 torsional shear cell experiments, and they showed very good agreement. During the aeration experiments, ambient air was injected through the sample using a stainless-steel base grid to have a homogeneous flow distribution. The air velocity was increased from no aeration to a fluidisation index FI < 0.4, at a varying shear rate $\dot{\gamma}$ (**Table 1**). All powders display a quasi-static behaviour under this range of aeration. The shear stress, however, was found to decrease with the increasing air velocity in agreement with the observation of Tardos et al. (1998). It is worth noting that unlike them, this work operated only in a batch mode and did not study the effect of an additional static layer of powder atop of the sample to prevent the expansion of the bed. For a fixed fluidisation index, a good agreement was found between the results obtained with samples with the same angle of internal friction, μ , while the shear stress, τ , associated with a higher μ was systematically lower. Yahia et al. (2020) demonstrated the potential of r^* to standardise the measurements in Couette shear testers. The authors compared the use of three virtual cells of a varying radius and a fixed bed height (Table 1). As expected, in every powder, the torque, T, depended on the dimensions of the virtual cell, increasing for an increasing radius. However, the shear stress τ computed at the optimal position, r^* , using the recorded torque, T, was the same for all the cells used.

These devices are still in development and quantitative comparison is necessary, but the selection of presented here shows the potential of Couette cells to investigate the departure from a quasi-static flow. The versatility of the device permits to operate at a wide range of rotational speeds, with or without an overload of static powder, with and without aeration, vibration or an imposed gravitational flow, and they allow varying the geometry with a sound scaling parameter. However, the computation of τ from T in each historical work is based on different assumptions, and the complete of information necessary to reconstruct it is missing from most of the studied. Not all of them operate under the free expansion of the bed, a wide range of particle properties and geometries is present, and the nature of the axial distribution of stress remains to be clarified. Nevertheless, the use of the optimal radial position, r^* , opens the way to establish a standard in the computation of the shear stress and the shear rate. At this point, a comparative analysis of the studies in Couette configurations is limited to the qualitative features summarised in Table 2. Overall, experiments find the expected behaviour at low $\dot{\gamma}$ where τ is independent of $\dot{\gamma}$ with and without aeration. As $\dot{\gamma}$ increases at a high FI aerated cells capture the departure from a quasi-static regime, whereby τ starts to increase for increasing $\dot{\gamma}$. This relation is modified with the operating $\dot{\gamma}$ and the level of aeration. The torque and the bulk viscosity decrease with the superficial gas velocity, and there are conflicting reports regarding the axial distribution of the stress, where both a linear and an exponential dependency with the bed height have been suggested.

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4.3 Mechanically stirred (agitated) beds

Mechanically stirred beds are used to study the highest range of shear rates under complete fluidisation. They measure the torque, T, required to rotate an impeller immersed in a powder bed, Fig. 11a. T depends on the structure of the powder and reflects its flowability. Depending on the impeller shape and its position in the bed, T could be used to compute a characteristic shear stress, τ . For example, Bruni et al. (2005; 2007) developed a mechanically stirred fluid-bed rheometer (msFBR) consisting of a flat impeller (36 mm diameter \times 7 mm height \times 0.7 mm thickness) that rotates at a fixed position inside an aerated bed. The test was conducted varying the impeller depth and the rate of aeration below and above the minimum fluidisation. The powder was preconditioned in every test by fully fluidising it and decreasing the aeration level to the desired value to remove any history effects. Bruni et al. (2005) explored the effect of the aeration rate $(0 \le FI \le 1)$, the impeller speed (0 to 8.79 rpm) and the depth ID on the torque, T, using alumina and soda glass beads. Under aeration, FI < 1, the torque, T, was found to reach a constant value at each speed only after a sufficiently long time, and as expected, it increased with the depth until reaching a plateau at the bottom end. In a later work, Bruni et al., (2007) proposed a model based on the Janssen equation and the Mohr-Coulomb yield criteria to predict the stress at the impeller depth, and evaluate the change in T at low consolidation resulting from the combined action of the sample weight, the aeration and the impeller position. This work studied alumina powders and glass beads varying the position of the impeller with or without aeration (FI < 1), and concluded that independently of the impeller depth, the aeration does not influence T. Tomasetta et al. (2012)

Table 2Summary of the experimental behaviour described in the cellslisted in Table 1.

Reference vs. main experimental observation	
r1	Adopts Bingham model; μ and τ_y decrease with u_g
r2	Measures T and deduces a hydrostatic stress profile (σ ~L). Captures intermediate flow for $\hat{\dot{\gamma}}_{\rm C} > 0.15$
r3	Proposes a vibrated virtual cell and r^* . Finds Newto- nian behaviour $\tau \sim \dot{\gamma}$ under vibration and low $\dot{\gamma}$.
r4	Adopts Newtonian model; μ decreases with ω
r5	Measures normal stresses consistent with a hydrostatic stress profile ($\sigma \sim L$); finds $\tau / \sigma = \tan(\mu) + b \dot{\gamma} ^{0.72}$
rб	Measures T decreases with u_g independently of rH.
r7	Measures normal stresses in agreement with Jensen Eq and in contradiction with a hydrostatic stress profile.
r8	Measures how T decreases with L and u_{g}
r9	Demonstrates the use of r^* in an aerated virtual cell; finds that τ decreases with u_g in quasi-static regime.



Fig. 11 Examples of stirred aerated/fluidised beds: (a) Depiction of the generic geometry (b) Qualitative evolution of the BFE with increasing gas superficial velocity, u_g , during a FT4 downwards test.

estimated the flow properties from the data reported by Bruni et al. (2007) developing a new procedure to compute the shear stress, τ , and the consolidation stress, σ , from the torque. τ was found to increase linearly with σ in a similar way to the yield locus characteristic a shear tester. The bulk friction coefficient, $\mu_{\rm b}$, was then simply computed by τ/σ . It was shown that the computed values of $\mu_{\rm b}$ were in a good agreement with the measurements obtained in a Schulze ring shear test.

The FT4 rheometer can also be used as a mechanically stirred aerated bed. The unit is equipped with a twisted stainless-steel rotated blade that moves downwards and upwards through the powder. As in all the FT4 tests, the powder is prepared in a conditioning cycle where the twisted blade moves through the sample rotating in a clockwise direction, creating a uniform, reproducible lightly packed sample (Freeman, 2007). Two tests can be performed with a mechanically stirred configuration: downwards and upwards. In both, the blade rotates in an anticlockwise direction. In a downwards test, the rotation of a twisted blade results in shearing while the axial movement applies a normal stress to the bed. The torque and the vertical force recorded in a downwards test can be used to derive a so-called Basic Flowability Energy (BFE) which represents the energy required for the blade to complete a full translation. The BFE is, therefore, a parameter specific to the FT4. It lacks universal meaning, but it allows a direct comparison of the flowability of different powders



at various aeration conditions. **Fig. 11b** illustrates the typical evolution of BFE with superficial gas velocity u_g . A non-dimensional aeration ratio (AR) defined as the ratio of BFE at no aeration to BFE at a given air velocity has been proposed as a way to classify flowability. If AR ~ 1 the powder is not sensitive to aeration, which is typical of very cohesive powders or a higher binder content. If AR >> 20, the powder displays a low cohesive strength, it is very sensitive to aeration and likely to be fluidised. There are many examples where the FT4 aeration test has been able to rank the flowability of powders (Freeman, 2007). For example, Gnagne et al. (2017) reported the properties of flours, Ono and Yonemochi (2020) studied the effect of additives in the flowability of ibuprofen and Ludwig et al. (2020) evaluated its behaviour under fluidisation.

Although the method is clearly able to rank powders, it does not provide a transportable set of properties. The complex geometry of the blade makes it difficult to evaluate the characteristic strain rate and the shear stress, but the combination of experimental and computational studies can help to address some of these limitations. The work of Hare et al. (2015; 2017) suggests that it is indeed possible to determine a characteristic τ for a powder in the FT4 aeration test. Hare et al. (2015; 2017) combined experiments and DEM simulations to determine the shear stress profile in the bed. In order to estimate the strain rate and shear stress they analysed the dynamic behaviour of a bed of large cohesive glass beads ($d_p = 1.7-2.1$ mm) during the FT4 aeration test and found that τ was be constant across the blade length and increased as the impeller penetrated the bed. Hare et al. (2017) later provided a similar framework to analyse the stress and strain rates, and Nan et al. (2017a; 2017b) combined computational and experimental work to study how aeration and shape affected the stress profiles in samples of soap roads, polyethylene and glass beads.

Oher commercially available stirred beds include the Anton Paar Powder Cell (APPC). This device works with the same principle as the msFBR (Bruni et al., 2005; 2007) recording the torque acting on an impeller immersed in an aerated powder bed. The bed can be operated either below or above the minimum fluidisation. The cell containing the powder is made of a glass cylinder with a porous bottom plate, and the unit is equipped with impellers of different shapes and wall conditions. Salehi et al. (2017b) used an APPC to study the effects of the impeller depth and the aeration rate on the torque acting on a flat blade impeller in samples of free-flowing powders, namely glass beads, alumina and sieved silica sand, up to the minimum fluidisation (0 < FI < 1). The dependency of T on the air velocity, the bed height and the impeller depth confirm the observations of Bruni et al. (2005; 2007). They proposed to use a fitting parameter as the "effectiveness" of the impeller to estimate T at different depths. The model is based on the assumption that the shearing occurs only within the cylindrical region captured by the impeller rotation. In a later work, Salehi et al. (2018) measured T under different geometries in non-aerated glass beads of different sizes. In a similar fashion to the works in an FT4, a combination of computational and experimental data was used to evaluate internal flow parameters such as the bulk friction coefficient between particles and between particles and the blade.

5. Conclusions

Classic shear cell devices and a broad array of ad-hoc experimental tests have served for decades as the standard to evaluate the flow threshold of cohesive industrial powders. However, looking only at the initiation of the flow is a rather simplistic view of the rheology of granular materials. It fails to capture their dynamic behaviour and the transition to intermediate and inertial regimes. These are fundamental aspects of the flow behaviour observed in natural systems and industrial units. In order to efficiently process powder, optimise unit operations and develop new technologies involving dense particle flows such as process, energy and additive manufacturing, one requires a precise understanding of all granular flow regimes. Dynamic tests and many flow configurations have been proposed as alternative ways to characterise the dynamic behaviour of a powder. However, even the simplest devices such as rotating drums, chutes or avalanches display a very complex flow pattern, and the resulting bulk properties are difficult to interpret.

It is important to move towards establishing a rigorous and transportable analysis of the data across different devices. This review provides an overview of the strategies developed in recent years to expand the usage of conventional shear cells from the quasi-static regime into the characterisation of intermediate and inertial flows by applying external actuation. However, the practical difficulties in operating at higher shear rates and the complex behaviour of granular matter make the development of flexible instruments very difficult. Commercially available units such as the FT4 rheometer or the Anton Parr Powder Cell have tackled this challenge using a rotational cell under aeration to achieve very small consolidation stresses. Many other customised devices have followed similar principles using modified testers, flow devices, fluidised bed rheometers and mechanically agitated beds. The main drawback of these units is linked to the assumptions employed to establish a relation between the registered torque and the characteristic stresses and shear rates. In this work, we have paid particular attention to the development of aerated Couette flow configurations to address some of these issues. Not only it is a flexible geometry with a tight and independent control normal and shear stress over a broad range of shear rates, but these units offer a direct way to harmonise the

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interpretation of data. They provide geometry-independent shear rates and stresses, and the introduction of the new virtual-cell concept removes most of the concerns associated to earlier units. However, their application is still limited, and further work is necessary to assess their viability as an industrial characterisation technique.

Acknowledgements

RO acknowledges financial support from the EPSRC (EP/N034066/1).

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Static and Dynamic Stickiness Tests to Measure Particle Stickiness[†]

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Abstract

Sticking of particles has a tremendous impact on powder-processing industries, especially for hygroscopic amorphous powders. A wide variety of experimental methods has been developed to measure at what combinations of temperature and moisture content material becomes sticky. This review describes, for each method, how so-called stickiness curves are determined. As particle velocity also plays a key role, we classify the methods into static and dynamic stickiness tests. Static stickiness tests have limited particle motion during the conditioning step prior to the measurement. Thus, the obtained information is particularly useful in predicting the long-term behavior of powder during storage or in packaging. Dynamic stickiness tests involve significant particle motion during conditioning and measurement. Stickiness curves strongly depend on particle velocity, and the obtained information is highly relevant to the design and operation of powder production and processing equipment. Virtually all methods determine the onset of stickiness using powder as a starting point. Given the many industrial processes like spray drying that start from a liquid that may become sticky upon drying, future effort should focus on developing test methods that determine the onset of stickiness using a liquid droplet as a starting point.

Keywords: stickiness, powders, caking, glass transition temperature, sintering

1. Introduction

Sticking of particles has a tremendous impact on numerous industries that process powders. Sticking can cause several issues, such as fouling and blockage of equipment, or caking of stored powder. It can also be used advantageously to produce agglomerates with beneficial properties. Why, how, and when particles stick together are critically important questions. In this review, we focus on the 'when' question by reviewing the experimental methods commonly used to determine the conditions under which sticking occurs. We hereby focus on the stickiness of hygroscopic amorphous powders, which play a major role in the food industry (Boonyai et al., 2004). Crystalline materials, which may also stick, but through a different mechanism (Kamyabi et al., 2017), are beyond this review's scope.

Whether two particles stick depends on their material and a wide variety of parameters, including their temperature, and moisture content. A common way to characterize

the stickiness of a material is to map the stickiness based on the environmental temperature and the moisture content. The moisture content can be described in terms of the particle's water mass fraction (x_w) , or the equilibrium environmental relative humidity (RH). The part of the parameter space for which the material is sticky is called the sticky region, which is bounded by the so-called sticky-point curve, $T_1(x_m)$, and the so-called tack boundary, $T_2(x_m)$, as illustrated in Fig. 1. Besides the environmental parameters, this map also illustrates the particle's material properties in the form of a boundary between the glassy state and the rubbery state, known as the glass transition temperature, $T_{a}(x_{w})$. The rubbery state has some overlap with the sticky region, and with further hydration becomes the liquid state (Roos, 2002). While particles are non-sticky in the glassy state, material properties, especially viscosity, drastically change upon transitioning to the rubbery state. Hence, the curves represented by the differences $T_1(x_w) - T_q(x_w)$ and $T_2(x_w) - T_q(x_w)$ are two meaningful measurements of the sticky-region that include the influence of temperature, moisture content, as well as the material. The distance between the sticky-point curve $T_1(x_w)$ and the glass transition curve $T_{a}(x_{w})$ often slightly depends on x_{w} (Palzer, 2005). Therefore, the onset of stickiness is commonly reported as a constant critical deviation from $T_{a}(x_{w})$, denoted as $(T-T_{a})_{c}$.



[†] Received 5 June 2020; Accepted 11 August 2020 J-STAGE Advance published online 19 September 2020

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Fig. 1 Map of temperature and moisture content showing the region in which a material is considered sticky. This region is enveloped by the sticky-point curve $(T_1(x_w))$, the tack boundary $(T_2(x_w))$, and the temperature above which the material decomposes. The sticky-point curve and tack boundary are often reported with respect to the glass transition temperature of the material (dashed line), which separates its glassy state from its liquid state. The difference $T_1(x_w) - T_g(x_w)$ is in literature more commonly referred to as $(T - T_g)_c$. Figure is modified from Lockemann (1999) and Kudra (2003).

Experimental stickiness tests generally aim to determine the sticky-point curve or the tack boundary by measuring stickiness for different temperatures and moisture contents. While most methods approach the sticky region from the glassy state to find $T_1(x_w) - T_q(x_w)$, a limited number of methods approach the sticky region from the liquid state to find $T_2(x_w) - T_a(x_w)$. Although the tack boundary is less well understood, it is known that the change in behavior is less sharp than near the sticky-point curve (Kudra, 2003). While the measured parameter may differ between the experimental methods, what all methods have in common is that they follow two steps: (1) a conditioning step, where the material is subjected to a specified temperature T and humidity RH for a certain time window and (2) a measurement step where the stickiness of the powder is measured (Boonyai et al., 2004). Whereas these steps are separated for some methods, they are intertwined for others. Hence, not only the duration of conditioning influences the sticky region's boundaries but also the used measurement method. While the influence of conditioning time is well understood (Kamyabi et al., 2017), the influence of particle motion in the conditioning and/or measurement step on the boundaries of the sticky region is still unclear. For skim milk powder, one of the most abundantly tested materials, a wide range for $T_1(x_w) - T_q(x_w)$ has been reported. For particles that are static during the conditioning step, values as low as 8 °C were reported for $T_1 - T_q$ (Verdurmen et al., 2006). By contrast, values as high as $T_1 - T_q = 63$ °C were reported for particles moving at tens of meters per second (Walmsley et al., 2014).

Following Verdurmen et al. (2006), we therefore distinguish between two classes of methods in this review. The first class is where the particles can be considered static during conditioning (not set in continuous motion through external means). The second class is where the particles are moving during conditioning. We refer to the first class of methods as *static stickiness tests* and to the second class as *dynamic stickiness tests*.

This review aims to provide an overview of the available methods to measure stickiness. As static stickiness tests, we describe various visual observation tests, the shear test, the penetration test, and the blow test. As dynamic stickiness tests, we describe the sticky-point test, the fluidized bed test, the particle gun, the cyclone test, the optical test, and the probe test. For each method, we describe how it can be used to determine either the sticky-point curve $T_1(x_w)$ or the tack boundary $T_2(x_w)$ of the sticky region. Additionally, we describe what we view to be the method's best application in industry. The overview of methods shows that particle velocity plays a significant role in the measured boundaries of the sticky region, illustrating the importance of choosing the most appropriate method for the application in mind.

2. Glass transition temperature

The glass transition temperature T_g marks the temperature where an amorphous material transitions from a glassy state to a rubbery state upon increasing temperature. While both states are fundamentally a liquid, the behavior of the glassy state is solid-like, being hard and brittle, and the rubbery state behaves like a highly-viscous liquid. The nature of the glass transition is the molecular freedom of movement, which is restricted in the glassy state (Roos, 2002).

The most common method to experimentally determine T_{q} is using differential scanning calorimetry (DSC), although several other methods are available (Li et al., 2019). In DSC, the T_q is found by subjecting the material in the glassy state to a temperature ramp and measuring the specific heat capacity. The specific heat capacity shows a characteristic change during the glass transition (Hogan et al., 2010; Roos, 2010). By repeating the experiment at different x_{w} , the curve for $T_{q}(x_{w})$ shown in **Fig. 1** can be experimentally constructed. Similarly, dynamic vapor sorption (DVS) can be used to measure the vapor sorption characteristics by applying a ramp in relative humidity at a fixed T while measuring the sample's mass. In the glassy state, water sorption only occurs at the surface, while the rubbery state also allows for bulk sorption, such that a characteristic change in the water sorption rate is observed at T_{a} (Burnett et al., 2004).

The glass transition temperature can also be estimated theoretically, for example using the Gordon-Taylor or Couchman-Karasz equation. The Gordon-Taylor equation can be used to determine the influence of water on the glass transition temperature $T_g(x_w)$ of a dry powder, based on the glass transition temperature of the anhydrous powder ($T_{a,s}$)



and pure water ($T_{\rm g,w}$), and the weight fraction of moisture, $x_{\rm w}$, as

$$T_{\rm g}(x_{\rm w}) = \frac{(1 - x_{\rm w})T_{\rm g,s} + kx_{\rm w}T_{\rm g,w}}{(1 - x_{\rm w}) + kx_{\rm w}}$$
(1)

with $T_{g,w} = -135$ °C (Roos, 2002). The constant k is often calculated from the densities ρ , $T_{g,s}$, and $T_{g,w}$ as $k = (\rho_s T_{g,s})/(\rho_w T_{w,s})$ (Katkov and Levine, 2004; Simha and Boyer, 1962). The Couchman-Karasz equation, while similar to Eq. (1), is based on thermodynamic additivity of specific heat capacity. Although different versions are reported, the so-called 'modified' version is found when using $k = \Delta C_{p,w}/\Delta C_{p,s}$ in Eq. (1). The changes in heat capacity ΔC_p at T_g can be found using DSC (Sochava, 1997). For $\Delta C_{p,w}$, 1.94 J K⁻¹ g⁻¹ is often used (Katkov and Levine, 2004; Roos, 2002). Katkov and Levine 2004 showed that the modified version of the Couchman-Karasz equation overestimated the T_g of mixtures and underestimated the plasticizing effect of water while they obtained a better fit using the so-called 'original' Couchman-Karasz equation

$$\ln (T_{\rm g}) = \frac{(1 - x_{\rm w})\ln (T_{\rm g,s}) + kx_{\rm w}\ln (T_{\rm g,w})}{(1 - x_{\rm w}) + kx_{\rm w}}$$
(2)

While the Gordon-Taylor and Couchman-Karasz equations are suitable for most simple systems and can be used to construct the curve for $T_g(x_w)$ in **Fig. 1**, they should be used with caution when considering complex mixtures (Katkov and Levine, 2004).

The glass transition temperature servers as a natural reference in the stickiness map and allows one to compare the stickiness of different type of materials. Similarly, the T_g serves as a reference in an attempt to come to a universal predictive equation of the dynamic viscosity in the rubbery state. The Williams-Landel-Ferry (WLF) equation relates the viscosity of a material to the distance from the T_g -curve $(T - T_g)$ as

$$\log_{10} \frac{\eta}{\eta_{\rm g}} = \frac{C_1 (T - T_{\rm g})}{C_2 + (T - T_{\rm g})} \tag{3}$$

with C_1 and C_2 two constants and η_g the viscosity at the glass transition temperature. While the WLF equation is often considered to be valid for temperatures up to $T_g + 100$ °C (Lomellini, 1992; Williams et al., 1955), it is only valid if correct values for the constants and η_g are chosen. Values of η_g are typically in a range between 10¹¹ Pa s to 10¹⁴ Pa s (Downton et al., 1982; Katkov and Levine, 2004; Murti et al., 2010; Palzer, 2005; Paterson et al., 2015; Wallack and King, 1988). Recently, the glass viscosity of freeze dried amorphous lactose was measured to be 1.1×10^{14} Pa s, although the authors suggest that further confirmation is required (Paterson et al., 2015). The wide variety of reported constants suggests that there is no universal set valid for different types of materials and different temperatures. Nevertheless, $(C_1, C_2) = (-17.44, 51.6 \text{ K})$ as originally

reported by Williams et al. (1955), are often considered to be universal (Aguilera et al., 1993; Murti et al., 2010; Palzer, 2005; Schulnies and Kleinschmidt, 2018; Wallack and King, 1988). Peleg (1992) found that these constants give large deviations when $T - T_q > 20$ °C, and suggested $(C_1, C_2) = (-10.5, 85.6 \text{ K})$, which better matched the experimental trend for the η_{q} of amorphous lactose measured by Paterson et al. (2015). However, $(C_1, C_2) = (-8.86,$ 101.6 K) also provided a good fit to other experimental data (Dagdug and García-Colín, 1998; Ferry, 1980). Others use material-specific constants, such as $(C_1, C_2) = (-14.5,$ 36.4 K), which were fitted for skim milk powder (Walmsley et al., 2014). Since the WLF equation is exponential, care should be taken in the choice of the constants when using the WLF equation to predict the dynamic viscosity. To illustrate the importance of this choice for a prototypical case $(T - T_{g} = 20 \text{ °C} \text{ and } \eta_{g} = 10^{12} \text{ Pa s})$, the constants by Williams et al. (1955) give $\eta = 1.3 \times 10^7$ Pa s, while the constants by Peleg (1992) gives $\eta = 1.0 \times 10^{10}$ Pa s, which is a difference of three orders of magnitude. As there are currently no clear rules of thumb on the selection of constants, we suggest that best practice would be to fit C_1 and C_2 to experimentally measured viscosity data.

The direct relation between viscosity and $T - T_q$ through the WLF equation leads to the natural question whether viscosity can be used as a predictor for stickiness. The success of viscosity as a predictor is expected to depend on the dominant mechanism of adhesion. For hygroscopic amorphous powders close to T_q , sticking is expected to occur primarily through immobile liquid bridging or viscoelastic deformation (Palzer, 2005). In case immobile liquid bridging primarily causes sticking, we generally expect viscosity to be more meaningful than when viscoelastic deformation primarily causes sticking. More specifically, using sintering theory by Frenkel (1945) and classic viscoelastic contact models, Palzer (2005) could predict the critical $T - T_{a}$ needed for sticking. However, this model did not successfully predict sticking of high velocity particle gun experiments (Murti et al., 2010). A contact model for adhesive elastic particles showed better results when predicting the critical $T - T_a$ for high velocity collisions (Walmsley et al., 2014). The mentioned works strongly suggest that viscoelasticity should be accounted for when predicting $(T - T_q)_c$ for collisions of particles in motion, and that the observed $(T - T_g)_c$ is a result of the colliding material's rheological behavior and the collision's kinetics.

3. Static stickiness tests

Testing stickiness of powders using static stickiness tests follows a general protocol. First, a powder bed is compressed under a stress σ to cause a certain amount of consolidation (**Fig. 2a**). Second, the powder is conditioned


by exposing it to an environment of controlled temperature and relative humidity (**Fig. 2b**). The duration of this conditioning step can be adjusted. When sufficiently long, the powder's moisture content is in thermodynamic equilibrium with the moisture in the environment such that x_w and *RH* are related through a vapor sorption isotherm. Third, a measurement is performed on the conditioned powder (**Fig. 2c**). Prior to the measurement, the powder can be considered static with little movement of the particles. Therefore, we refer to this class of tests as static stickiness tests, which are deliberately different from the dynamic stickiness tests in which the particles are actively set in continuous motion during the conditioning and measurement step. Next, we describe the different static stickiness tests.

3.1 Visual observation

The most straightforward form of analysis is through visual observation. Typically, a sample with a specified dry matter content is placed in a closed container. After conditioning it at a given temperature, the container is turned upside down to see whether any particles are stuck to the bottom. This procedure is repeated at different temperatures until particles noticeably stick to the bottom, which is identified as the sticky-point temperature (Palzer, 2005). By repeating this procedure for different moisture contents, the sticky-point curve $T_1(x_w)$ in **Fig. 1** can be

constructed. An alternative visual observation test is one in which the powder's temperature is increased stepwise while observing changes in the appearance of the powder bed (Tsourouflis et al., 1976; Verdurmen et al., 2006).

3.2 Shear test

Shear tests are used to characterize powder stickiness by measuring the powder's response to shear stress. Two common approaches are uniaxial compression and shearing in shear cells. The uniaxial compression approach consolidates the bed with normal stress σ and then compresses along one axis until failure. The failure stress $\sigma_{\rm f}$ for different values of σ gives a yield locus that can be used to find the unconfined yield strength σ_c by drawing a Mohr circle starting at $\sigma = 0$ Pa (Schulze, 2008). The unconfined yield strength σ_c is used as the parameter for bed strength and can be determined for different environmental T and RH (Fitzpatrick et al., 2007b; Hartmann and Palzer, 2011). In order to find a sticky-point curve $T_1(x_w)$, a critical bed strength, which is characteristic for a sticky powder, must be determined first. It can be empirically determined before testing using the same or comparable materials (Palzer and Zürcher, 2004).

Similarly to uniaxial compression, shear cells can be used to determine σ_c and acquire $T_1(x_w)$ by defining a critical σ_c for the bed strength of a sticky powder (Hartmann and Palzer, 2011; Schulnies and Kleinschmidt,



Fig. 2 An overview of the static stickiness tests. a) In the consolidation step, the powder is compressed under a stress σ . b) In the conditioning step, the powder is subjected to temperature *T* and relative humidity *RH* for a specified duration. c) The measurement of stickiness proceeds differently per test.



2018). However, shear cells improve on result consistency by preshearing before measuring the failure stress. Preshearing to steady-state at normal stress σ_1 eliminates any stress history, for example, due to filling (Schulnies and Kleinschmidt, 2018). After preshearing, the shear stress is reversed to reduce the shear stress to zero. Subsequently, the sample is sheared to failure while measuring shear stress σ_{τ} under normal stress σ_2 so that $\sigma_1 < \sigma_2$ (overconsolidation), which ensures a peak is observed for the failure stress (Schulze, 2008). By shearing to failure at different σ_2 while preshearing at identical σ_1 a yield locus can be found. From this point on, the acquisition of σ_c and $T_1(x_w)$ is similar to uniaxial compression.

Besides acquiring the sticky-point curve, shear tests have other commonly used applications related to stickiness and powder cohesion. Shear tests are commonly used to quantify the powder flowability. The flowability is described in terms of the flow function, which is the inverse slope in a plot of unconfined yield strength σ_c versus normal stress σ (Fitzpatrick et al., 2007b; Jenike, 1964; Papadakis and Bahu, 1992; Schulze, 2008). Shear cells can also be used to measure wall friction. This is done by replacing the bottom ring of a shear cell with the wall material. When choosing the wall material similar to industrial surfaces or packaging materials, the adhesion of powder to these substrates can be measured (Papadakis and Bahu, 1992; Schulze, 2008).

Commonly used examples of shear cells are the manual Jenike shear cell (Jenike, 1964), the automated Schulze ring shear test (Schulnies and Kleinschmidt, 2018), or the more recent Freeman FT4 Powder Rheometer (Freeman, 2007) and Anton Paar MCR rheometers (Anton Paar GmbH, 2020; Groen et al., 2020). Conveniently, both the Freeman and Anton Paar powder rheometers can quickly change environmental T and RH independently through powder bed aeration with conditioned airflow (Freeman, 2007; Groen et al., 2020; Mitra et al., 2017). Besides uniaxial compression and shear cells, other types of shear tests for measuring flowability have been reported (e.g., Warren Spring cohesion tester, Peschl shear cell). These were not described as their application to find $T_1(x_w)$ was not found in literature (Pasley et al., 1995).

3.3 Penetration test

Penetration tests are similar to the uniaxial compression tests, but use a puncher with a diameter of 1 mm to 2 mm to penetrate the powder bed to a preset depth (Knight and Johnson, 1988). Measurement of the required penetration force F_p , which is a measure for bed strength (Özkan et al., 2002; 2003), is done after conditioning at a fixed *T* and *RH* for a given time. Through repetition, while varying these conditions, the sticky-point curve $T_1(x_w)$ is found for the combinations of *T* and *RH*, where the measured F_p equals a predetermined critical value for which the powder is

considered sticky (Özkan et al., 2003).

3.4 Blow test

The blow test uses a small thin tube to blow air at a powder bed surface. The tube is placed millimeters above the surface at an angle of 45°. The airflow through the tube is increased until particles dislodge from the surface of the conditioned powder bed, which is the endpoint of the blow test. The flow rate of air at which particles start dislodging is a measure for bed strength (Paterson et al., 2001). The sticky-point curve $T_1(x_w)$ is found at the *T* and *RH* where the airflow to dislodge particles reaches a predetermined critical value for which the powder is considered sticky (Foster et al., 2005; Paterson et al., 2005).

A benefit of the blow test is the ability to test multiple times without needing to repeat the consolidation and conditioning step. The powder bed sits on a distributor plate, which sections the powder into multiple parts with an equal amount of powder. Each section of powder is conditioned with the same T and RH and can be measured separately by rotating the thin tube. Therefore, the blow test is convenient when interested in temporal measurements, such as determining the rate of bed strength increase (Paterson et al., 2005).

3.5 Comparison of tests

While simplicity is a strength of the visual observation tests, it is also their greatest weakness. The accurate detection of the sticky-point temperature relies on the observer's experience. Based on caking theory, we expect that visible changes in powder properties occur after a high degree of agglomeration has taken place (Kamyabi et al., 2017). Hence, human observers can miss the onset of stickiness, which would cause an over-prediction of the sticky-point temperature. The onset of stickiness can be more precisely quantified with the other tests. Based on the literature, we find that shear tests are more accurate than penetration tests, with less scatter of data and time consolidation effects that are easier to detect (Knight and Johnson, 1988; Schwedes, 2003). Based on these findings, we recommend using uniaxial compression or shear cells instead of penetration tests, in line with Knight and Johnson (1988), who recommended to only use penetrometry in support of shear cell experiments. While shear tests are applied to the bulk of the powder, the blow test is applied to the powder's surface, suggesting that the blow test mostly tests the surface conditions. Blow tests nevertheless create channels in the powder bed (Billings et al., 2006; Paterson et al., 2005), indicating that the bulk is strongly affected by blow test. Hence, we expect that blow tests can be used to determine (bulk) stickiness, similarly to the shear tests. An advantage of the shear tests over the blow test is that the compression

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during consolidation can be maintained during conditioning, while an advantage of the blow test over the shear tests is that multiple measurements can be performed without having to repeat the consolidation and conditioning steps.

The shear, penetration, and blow tests can be used to quantify bed strength for different T and RH based on the measured parameter (yield strength, penetration force, flow rate). To, in turn, relate bed strength to stickiness, a predetermined value of the critical bed strength is required at which the powder of interest is considered sticky. A way to overcome having to predetermine a critical bed strength is by considering the temporal behavior. Experiments with the blow test, for example, show an initial linear increase of bed strength with time (Foster et al., 2006; Paterson et al., 2005). Similar experiments with shear cells are timeconsuming since each test requires repetition of consolidation and conditioning, but suggest a similar linear increase of bed strength with time (Fitzpatrick et al., 2007a; 2007b; 2008). By measuring the rate (i.e., slope) of increase for a range of $T - T_{q}$, one can infer the sticky-point curve $T_{1}(x_{w})$ by plotting the rate versus $T - T_q$ and extrapolating to arate of zero. In case the critical bed strength is not available a priori, studying the temporal behavior to determine the rate of bed strength increase as a function of $T - T_q$ provides a means to construct the sticky-point curve $T_1(x_w)$.

3.6 Application areas of static stickiness tests

Generally, the static stickiness methods are useful in predicting the long-term behavior of powder during storage, transport, or in packaging. In these situations, particles may stick together under the influence of humidity in a process known as caking. This process comprises multiple steps. Firstly, environmental conditions cause particle surfaces to become viscous. Contacting liquid particle surfaces become connected through liquid bridges. Secondly, the liquid bridges that formed grow in size, increasing powder

 Table 1 List of methods to measure dynamic stickiness

cohesion. Thirdly, the pores that existed between particles disappear as the liquid fills up the pores (Kamyabi et al., 2017). During the caking process, the bed strength initially increases with time until a maximum value is achieved. As the process continues, the bed strength starts to decrease, attributed to partial crystallization of material to non-sticky crystals (Fitzpatrick et al., 2007b), as well as a decreased liquid bridge viscosity due to increased liquid adsorption (Hartmann and Palzer, 2011). Static stickiness tests are particularly suitable for assessing the progress of caking by monitoring bed strength as a function of time. Shear tests are particularly useful because they can emulate storage environment conditions in a warehouse or transport vehicle by maintaining a certain level of compression during conditioning and measurement. Using shear cells where the powder can be sheared against a wall material is also applicable to measure powder stickiness in food packaging.

4. Dynamic stickiness tests

The class of dynamic stickiness tests covers the tests where particles are not static during conditioning, but set in continuous motion through external means. This introduces particle velocity or contact time between particles as an additional relevant parameter. An overview of dynamic stickiness tests is listed in **Table 1**, showing the measured parameter and the most suitable application. Most dynamic stickiness tests approach the sticky region from the glassy state, while just a few approach it from the liquid state.

4.1 Sticky-point test

The sticky-point test is the earliest reported method to measure stickiness, hence the name (Lazar et al., 1956). This test has also been referred to as a propeller-driven test (Boonyai et al., 2004). As shown in **Fig. 3**, the device

Table 1 List of methods to measure dynamic stickiness			
Method	Measured parameter	Application	
Sticky-point test	Torque	Powder mixing	
Fluidized bed	Bed collapse/Pressure drop	Fluidized beds:	
		Preventing bed collapse	
		Granulation	
Particle gun	Deposited mass	Pneumatic transport	
		Cyclones	
Cyclone test	Visual change	Pneumatic transport	
		Cyclones	
		Fluidized beds	
Optical test	Scatter intensity	Versatile application, opaque powder	
Probe test	Tensile force	Droplet evaporation	



uses a container in which a powder with known moisture content x_w is placed. The sample container is submerged in a heating medium to control the powder's temperature. The sample is continuously stirred at fixed angular velocity with a stirring device, and the required torque τ is measured. Typically, a temperature ramp is imposed where the temperature is slowly increased until the powder transitions from the glassy to the rubbery state. Above T_g , the cohesive forces increase. Further increase of the temperature leads to particles sticking together, leading to a sharp increase in the required τ . The temperature where this sharp increase is observed is identified as the sticky-point temperature. By repeating the test with different x_w , the sticky-point curve $T_1(x_w)$ can be found.

Detection of the sticky-point in the earliest versions relied on manual stirring. When the stirring had become noticeably more demanding, the sticky-point was reached (Downton et al., 1982; Lazar et al., 1956). More accurate detection methods use automatic stirrers or shear cells equipped with stirrers, which record the τ required for stirring (Özkan et al., 2002; Wallack and King, 1988). Recently, the method has been further improved by utilizing aeration in an Anton Paar rheometer equipped with a propeller (Groen et al., 2020). The option to aerate the powder is used to fluidize the powder, which occurs at a sufficiently high airflow velocity. The powder conditions are controlled by changing the T and RH of the airflow, instead of using a heating medium surrounding the container. The propeller stirs the fluidized powder and measures the required τ . The required τ is substantially smaller than without fluidization, although the rheometers are sufficiently sensitive (Groen et al., 2020). The benefit of aeration or fluidizing is that environmental conditioning occurs rapidly by changing the air's temperature and humidity. In our view, this makes the sticky-point test combined with fluidizing the powder a promising method for measuring dynamic stickiness, both in terms of accuracy and a shorter experimental time.

Besides applying the sticky-point test to free-flowing powder, it has also been used to measure the stickiness of drying liquids. Hence, instead of determining the stickypoint curve $T_1(x_w)$, the tack boundary $T_2(x_w)$ is determined. Kudra (2003) used a laboratory batch dryer equipped with a stirrer to measure the stickiness of drying sludge. They found that the temperature where the torque substantially increased was different from the $T_1(x_w)$ that is found when approaching from the glassy state. The conclusion was that most materials have a sticky-region in which they are sticky (Kudra, 2003).

4.2 Fluidized bed

As discussed for the sticky-point test, the fluidization of powder reduces the required conditioning time. However, because powder fluidization is highly sensitive to powder cohesiveness, the fluidized bed in isolation is also suitable to measure stickiness. In a fluidized bed, which is shown in Fig. 4, a powder bed sits in a column while airflow is applied at the bottom. Fluidization causes expansion of the powder bed so that the powder displays fluid-like behavior with a high degree of mixing. The sticky-point curve's acquisition goes as follows: The T or RH of the fluidizing air is increased stepwise. Most commonly, a RH ramp is used at a fixed T by increasing the airflow's humidity. As the cohesiveness increases, there is a point where the fluidized bed collapses (defluidization). The conditions where the collapse of the powder bed is observed, visually, or using pressure drop measurements, is the sticky-point T_1 (Palzer, 2005; Verdurmen et al., 2006). By repeating the RH ramp at different temperatures, the sticky-point curve $T_1(x_w)$ can be drawn.

In many cases, fluidized bed collapse is detrimental when it occurs. Hence, much research has been done on the detection and prevention of bed collapse (Bartels et al., 2008). Methods such as the attractor comparison method can be used to detect early changes in the bed that indicate an upcoming collapse (Van Ommen, 2001) and have been used to determine the sticky-point curve $T_1(x_w)$ (van



Fig. 3 A sticky-point test. A powder with known moisture content is placed in a temperature-programmable water bath. The powder is stirred at a fixed angular velocity, and the required torque τ is measured.



Fig. 4 A fluidized bed test. The humidity or temperature of the conditioned airflow is increased stepwise until the powder bed collapses.

der Knaap, 2006; Verschueren et al., 2007). When such detection methods are implemented, the sensitivity of the fluidized bed as a stickiness test is expected to be high.

4.3 Particle gun

The particle gun has been designed to measure the sticking of high-velocity particles to a wall and is shown in Fig. 5. It is a duct through which conditioned air is flowing at high velocity with a target plate at the far end of the duct. For each experiment, a sample of approximately 25 g powder is introduced into the duct. The particles become entrained in the conditioned air-jet shortly until eventually impacting the target plate. Due to the short exposure of particles to the air, the particle gun relies heavily on the rapid acclimation of the powder surface to environmental conditions. The short acclimation time has consequences for liquid bridge formation as the thin surface region that has adsorbed vapor limits their potential width (Murti et al., 2010). The measured parameter is the percentage of injected powder deposited on the target plate. Plotting this parameter versus $T - T_{a}$ shows negligible 0 % deposition until a critical value of $T - T_q$ is reached. Above this temperature, deposition is observed and increases linearly with $T - T_{a}$. The temperature where deposition starts increasing is taken as $T_1(x_w)$ (Zuo et al., 2007).

4.4 Cyclone test

The cyclone test, shown in **Fig. 6**, uses a cyclone in which conditioned air is circling (Boonyai et al., 2002). When the air is at a steady-state, approximately 1 g of powder is injected at the top of the cyclone. When conditions are such that the powder becomes sticky, particle lumps and powder deposition on the cyclone are observed within minutes. Longer experimental times lead to full immobilization of the powder. The experiment starts at a low *RH* of the air and is increased stepwise until lumping and deposition are observed visually, which marks a point on the sticky-point curve $T_1(x_w)$.

4.5 Optical test

Lockemann (1999) proposed an optical test, shown in **Fig. 7**, which uses changes in reflectivity to determine the sticky-point curve. The proposed optical test consists of a rotating test tube containing the free-flowing powder with known (x_w) . The tube is inserted into an oil bath with a programmable temperature. A near-infrared source emits light to the sample while a fiber-optical sensor records the back-scattered signal. The sensor is also immersed in the oil-bath to prevent any refraction of the signal. When particles in the tube stick together, the powder flowability changes, which is observed as a sudden change in reflectivity. This marks the sticky-point temperature T_1 (Lockemann, 1999). The experiment has to be repeated for different x_w to determine $T_1(x_w)$.

4.6 Probe test

The probe test is the only method that is solely applicable to measure stickiness when starting from the liquid state. Hence, instead of the sticky-point curve $T_1(x_w)$, the tack boundary $T_2(x_w)$ is found. The probe test can be applied to liquid films or droplets (Chen J. et al., 2008; Werner et al., 2007a). The approach for either is similar.



Fig. 6 A cyclone stickiness test. Conditioned airflow is used to circulate a powder sample through the cyclone. Non-sticky particles remain entrained in the cyclone, while sticky particles can agglomerate or stick to the cyclone wall.



Fig. 5 The particle gun. Conditioned air flows with high velocity through an air duct. The powder is introduced through a funnel, and the entrained particles hit the target plate. Particles either bounce off or deposit on the plate.



Fig. 7 The optical test. A rotating sample tube is placed in a heated water bath. A fiber-optical sensor illuminates the sample and receives scattered light. Redrawn from Lockemann (1999).



The droplet probe test is shown in Fig. 8 and goes as follows. Droplet evaporation is monitored gravimetrically by placing the droplet on a scale (Werner et al., 2007a, 2007b). At some point during evaporation, a probe is lowered with a fixed speed to touch the droplet's surface and then retracted, also with a fixed speed, while the required force for retraction is measured. Hence, this approach is similar to a force measurement with Atomic Force Microscopy (Fabre et al., 2016). The peak tensile force F_{TU} is then determined, which is a measure of the tack, or stickiness, of the sample (Hammond, 1965; Kambe and Kamagata, 1969). By plotting F_{TU} versus drying time, a point is found where F_{TU} increases substantially, marking the tack boundary $T_2(x_w)$ with x_w determined gravimetrically based on the initial solids concentration and the measured weight loss. It should be noted that the measured $F_{\rm TU}$ is influenced by the probe speed and material (Adhikari et al., 2007; Green, 1942). Besides x_w , the sample's temperature T also changes during evaporation, which should be accounted for when determining $T_2(x_w)$ (Schutyser et al., 2019).

4.7 Comparison of tests

The particle gun, fluidized bed, cyclone test, and optical test use a powder as a starting point, approaching the sticky region from the glassy state to find the sticky-point curve $T_1(x_w)$. The probe test starts from the liquid state and hence can be used to determine the tack boundary $T_2(x_w)$. The sticky-point test can be used starting from the glassy or liquid state and is hence suited for determining both boundaries. The influence of inter-particle contact time was already observed for the static stickiness tests investigating caking. The longer the powder bed is subjected to environmental conditions where the powder will cake, the stronger the powder bed becomes. Control over particle motion and contact time in the dynamic stickiness tests provides a means to investigate the influence of motion within a sample on the boundaries of the sticky region.

Particle motion depends on the angular velocity of the stirrer or the container in the sticky-point and optical tests,



Fig. 8 The probe test. A probe is lowered until it touches the evaporating droplet. The probe retracts, and the required tensile force $F_{\rm TU}$ is measured. The droplet evaporation is monitored gravimetrically. Redrawn from Boonyai et al. 2004.

on the air velocity in the fluidized bed, cyclone test, and particle gun, and the probe speed in the probe test. A key challenge, in comparing these tests or studying the influence of particle motion on the boundaries of the sticky region, is that particle motion largely differs in all these tests. Even for a single test at a single condition, particle motion may be heterogeneous. In a sticky-point test, for example, stirring can cause the powder to distribute inhomogeneously in the stirring vessel, e.g., due to the stirrer digging channels in the powder. Similarly, in a fluidized bed, the particle velocities are inhomogeneous, mostly due to the common occurrence of bubbling (Seville et al., 2000). Hence, quantification of the relative velocity between the particles, and the resulting inter-particle contact time, presents a challenge, apart from the particle gun where the particle impact velocity may be controlled and quantified (Murti et al., 2010; Walmsley et al., 2015; Zhao, 2009).

The clearest influence of particle motion has been observed with the particle gun, as shown in **Fig. 9**. The data by Murti et al. (2010) shows a minimal increase for $(T - T_g)_c$ with increasing v_i . The data by Walmsley et al. (2015) shows a sharp increase of $(T - T_g)_c$ with increasing v_i , although, at $v_i > 20$ m s⁻¹, the effect appears to level off. A similar trend was observed by Zhao (2009) where v_i ranged from 10 m s⁻¹ to 45 m s⁻¹. These particle gun experiments show that a larger v_i shifts $T_1(x_w)$ to higher temperatures so that $(T - T_g)_c$ is increased.

The influence of particle motion also becomes apparent when different methods are compared with each other. A static method where the visual change of an SMP bed was used to find $(T - T_g)_c$ was compared with a dynamic fluidized bed method where the pressure change was used to find $(T - T_g)_c$ (Verdurmen et al., 2006). Over an



Fig. 9 Velocity-dependence of $(T - T_g)_c$ using skim milk powder and the particle gun. Triangles \blacktriangle are data by Walmsley et al. (2015); circles \bullet are data by Zhao (2009), and squares \Box are data by Murti et al. (2010). Note that the data cannot be directly compared between authors as different experimental settings were used. Error bars indicate the experimental range for $(T - T_g)_c$ that was reported by the respective authors. The dashed trendlines are to guide the eye.



experimental range of RH = 12 % to 30 %, the average offset of the sticky-point curve to the T_g was determined. The static test resulted in an average offset of $T - T_g = 13$ °C and the dynamic stickiness test resulted in an average offset of $T - T_g = 18$ °C. Another example is a comparison between the dynamic fluidized bed and particle gun tests. The $(T - T_g)_c$ was obtained for both methods using various types of skim and whole milk powder. While the results varied, for 6 out of 8 samples, the $(T - T_g)_c$ was lower for the fluidized bed by ≈ 10 °C to 15 °C. For the other two samples, the two methods provided similar results (Murti et al., 2010; Zuo, 2004). Based on these results, we strongly recommend matching the velocity of the particles in the dynamic stickiness test to the application in mind to achieve the most accurate $T_1(x_w)$.

In an attempt to further clarify the influence of particle motion on $(T - T_g)_c$, data from dynamic stickiness tests was gathered in **Table 2**. No data was found for the optical test and data for the probe test could not be used to find $(T - T_g)_c$. For each experiment, the impact velocity v_i of particle collisions was estimated. For the particle gun, the v_i was chosen as the air jet velocity. For the sticky-point test, v_i was estimated as the maximum angular velocity of the stirrer. For the fluidized bed, an average particle velocity \hat{v}_p was estimated using Eq. (4), with U the superficial velocity and $U_{\rm mf}$ the minimum fluidization velocity (Ennis et al., 1991). The constant α was estimated from Seville et al. (2000) to be $\alpha = 0.53$.

$$\hat{v}_{\rm p} = \alpha (U - U_{\rm mf}) \tag{4}$$

For the data where v_i could be estimated, no clear trend with $(T - T_g)_c$ could be found. Nonetheless, a wide range of $(T - T_g)_c = -5$ °C to 90 °C has been reported. Further analysis indicated that, besides v_i , material and experimental differences can also play a substantial role in determining $(T - T_g)_c$, some of which is highlighted below.

Some outliers can be explained by material differences, e.g. the $(T - T_g)_c = 90$ °C is for a skim milk powder (SMP) with 80 % protein, which is known to decrease stickiness (Hogan and O'Callaghan, 2010). Another example is the low value of -5 °C for a fluidized bed experiment using amorphous lactose. Using a range of RH = 7 % to 32 %, the results were $(T - T_g)_c = -5$ °C to 3.8 °C with a single outlier of $(T - T_g)_c = 21$ °C for RH = 53 %, the highest humidity tested. Amorphous lactose is known for its early onset of stickiness (Zuo et al., 2007) and crystallization (Schulnies and Kleinschmidt, 2018). We expect the latter could have played a role in the outlier as crystallization reportedly reduces liquid bridge strength (Fitzpatrick et al., 2007b).

However, even for similar materials, the deviation can be quite large. Using SMP in a particle gun with a velocity of 15 m s⁻¹ the $(T - T_a)_c$ was found to be 34 °C to 36 °C by Murti et al. (2010) and 57 °C to 61 °C by Walmsley et al. (2014). Two experimental differences explained this deviation. In the experiment of Walmsley et al. (2014), the deposition was only measured for the air jet's impingement location, not for the entire target plate. Particles that stray from the jet direction move through the air with undefined T and RH. Hence, the surface conditions of stray particles cannot be accurately determined. Additionally, the target plate was heated to match the temperature of the air jet. The plate temperature $T_{\rm p}$ can play an important role and is often a relevant industrial parameter, e.g., in dryers, pneumatic ducts, fluidized beds, and cyclones (Walmsley et al., 2014). A higher $T_{\rm p}$ is known to reduce the amount of wall deposition (Chen X.D. et al., 1993). Walmsley et al. (2014) found reduced deposition for higher T_p , which was consistent regardless of the used v_i . Such wall temperature effects are also found outside of food processing, such as cold spray deposition (Khalkhali and Rothstein, 2020). The improvements of the particle gun made by Walmsley et al. (2014) show that the experimental conditions influence the resulting $T_1(x_m)$. Hence, the experimental conditions need to be accurately chosen when stickiness tests are used for predicting powder processing parameters.

4.8 Application areas of dynamic stickiness tests

The moving nature of the particles in dynamic stickiness tests makes these tests useful for predicting the behavior of powder in most of powder production and processing equipment. However, it makes them unsuitable for measuring powder caking. The application of the dynamic tests will depend on the impact velocity v_i of collisions and whether particle-particle or particle-wall collisions are tested.

The particle gun can measure the highest impact velocity of all the reviewed methods and involves particle-wall collisions. Initially, an impact velocity of 20 m s⁻¹ was chosen for its similarity to industrial cyclones (Zuo et al., 2007). The high impact velocity makes it a useful method to predict stickiness for high-velocity pneumatic handling, dried material colliding with spray dryer walls, or industrial cyclones. Additionally, by changing the target plate's material or dimensions, the influence of wall material or impact angle can also be investigated (Murti et al., 2010; Walmsley et al., 2015).

The sticky-point test and fluidized bed have continuously moving powder, making these tests useful for various industrial applications involving moving powders such as powder mixing, blending, and milling. Since many industrial processes incorporate a fluidized bed, a stickiness test using fluidized powder will be most applicable to the fluidized bed itself. Limitations of the stirrer's angular velocity and the velocity of fluidization airflow make the sticky-point test and fluidized bed ill-suited for



 Table 2
 A selection of the reviewed literature for dynamic stickiness tests.

Material	Method	$(T - T_g)_c$ (°C)	v _i (m s ⁻¹)	Ref.
Sucrose & fructose	Sticky-point test	9 to 26 ^a	—	Downton et al., 1982
Amorphous lactose	Fluidized bed	-5 to 21	0.055 ± 0.055^{b}	Zuo et al., 2007
Amorphous lactose	Particle gun	19 to 37	20	Zuo et al., 2007
Amorphous lactose	Particle gun	36 to 40 ^a	20	Paterson et al., 2007a
Coffee creamer (maltose)	Fluidized bed	10 to 20 ^a	0.05 ± 0.025^{b}	Groen et al., 2020
High fat cream powder	Particle gun	38	20	Paterson et al., 2007b
Low fat cream powder	Particle gun	26	20	Paterson et al., 2007b
SMP15	Fluidized bed	10	—	Hogan and O'Callaghan, 2010
SMP25	Fluidized bed	22	—	Hogan and O'Callaghan, 2010
Maltodextrin DE21	Fluidized bed	47 to 62	—	Palzer, 2005
SMP55	Fluidized bed	45	—	Hogan and O'Callaghan, 2010
SMP80	Fluidized bed	90	—	Hogan and O'Callaghan, 2010
Orange juice powder	Sticky-point test	17 to 25 ^a	—	Brennan et al., 1971
SMP	Fluidized bed	14 to 23	—	Verdurmen et al., 2006
SMP	Fluidized bed	29	—	Hogan and O'Callaghan, 2010
SMP	Fluidized bed	25 to 34	0.01	Murti et al., 2010
SMP	Sticky-point test	23	0.3	Hennigs et al., 2001
SMP	Cyclone test	11.4	—	Intipunya et al., 2009
SMP $d < 45 \ \mu m$	Particle gun	8.2	10.3	Zhao, 2009
SMP $d < 45 \ \mu m$	Particle gun	14.8	19.4	Zhao, 2009
SMP $d = 45 \ \mu m$ to 65 μm	Particle gun	11.6	10.3	Zhao, 2009
SMP $d = 45 \ \mu m$ to 65 μm	Particle gun	23.5	19.4	Zhao, 2009
SMP	Particle gun	18.6	10.3	Zhao, 2009
SMP	Particle gun	30.1	14.8	Zhao, 2009
SMP	Particle gun	39	19.4	Zhao, 2009
SMP	Particle gun	53.4	45.6	Zhao, 2009
SMP	Particle gun	34	4.5	Walmsley et al., 2015
SMP	Particle gun	48	5.4	Walmsley et al., 2014
SMP	Particle gun	43	6.5	Walmsley et al., 2015
SMP	Particle gun	30 to 31	10	Murti et al., 2010
SMP	Particle gun	34 to 36	15	Murti et al., 2010
SMP	Particle gun	57 to 61	15	Walmsley et al., 2014
SMP	Particle gun	32 to 35	20	Murti et al., 2010
SMP	Particle gun	60 to 63	25	Walmsley et al., 2014
SMP	Particle gun	33 to 43	30	Murti et al., 2010
Tomato powder	Sticky-point test	36 to 41 ^a	—	Lazar et al., 1956
White cheese powder	Particle gun	28	20	Paterson et al., 2007b
Whole milk powder	Fluidized bed	23 to 38	0.09	Zuo et al., 2007
Whole milk powder	Particle gun	38 to 61	20	Zuo et al., 2007
Whole milk powder	Sticky-point test	36 to 41 ^a	1.0	Özkan et al., 2002

^a The $(T - T_g)_c$ was not directly obtainable from the paper, instead, it was calculated using Eq. (1) and Eq. (2). ^b A range for fluidization velocity was reported, authors did not test the influence of velocity. SMP15: Skim milk powder with 15 % protein, similar for SMP25, SMP55, and SMP80. Ranges for $(T - T_g)_c$ are mostly due to experimental scatter.



high-velocity processes such as spray drying or pneumatic handling. Further work on the influence of the intensity of continuous mixing on the sticky-point is required to choose experimental conditions for specific applications when using the sticky-point test and the fluidized bed. Using the sticky-point test with a fluidized powder solves some of the issues of the individual methods. However, sensitive equipment is necessary to measure the smaller increase of torque at the sticky-point, compared to without fluidization, which is possible with advanced rheometers (Groen et al., 2020).

The cyclone test was proposed as an alternative for the fluidized bed test, while we expect it to achieve sufficient particle motion to be an alternative for the particle gun as well. Boonyai et al. (2004) suggested that the cyclone test's primary advantage over the fluidized bed is that the cyclone test measures both adhesion and cohesion while the fluidized bed measures only cohesion. Therefore, the cyclone test would be more suitable to predict stickiness in spray drying, fluidized beds, and pneumatic handling of powders (Boonyai et al., 2004). However, it is difficult to judge this statement since, besides the original paper by Boonyai et al. (2002), we only found one application of the cyclone test in literature (Intipunya et al., 2009).

The optical test can be used if the tested material scatters near-infrared light (Boonyai et al., 2004). Since it was proposed, no further experiments using this method have been reported to our knowledge. Hence, no judgment of its applicability can be made momentarily. Still, commonly tested powders such as amorphous lactose and various milk powders are all opaque, indicating that this method could be applied to these powders.

The most prominent application for the probe test is the droplet evaporation phase of spray drying. However, the use of a bulk moisture content severely limits this application. Werner et al. (2007a) measured the stickiness of an evaporating droplet with the probe test. The onset of stickiness occurred much earlier than expected based on the droplet's bulk moisture content, which indicated solute had accumulated at the droplet surface. Hence, the gravimetrically determined droplet water content is an unhelpful parameter for determining $T_2(x_w)$, which makes the probe test not applicable to industrial processes involving rapid evaporation. Crucially, this includes spray drying, for which there is no adequate method to predict droplet stickiness in the initial evaporation phase. Future methods should focus on the drying droplet's surface conditions for finding the tack point $T_2(x_w)$, either through direct measurement or by modeling the gradient formation under the influence of evaporation (Adhikari et al., 2005).

5. Conclusion

In this review, we provided an overview of methods that

measure the stickiness of amorphous powders relevant in the food industry. The reviewed methods included visual observation tests, shear tests, the penetration test, the blow test, the sticky-point test, the fluidized bed, the particle gun, the cyclone test, the optical test, and the probe test. For each method, we described how either the sticky-point temperature $T_1(x_w)$ or the tack boundary $T_2(x_w)$ can be determined. We have classified the methods based on the particle mobility during the conditioning and measurement steps into *static stickiness tests* and *dynamic stickiness tests*.

Static stickiness tests have limited particle motion during the conditioning step, which can be as long as desired. Therefore, these tests are particularly suitable to measure the caking rate of powder beds. Hence, industrial applicability is predominantly in predicting the long-term behavior of powder during storage or in packaging. Static stickiness tests have shown that the caking rate can be related to $T - T_g$ when $T - T_g > (T - T_g)_c$, although the nature of the relation is dependent on the used method. Nonetheless, this approach gives much insight into the stability of stored powders.

Dynamic stickiness tests involve particles with significant particle motion during the conditioning and measurement step. The particle gun is a good method to measure stickiness during particle-wall impacts, while the combination of the sticky-point test and fluidized bed measure stickiness for particle-particle collisions and continuously mixed systems. A wide range of testing conditions can be achieved by varying the impact velocity or contact time between particles. Hence, information from dynamic stickiness tests is highly relevant to the design and operation of powder production and processing equipment. Dynamic stickiness tests have shown that velocity plays an important role in the location of the sticky region, with larger velocity shifting the sticky-point curve $T_1(x_w)$ to higher temperatures so that a larger $(T - T_q)_c$ is obtained.

An essential type of stickiness test that is lacking is a dynamic test that measures particle stickiness when moving from the liquid state to the sticky-region, hence, finding the tack boundary $T_2(x_w)$. Much unclarity exists for when evaporating solute containing droplets are sticky, while this is hugely relevant for spray drying, which is one of the most used processes in the food processing industry. The probe method does approach the sticky-region from the liquid state, but the reliance on the droplet's bulk properties makes it unable to determine values for $T_2(x_w)$. Further work in predicting the surface stickiness, either through direct measurement or by modeling the gradient formation under the influence of evaporation, is required to predict droplet stickiness.



This scientific work is supported by the Netherlands Organization for Scientific Research (NWO) (grant number 15459).

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Erik Sewalt MSc obtained his MSc in Food Technology at Wageningen University & Research. His specialization was Sustainable Food Process Engineering. His MSc thesis was about modeling the diffusion of pepsin in protein gels to understand food breakdown. He did an internship on in-vitro digestion of protein-rich food at University of California, Davis, USA. From October 2017, he became a PhD candidate at TU Delft, Faculty of Applied Sciences, Product and Process Engineering. His research activities as PhD candidate revolve around understanding the agglomeration of evaporating droplets in spray drying.



Authors' Short Biographies



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Gabrie M.H. Meesters

Dr Gabrie Meesters has 27 years of industrial formulations experience at Gistbrocades, Genencor International and DSM. He has 23 years of experience as a part-time professor at TU Delft in particle technology and product design. From January 2019, he became a full-time assistant professor at the TU Delft, Faculty of Applied Sciences, Product and Process Engineering. He is a contributor to several books on formulation. He is the editor of three books on product design and solids processing. He published over 70 refereed papers, has more than 20 patents and supervised more than 100 BSc, MSc and PhDs. He is a regular speaker at conferences and workshops. He was the organizer of the 2010 Partec and the 2010 World Congress on Particle Technology in Nuremberg, Germany.

Inertial Impaction Technique for the Classification of Particulate Matters and Nanoparticles: A Review[†]

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Abstract

Inertial impactors are applied widely to classify particulate matters (PMs) and nanoparticles (NPs) with desired aerodynamic diameters for further analyses due to their sharp cutoff characteristics, simple design, easy operation, and high collection ability. A few hundred papers have been published since the 1860s that addressed the characteristics and applications of the inertial impactors. In the last 30 years, our group has also carried out lots of studies to contribute to the design and the improvement of inertial impactors. With our understanding of inertial impactors, this article reviews previous studies of some typical types of the inertial impactors including conventional impactors, cascade impactors, and virtual impactors and the parameters for design consideration of these devices. The article also reviews some applications of the inertial impactors, which are mass concentration measurement, mass and number distribution measurement, personal exposure measurement, particulate matter control, and powder classification. The synthesized knowledge of the inertial impactor in this study can help researchers to design an inertial impactor with an accurate cutoff diameter, a sharp collection efficiency curve, and no particle bounce and particle overloading effects for long-term use for PM classification and control purposes.

Keywords: inertial impactor, cascade impactor, virtual impactor, nanoparticles, sampling

1. Introduction

There was a great demand to develop devices for collecting airborne particles of different sizes to study the effect of particulate matters (PMs) on human health (Anderson J.O. et al., 2012). In the period from 1860 to 1880, researchers discovered that inertial impactors can be used to collect airborne particles for further analysis (Marple V.A., 2004). The inertial impactors including the conventional impactor, cascade impactor, and virtual impactor can classify particles into different size ranges based on particle's inertia. In the inertial impactors, when the airflow is forced to change the direction, the particles with sufficient inertia escape the turning flow while the particles with less inertia remain in the flow resulting in the particle size-based classification. A burst of development of the inertial impactors has exploded since 1945 when the first cascade impactor (a series of conventional impactors) was developed to collect size-fractionated airborne particle samples with a high collection efficiency to obtain the particle mass distribution (May K.R., 1945). Since the 1970s, researchers computed the flow field and particle trajectories within the impactor by using the finite difference methods and showed that the impactor has a sharp cutoff characteristic (McFarland A.R. et al., 1978). Thereafter, the impactor was considered as a standard device for PM classification based on particle aerodynamic diameter.

The virtual impactor was developed later since 1966 (Conner W.D., 1966) with a feature not found in the conventional impactor, in which particles are collected in a probe instead of on the collection plate to avoid particle bounce. The virtual impactor also attracted lots of interest from researchers for PM classification since two particle size fractions can be collected for further analysis as the design theory was studied and better understood (Marple V.A. and Chien C.M., 1980; Zahir M.Z. et al., 2018). Since 1970 until now, inertial impactors have been used extensively for various purposes such as (i) size-based classification for mass concentration measurement (Le T.C. and Tsai C.J., 2017; Le T.C. et al., 2019), (ii) particle mass distribution measurement (Marple V.A. et al., 1991; Demokritou P. et al., 2004a), (iii) chemical composition measurement (Marple V.A. et al., 1991), (iv) personal exposure measurement (Tsai C.J. et al., 2012b), and (v) nanoparticle (NP) measurement (Chow J.C. and Watson J.G., 2007).

The main reasons behind the diverse application of the



[†] Received 4 December 2019; Accepted 6 February 2020 J-STAGE Advance published online 31 March 2020

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inertial impactors are their sharp separation, high collection abilities, relatively simple design, and easy operation. But several limitations are inherent to the impactors such as particle bounce and re-entrainment (Turner J.R. and Hering S.V., 1987; Fujitani Y. et al., 2006), particle overloading (Tsai C.J. and Cheng Y.H., 1995; Demokritou P. et al., 2004b), and particle loss (Fang C. et al., 1991; Durand T. et al., 2014), which can degrade their performance. Moreover, some typical characteristics of the inertial impactors such as the cutoff diameter, the sharpness of collection efficiency curve, and the properties of the impaction substrate should be understood well since PMs have different sizes, shapes, types, compositions and characteristics (Loo B.W., 1975; Hinds W.C., 1999). There have been many studies conducted to resolve these issues from 1970 onward, which are reviewed in detail in Section 2.

In the last 30 years, our group has also carried out lots of studies to contribute to the design and the improvement of inertial impactors. In 1995, an impactor with an inverted conical cavity as the collection plate was developed to eliminate the particle bounce and re-entrainment and enhance the loading capacity (Tsai C.J. and Cheng Y.H., 1995). This design was studied further by other researchers (Chang M. et al., 1999; Kim D.S. et al., 2006; Kim Y.J. and Yook S.J., 2011; Kim W.G. et al., 2013) and used for the development of the EPA (Environmental Protection Agency) PM_{2.5} well impactor ninety-six (WINS) (Peters T.M. et al., 2001). Some different personal samplers were developed to measure respirable particles and NPs for the exposure assessment at workplaces such as personal inertial impactor (Huang C.H. et al., 2006) and novel active personal nanoparticle sampler (PENS) (Tsai C.J. et al., 2012b). The PENS was used for further studies by other research groups (Hsiao T.C. et al., 2010; Hsiao T.C. et al., 2011; Sung G. et al., 2018) or for field measurements (Young L.H. et al., 2013; Zhou Y. et al., 2014; Zhu C.S. et al., 2016; Asbach C. et al., 2017; Zhu C.S. et al., 2017). Some commercial sampling devices were studied to improve their sampling performance at our laboratory. We found the inter-stage loss of NP clogging in the last four stages of the micro-orifice uniform deposit impactor (MOUDI) due to its step-wised nozzle structure with abrupt contraction (Liu C.N. et al., 2013b) and developed the NCTU micro-orifice cascade impactor (NMCI) with smooth nozzle shape to eliminate these problems (Chien C.L. et al., 2015). The sampling performance of the standard EPA louvered PM₁₀ inlet and PM_{2.5} WINS inlet was studied and the particle bounce, re-entrainment, and particle overloading effects of these devices were found (Le T.C. and Tsai C.J., 2017; Le T.C. et al., 2019). The non-bouncing modified louvered PM10 (M-PM10) inlet and the modified WINS (M-WINS) were developed for the long-term sampling purpose without the need for frequent maintenance. A multi-filter PM₁₀ and PM_{2.5} sampler (MFPPS) which consists of PM₁₀ and PM_{2.5} impactors was developed for collecting multiple samples of PM₁₀ and PM_{2.5} simultaneously for different analyses or comparison tests of different devices (Liu C.N. et al., 2011). Besides, numerous theoretical and experimental studies have been carried out by our group, which explored fundamental issues of the inertial devices including the effect of gravity on particle collection efficiency (Huang C.H. and Tsai C.J., 2001), the influence of impaction plate diameter and particle density on the collection efficiency of inertial impactors (Huang C.H. and Tsai C.J., 2002a), the effect of porous metal (Huang C.H. et al., 2001; Huang C.H. and Tsai C.J., 2002b; Huang C.H. and Tsai C.J., 2003) and porous foam (Huang C.H. et al., 2005) as the impaction substrate on the cut-size and collection efficiency, and the influence of the relative humidity (RH) on NP concentration and particle mass distribution measurements by the MOUDI (Chen S.C. et al., 2011).

With our understanding of inertial impactors, this article aims to synthesize the existing knowledge of impactor design and discuss future perspectives in the applications of inertial techniques to classify PMs, NPs, and powder. The design principle, cutoff characteristics, and the advantages and disadvantages of each type of inertial impactors are reviewed. Some typical applications of inertial impactors including mass concentration measurement, mass and number distribution measurement, personal exposure measurement, PM control, and powder classification are discussed. Two types of inertial impactors including the conventional impactor and the virtual impactor are covered.

2. Principle and design consideration

The types and principles of the inertial impactors are presented in textbooks (Hinds W.C., 1999; Marple V.A. and Olson B.A., 2011) and are described briefly here to support the design and application considerations. The description and pros and cons of each type of inertial impactors are summarized in **Table 1**. The lists of their commercial devices can be found in Watson J.G. and Chow J.C. (2011).

2.1 Conventional impactor and cascade impactor

A conventional single-stage impactor consists of a single or multiple nozzles which are either round- or rectangular-shaped and an impaction plate below the nozzle as shown in **Fig. 1a**. When the particle-laden air passes through the nozzle(s) and makes a turn above the impaction plate, particles with sufficient inertia are not able to follow streamlines and impact on the collection plate while particles with less inertia will flow out of the



Brief description		Pros and cons	Typical devices	References
Single-stage, single- nozzle impactor	The impactor consists of a single nozzle and an impaction plate, used to collect parti- cles smaller than a certain size.	<i>Pros:</i> Simple configuration, easy operation, and low cost. <i>Cons:</i> Low flow rate, large cut-size, and possible particle bounce, particle overloading, and particle loss.	EPA $PM_{2.5}$ WINS; EPA louvered PM_{10} inlet; EPA flat-topped PM_{10} inlet	McFarland A.R. et al., 1984; Peters T.M. et al., 2001; Tolocka M.P. et al., 2001
Single-stage, multi-nozzle impactor	The impactor consists of a nozzle plate with multiple nozzles and an impaction plate, used to collect parti- cles smaller than a certain size.	Pros: Simple configuration, easy operation, a wide range of flow rates, and a smaller cut-size. Cons: Particle bounce, particle overloading, particle loss, and multiple jet interactions.	EPA Hivol PM ₁₀ impactor (1133 L/ min); Harvard sharp- cut impactor (10 and 20 L/min)	McFarland A.R. et al., 1984; Turner W.A. et al., 2000
Cascade impactor	The impactor is a series of multi-nozzle impactors, used to measure particle mass distribution.	<i>Pros:</i> It can measure particle mass distribution ranging from 10 nm to 10 μm. <i>Cons:</i> Possible overloading, particle re-entrainment, and interstage loss.	MOUDI; MOUDI-II; Andersen cascade impactor; NMCI	Andersen A.A., 1966; Marple V.A. et al., 1991; Chien C.L. et al., 2015
Low pressure impac- tor (LPI)	The cascade impactor operates at low pressure condition.	<i>Pros:</i> It can measure particle mass distribution of NPs down to 10 nm. <i>Cons:</i> High pressure drop.	Berner-type low-pres- sure impactor	Berner A., 1972
Electrical low pres- sure impactor (ELPI)	The device consists of a charger and a cascade impactor cou- pled with electrome- ters, used to measure particle number concentrations electri- cally	Pros: Automatic and nearly real-time measurement with a response time of less than 5 s. Cons: Possible particle bounce unless the oil-coated sin- tered-metal substrate is used; Resolution is not good for NPs.	Dekati [@] ELPI	Keskinen J. et al., 1992; Järvinen A. et al., 2014
Virtual impactor	The impactor consists of a single nozzle and a single collection probe, used to collect two particle size	Pros: No particle bounce and particle loading effect; Simultaneous measurement of two particle size ranges. Cons: Contamination of coarse	Dichotomous sampler	McFarland A.R. et al., 1978

particles by particles smaller than the cut-size; Particle loss; Use of two flow meters.

Table 1 Types of inertial impactors.

impactor and are either collected by a filter for further analyses or measured directly by an aerosol instrument (Marple V.A. and Olson B.A., 2011). In order to classify particles into many size ranges, a series of single-stage impactors are used, which is called cascade impactor (Marple V.A. and Olson B.A., 2011). The successive stages are designed to provide progressively higher jet speeds and/or reduced pressures so that the average aerodynamic size of particles collected at each stage is progressively smaller. Many nozzles (multi-nozzle) are

fractions.

mainly used to increase the airflow rate. These nozzles are drilled on a nozzle plate which is placed on the top of the impaction plate with a given jet-to-plate distance.

2.1.1 Design theory

The design theory of the conventional impactor is based on the numerical modeling of the flow field and the equations of particle motion by Marple and co-workers (Marple V.A. and Rubow K.L., 1986). The performance of the inertial impactor is characterized by the collection





Fig. 1 Inertial impactor problems (a) normal case (b) particle bounce, (c) particle overloading, and (d) particle loss.

efficiency curve, which is an "S" shape curve due to the non-ideal and non-uniform flow field in the impactor. The collection efficiency curve is represented by the cutoff aerodynamic diameter (D_{pa50}), which is the aerodynamic diameter for 50 % collection efficiency, and the sharpness or geometric standard deviation (GSD \geq 1.0) of the particle collection efficiency curve. The GSD is calculated as (Marple V.A. and Olson B.A., 2011)

$$GSD = \sqrt{\frac{D_{pa84}}{D_{pa16}}}$$
(1)

where D_{pa84} and D_{pa16} are the aerodynamic diameters for 84 % and 16 % collection efficiencies, respectively. The most important parameter that governs the collection efficiency is the Stokes number (*Stk*) which is used to predict whether a particle will impact on the impaction plate or follow the air streamlines to exit the impactor. *Stk* is the ratio of the particle's stopping distance to the characteristic dimension of the nozzle and is calculated as follows (Marple V.A. and Olson B.A., 2011)

$$Stk = \frac{\rho_{\rm p} D_{\rm p}^2 C_{\rm c} (D_{\rm p}) U_0}{9\mu W} = \frac{\rho_{\rm p0} D_{\rm pa}^2 C_{\rm c} (D_{\rm pa}) U_0}{9\mu W}$$
(2)

where ρ_p is the particle density (kg/m³), ρ_{p0} is the unit density (1000 kg/m³), C_c is the slip correction factor, U_0 is

the air jet velocity (m/s), D_p is the particle diameter (m), μ is the dynamic air viscosity (kg·s/m²), and *W* is the diameter or the width of nozzle (m). Stk_{50} is the Stokes number for 50 % collection efficiency. For an impactor, Stk_{50} is usually fixed under optimized conditions, and D_{pa50} can be calculated as the following equation (Marple V.A. and Olson B.A., 2011):

$$D_{\rm pa50} = \sqrt{\frac{9\mu W}{\rho_{\rm p0} C_{\rm c} (D_{\rm pa50}) U_0}} \sqrt{Stk_{50}}$$
(3)

Jet Reynolds number (Re) is another parameter governing the flow field and the particle collection efficiency. Reinfluences the sharpness of the collection efficiency curve more than the cutoff diameter. Re of the round-nozzle impactor is expressed as (Marple V.A. and Olson B.A., 2011)

$$Re = \frac{\rho_a W U_0}{\mu} \tag{4}$$

where ρ_a is the air density (kg/m³). The inertial impactors will have sharp and nearly the same collection efficiency curves with a fixed *Stk*₅₀ of 0.24 (round nozzle) or 0.59 (rectangular nozzle) if *Re* ranges from 500 to 3000.

The S/W ratio, which is the jet-to-plate distance (S) divided by W, also influences the collection efficiency. An



impactor will have a sharp efficiency curve if S/W is greater than 1.0 for a round-nozzle impactor and greater than 1.5 for a rectangular-nozzle impactor (Marple V.A. and Rubow K.L., 1986). S/W usually ranges from 1 to 5 to eliminate the effect on Stk_{50} for single nozzle impactors (Marple V.A. and Liu B.Y., 1974). Furthermore, in order to provide a sufficient time for the particles to accelerate to the fluid velocity, the throat length (T) divided to W(T/W) should be larger than 1.0 and the entrance of the nozzle should be tapered or conical (Marple V.A. and Willeke K., 1976). In addition, the effect of particle gravity on the increasing particle collection efficiency was found when Re is below 1500 (Huang C.H. and Tsai C.J., 2001). Other parameters influencing the collection efficiency curves are the impaction plate diameter, the particle density (Huang C.H. and Tsai C.J., 2002a) and the design of impaction surfaces (Tsai C.J. and Cheng Y.H., 1995; Tsai C.J. and Lin T.Y., 2000). A small impaction plate will cause an increase in the cutoff diameter (Huang C.H. and Tsai C.J., 2002a) while a small impaction well will decrease the cutoff diameter due to the secondary impaction on the wall of the well (Hu S. et al., 2007).

It is noted that the above design considerations are not only suitable for singe-nozzle, single-stage impactor but also applicable for the multi-nozzle, multi-stage impactor with nozzles far enough from each other. If the nozzles are too close, nozzle crossflow interaction occurs, which affects the collection efficiency of the multi-nozzle impactor (Fang C. et al., 1991; Kwon S.B. et al., 2002). The cross-flow parameter, which is a function of the number of nozzles, nozzle diameter, and nozzle cluster diameter. should be less than 1.2 to eliminate the effect of the crossflow interaction (Fang C. et al., 1991). Other previous studies showed that the cutoff characteristics of the multi-nozzle impactor are also effected by S/W and Re even if they fall in the recommended range for the singlenozzle impactor (Gudmundsson A. et al., 1995; Kwon S.B. et al., 2002; Yao M. and Mainelis G., 2006). The cutoff characteristics of successive stages of the cascade impactor with the $D_{pa50} < 100$ nm was found to be very sensitive to S/W (Arffman A. et al., 2011; Tsai C.J. et al., 2012b; Liu C.N. et al., 2013b). In the multi-nozzle impactor, the secondary deposit of particles due to the jet interaction leads to the differences between the theoretical and experimented collection efficiencies and the less sharp collection efficiency and lower Stk (Rocklage J.M. et al., 2013; García-Ruiz E. et al., 2019).

To achieve smaller cut-sizes in the lower stages of the cascade impactor, multiple micro-orifice impactors (MOIs) or low pressure impactors (LPIs) are used. In the LPIs, particles with a very small cutoff diameter (e.g. $0.05 \ \mu m$) are collected due to the increase of the slip correction factor with the decrease in the pressure. A large vacuum pump to draw the air through the nozzles at a

high flow velocity is needed which creates a large pressure drop for the impaction to take place at low pressure (e.g. 3 kPa). The nano-size cutoff diameter (e.g. 2 or 5 nm) can also be achieved by expanding the aerosol into an evacuated region creating hypersonic impaction conditions (Fernandez de la Mora J. and Schmidt-Ott A., 1993). These low pressure impactors may have the evaporation loss of semi-volatile particle materials (SVM) (Biswas P. et al., 1987). In comparison, in the MOIs, the smaller cutoff diameter is obtained by using numerous small microorifices, which provide the desirable flow rate at a relatively low pressure drop. The evaporation loss of SVMs was shown to be eliminated in the MOIs if the pressure drop is less than 40 kPa (Fang C. et al., 1991). The cascade impactor can be developed with the above design considerations and calibrated with the standard method presented by Marple V.A. and Olson B.A. (2009). The consideration of designing an inertial impactor with a smaller cut-size, a sharper collection efficiency curve, and a higher flow rate is summarized in Table 2.

There major drawbacks of the conventional impactor are particle bounce, particle overloading and particle loss as shown in **Fig. 1b–d**. Since these effects can cause the shift of the cutoff diameter and the collection efficiency curve leading to incorrect PM measurement, numerous researches have studied these problems to find out the solutions (Liu C.N. et al., 2013b; Le T.C. and Tsai C.J., 2017; Le T.C. et al., 2019).

2.1.2 Particle bounce effect

Particle bounce occurs when the impactor plate is unable to absorb the kinetic energy of the incident particles completely (Fig. 1b). The particles are not retained by the surface, resulting in the lower particle collection efficiency for particles larger than the cutoff diameter (John W. et al., 1991; Bateman A.P. et al., 2013). The rebound particles can be collected on the after filter or a subsequent stage resulting in the positive bias of PM measurement or the shift of the mass distribution toward smaller aerodynamic sizes (Marple V.A. and Olson B.A., 2011; Jain S. and Petrucci G.A., 2015). The particle bounce depends on the adhesion energy between particles and the impaction surface, the energy loss mechanisms in particles (dissipation energy) and the initial velocity (or kinetic energy) of particles (Bateman A.P. et al., 2013; Jain S. and Petrucci G.A., 2015). After impaction, the incident kinetic energy is balanced by several energy relaxation terms including dissipation energy, adhesion energy, and rebound energy. Rebound energy that is greater than the sum of dissipation and adhesion energies will result in particle bounce. Physical properties of particles such as hygroscopicity, size, density, phase, elasticity, and hardness can also play an important role in particle bounce behavior (Matthew B.M. et al., 2008; Bateman A.P. et al., 2013;



Requirements	Solutions	Limitations	References
To decrease the cut-size by	increasing the flow rate	<i>Re</i> numbers should be in the range of 500–3000 to achieve a sharp collection efficiency curve	Marple V.A. and Rubow K.L., 1986
	decreasing the diameter or width of nozzles	It may cause an increased pressure drop and it is hard to fabricate the micro-size nozzles	Berner A., 1972; Marple V.A. et al., 1991
	decreasing the jet-to-plate distance	It may cause an increased pressure drop if S/W is ≤ 1.0 for round-nozzle impac- tors and ≤ 1.5 for rectangular-nozzle impactors	Chien C.L. et al., 2015
	increasing nozzle throat length	$T/W \ge 1.0$	Marple V.A. and Liu B.Y., 1974
	increasing the impaction plate diameter	It is applicable as $Re < 1500$	Huang C.H. and Tsai C.J., 2002a
	using the elliptical concave impaction plate	It is applicable for round-nozzle impactor	Kim Y.J. and Yook S.J., 2011
	gravitation force assistance	It is applicable as $Re < 1500$	Huang C.H. and Tsai C.J., 2001
	reducing the pressure by using high jet velocities	Evaporation of semi-volatile compounds	Chen S.C. et al., 2007; Arffman A. et al., 2011
To increase the sharpness of the	reducing the nozzle throat length	$T/W \le 1.0$. It is just applicable for low pressure impactors	Arffman A. et al., 2011
collection efficiency curve by	using an additional punched impaction plate	It is a complicated configuration	Cheon T.W. et al., 2017
	using horizontal inlet with rectangular-slit-nozzle	It is a complicated configuration	Kim M.K. et al., 2014
To increase the flow rate by	increasing the number of nozzles	<i>W</i> should be ≥ 0.04 cm to lower fabrication cost	Chien C.L. et al., 2015
	using rectangular nozzles	The less sharp collection efficiency curve was found	Kim M.K. et al., 2014

Table 2 Design considerations of inertial impactors.

Kang M. et al., 2015; Chen M. et al., 2016). It was reported that liquid and liquid-coated particles were collected with an efficiency of nearly 100 %, while the collection efficiency of solid particles could be as low as 20 % (Matthew B.M. et al., 2008).

To increase the adhesion energy and minimize the solid particle bounce, the impaction plate is usually coated with vacuum grease, vacuum oil or silicone oil (Turner J.R. and Hering S.V., 1987), covered by a glass-fiber filter (GFF) saturated in water (Dunbar C. et al., 2005), or soaked in vacuum oil (Vanderpool R.W. et al., 2007). Use of rough impaction plates (Marjamäki M. and Keskinen J., 2004), porous substrate (Huang C.H. et al., 2001; Huang C.H. and Tsai C.J., 2003; Huang C.H. et al., 2005), or specially designed impaction plate (Kim Y.J. and Yook S.J., 2011; Kim W.G. et al., 2013) can also reduce particle bounce. For the coated substrate, the type and the thickness of the coating material also affect the particle bounce. If the coating materials interfere with chemical analysis (Wang L. et al., 2005; Fujitani Y. et al., 2006), an uncoated impaction surface is preferred (Kang M. et al., 2015). In addition, the relative humidity of incoming aerosols conditioned to a higher value (> 70 %) can minimize particle bounce, due to the increase in the adhesion energy by capillary force between adsorbed water on the particle and the impaction plate (Chen S.C. et al., 2011; Bateman A.P. et al., 2013).

2.1.3 Particle loading effect

Although the coating materials help to reduce the particle bounce effectively, the particle loading effect occurs when too many particles are collected on the impaction substrate after a long sampling period (**Fig. 1c**). When the grease-coated impaction plate is loaded heavily with particles, the incident particles strike on previously deposited solid particles rather than the coated plate, resulting in



possible particle bounce (Tsai C.J. and Cheng Y.H., 1995). Moreover, the particle blow-off problem may take place when heavily loaded particles are swept away from the substrate by high-velocity jet flow.

Therefore, the net effects of substrate overloading are similar to particle bounce: lower collection efficiencies for particle larger than the cut-size and the shift of the measured size distribution toward the smaller particle sizes (Tsai C.J. et al., 2012b). The problem of particle overloading can be overcome by reducing the sampling time since it affects the amount of particles collected. Many methods have been proposed to increase the particle loading capacity on the impaction substrate to extend the sampling period, including the special designs of impaction plates (Tsai C.J. and Cheng Y.H., 1995), oil-soaked filters (Peters T.M. et al., 2001), oil-coated impaction substrate (Tsai C.J. et al., 2012b), multi-hole impactor with Trypticase Soy Agar (TSA) substrate (Lai C.Y. et al., 2010) or rotating substrates (Marple V.A. et al., 1991; Tsai C.J. et al., 2012b).

However, when the oil-coated filter substrate is used to eliminate particle bounce, the particle loading effect can still occur since the oil, which has a lower viscosity than the grease, wicks up through the previously deposited particle layer by the capillary action, and eventually leads to the pile-up of the deposited particles on the substrate. This causes the shift of the cutoff diameter and collection efficiency curve to the smaller sizes leading to incorrect PM measurements (Kenny L.C. et al., 2000; Vanderpool R.W. et al., 2001). Even with the rotating stage design in the MOUDI (Marple V.A. et al., 1991), it is expected that several tens of layers of deposited particles will appear on the grease-coated stage for particle bounce and loading effect to occur when the typical stage inlet aerosol mass concentration is 10–20 µg/m³ during 24-h sampling (Tsai C.J. and Cheng Y.H., 1995). The special designs of impaction cavities and wells have better performance compared to that of flat impaction surfaces since rebound particles can be retained (Tsai C.J. and Cheng Y.H., 1995; Peters T.M. et al., 2001).

An M-PM₁₀ impactor with oil-soaked GFF substrate supported by a porous metal disc as shown in **Fig. 2** was designed to avoid the particle bounce and overloading effects (Le T.C. et al., 2019). In the M-PM₁₀ impactor, there is a 1-mm layer of oil remaining on the top of the substrate and the pores of the porous metal disc are filled with vacuum oil to enhance the loading capacity. With these improvements, the modified PM₁₀ impactor showed a good sampling performance with a bias of less than \pm 10 % during 30 sampling days. Based on the concept of water-saturated GFF substrate of Dunbar C. et al. (2005) and impaction well (Peters T.M. et al., 2001), a PM_{2.5} impactor with the water-wetted GFF substrate modified from the WINS was developed by our group as shown in



Fig. 2 Schematic diagram of the $M-PM_{10}$ impactor (Le T.C. et al., 2019).



Fig. 3 Schematic diagram of the M-WINS (Le T.C. and Tsai C.J., 2017).

Fig. 3. This impactor design not only can eliminate the particle bounce by using the water-wetted GFF impaction substrate but also avoid the particle overloading effect by injecting a small amount of water upward to wash the deposited particles off the impaction surface continuously (Le T.C. and Tsai C.J., 2017). Instead of using water, the M-WINS can inject vacuum oil periodically to wash off particles to save oil consumption. Washing impaction substrate to eliminate particle bounce and particle overloading effects can be applied to different types of impactors as well.

2.1.4 Particle loss effect

Particle loss is another limitation of inertial impactors (**Fig. 1d**). Instead of being collected on the impaction substrate, particles can also deposit on the inner walls of the impactor, including the nozzle and the casing, leading to the underestimation of the collection efficiency and the distortion of the measured mass distribution. Large particles can be lost by impaction while nanoparticles can be

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lost by convention-diffusion. The losses may vary with particle properties. If particles are liquid or sticky, they will adhere to any surface upon contact with it. Some of dry particles, however, may rebound when they hit the surface and remain airborne. Experimental and theoretical studies have been conducted for determining the particle losses by impaction and diffusion (Chen S.C. et al., 2007). The inertial loss of large particles normally occurs on the contractions which connect the big inlet tube to the small nozzle or on the surface of nozzle plate (Durand T. et al., 2014; Kumar A. and Gupta T., 2015a, 2015b).

Another particle loss in the cascade impactor is the inter-stage particle loss, which occurs in the inter-stage space above the intended stage to collect particles. The inter-stage loss is due to turbulent particle deposition when they pass through sharp corners or obstructions between two adjacent stages (Marple V.A. et al., 1991). Typically, significant particle loss occurs in the lower stages of the cascade impactors due to diffusion-convention (Demokritou P. et al., 2002b; Watson J.G. and Chow J.C., 2011). The NMCI with smooth nozzles could minimize the convection-diffusion particle deposition in the nozzle (Liu C.N. et al., 2013b). In another study, 80 % of particle loss was found to concentrate around the nozzles and 20 % on the impaction plate in a stage of the DLPI (Dekati[®] Low-Pressure Impactor) (Durand T. et al., 2014).

Some conventional impactors were designed by changing the geometry of the impactor to enhance the collection efficiency to obtain a lower cut-size, including using the horizontal inlet to concentrate particles in the central axis of nozzle (Kim M.K. et al., 2014; Kim W.G. et al., 2014; Heo J.E. et al., 2018), using an additional punched impaction plate installed between the nozzle outlet and impaction plate (Cheon T.W. et al., 2017), and the combination of the impactor and the initial filter to achieve a sharp collection efficiency curve (Zhang T. et al., 2017; Zhang X. et al., 2018). **Table 3** lists the design solutions to resolve the problems of conventional impactors.

2.2 Virtual impactors

The virtual impactor is another type of inertial impactors, which consists of the nozzle(s), and the collection probe(s) (Marple V.A. and Olson B.A., 2011). In the virtual impactor, the collection probe diameter (*D*), which is slightly larger than *W*, is used to replace the collection plate of the conventional impactor to eliminate particle bounce and particle overloading effects (Loo B.W., 1975). Particles with sufficient inertia are retained in a relatively stagnant air passing through the collection probe while particles with less inertia follow the airflow to exit the impactor. The minor flow (Q_1) is about 5–20 % of the total air flow (*Q*) or the major flow (Q_0) is about 80–95 % of the total air flow (Hinds W.C., 1999).

Many studies have been conducted to examine the cutoff characteristics and the influencing parameters of the virtual impactor of the basic design (McFarland A.R. et al., 1978; Marple V.A. and Chien C.M., 1980; Lim K.S. and Lee K.W., 2006). They concluded that the theoretical cutoff characteristics of the virtual impactors are similar to those of conventional impactors, which are mainly governed by Stk and Re (Marple V.A. and Chien C.M., 1980). The other parameters such as collection probe/nozzle diameter ratio, nozzle length, entrance cone angle, and nozzle to collection probe distance do not have an important effect on the collection efficiency. Although the value of D/W does not affect the cutoff characteristic, it should be less than 1.49 to eliminate the flow field effect. The cutoff diameter increases as the minor and major flow ratio $(Q_1/$ Q_{0}) decreases (McFarland A.R. et al., 1978; Marple V.A. and Chien C.M., 1980). The virtual impactor avoids the particle bounce effect without using the impaction plate, but an intrinsic disadvantage of the virtual impactor is the contaminations of coarse particles in the major flow by fine particles. That is, a portion of particles less than the cutoff diameter will remain in the minor flow or the socalled minor flow contamination. A virtual impactor with reduced fine particle contamination was designed by confining the aerosol flow within a central core enveloped by a sheath of clean air (Chein H. and Lundgren D.A., 1993). The opposing jets design and the introduction of a clean air core as the envelope around the particle-laden stream were also used to eliminate fine particle contamination.

Another major disadvantage of the virtual impactor is the particle internal losses which affect the cutoff diameter significantly (Xu Z., 1991). Particles are normally lost at the upper edge of the collection probe or on the backside of the probe plate. The particle loss is affected by D/W, Re, Q_1/Q , the nozzle protruding through the nozzle plate, the shape of the collection probe inlet, and the alignment of the axes of the nozzle and the collection probe. High particle losses occur for particles having a diameter close to the cutoff point (Marple V.A. and Chien C.M., 1980). The particle loss can be reduced by proper contouring of the probe entrance, decreasing Re, and increasing Q_1/Q_0 and S/W ratio (Marple V.A. and Chien C.M., 1980). The particle loss can be reduced by increasing D/W but it may reduce the sharpness of the particle collection efficiency curve. Certain values of the throat length of the probe opening, the radius of the rounded shoulder of the probe opening, and the diameter of the lower surface of the nozzle required to reduce the particle loss were suggested (Marple V.A. and Chien C.M., 1980). It is summarized that D should be about 30–50 % larger than W, the radius on the inside of the collection probe inlet is about 30 % of W, the nozzle should protrude two to three times W through the nozzle plate, S should be about 1-1.8 times W, and the axes of the nozzle should be



Problems	Solutions	Pros and cons	References
Particle bounce	Using glass fiber filter or Teflon filter as an impaction substrate	<i>Pros:</i> Simple and no chemical interference <i>Cons:</i> Expensive	Marple V.A. et al., 1991
	Greased substrate	Pros: Easy implementer Cons: Can't be suitable for chemical analysis; Particle overloading effect	Turner J.R. and Hering S.V., 1987; John W. et al., 1991
	Oiled substrate	<i>Pros:</i> Cheap, high loaded mass, low viscosity, and uniform coating <i>Cons:</i> Particle loading effect and oil evaporation	Turner J.R. and Hering S.V., 1987; Peters T.M. et al., 2001; Le T.C. et al., 2019
	Porous metal substrate	<i>Pros:</i> No chemical interference <i>Cons:</i> The shift of the collection efficiency curve and cutoff diameter; Less sharp curve	Huang C.H. et al., 2001; Huang C.H. and Tsai C.J., 2002b; 2003
	Foam substrate	<i>Pros:</i> No chemical interference <i>Cons:</i> The shift of the collection efficiency curve and cutoff diameter; Less sharp curve	Huang C.H. et al., 2005
	Water substrate and water washing	<i>Pros:</i> No chemical interference; Can be used to collect samples for chemical analysis; Long-term use <i>Cons:</i> Pumps are needed to inject and drain water	Dunbar C. et al., 2005; Le T.C. and Tsai C.J., 2017
	Cavity-type impaction substrate	<i>Pros:</i> No energy, solutions or materials are needed <i>Cons:</i> The curve is not very sharp	Tsai C.J. and Cheng Y.H., 1995
	Elliptical concave impaction plate	<i>Pros:</i> No chemical interference <i>Cons:</i> The determination of dimensions is needed; It just helps trap some re-bound particles	Kim W.G. et al., 2013
	Cup impactor	<i>Pros:</i> No chemical interference <i>Cons:</i> Special design; The cut-size can't be predicted	Kim D.S. et al., 2006
	Using virtual impactor	<i>Pros:</i> Two size fractions <i>Cons:</i> Fine particle contamination; High particle loss near the cut-size.	McFarland A.R. et al., 1978; Marple V.A. and Chien C.M., 1980
Particle over- loading	Oiled substrate	<i>Pros:</i> Cheap and high loaded mass <i>Cons:</i> Short-term use and oil evaporation	Turner J.R. and Hering S.V., 1987
	Porous metal substrate	<i>Pros:</i> High loaded mass <i>Cons:</i> The shift of the collection efficiency curve and cutoff diameter; Less sharp curve	Huang C.H. et al., 2001
	Continuous water washing	<i>Pros:</i> Long-term use without frequent maintenance <i>Cons:</i> Pumps are needed to inject and drain water	Le T.C. and Tsai C.J., 2017
	Rotated impaction plate	<i>Pros:</i> Long-term use <i>Cons:</i> A motor is needed; Coated substrate; Complicated configuration	Marple V.A. et al., 1991; Tsai C.J. et al., 2012b
Particle loss	Horizontal inlet in virtual impactor	<i>Pros:</i> High collection efficiency <i>Cons:</i> Complicated configuration	Heo J.E. et al., 2018
	Smooth nozzles	<i>Pros:</i> No particle clogging <i>Cons:</i> Need special technique to fabricate microsize nozzles	Fang C. et al., 1991; Liu C.N. et al., 2013b; Chien C.L. et al., 2015
Multiple-jet interaction	The symmetrical arrangement of nozzles	<i>Pros:</i> Uniform deposition <i>Cons:</i> Not enough study	Kwon H.B. et al., 2018

Table 3 Solutions of inertial device problems	s.
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aligned closely to that of the collection probe (Hinds W.C., 1999).

Some special designs of the virtual impactor to eliminate particle loss and improve the collection efficiency were developed. This includes the slit virtual impactor assembled with an orifice installed upstream of the acceleration nozzle to concentrate the minor flow at the center of the collection probe (Lim K.S. and Lee K.W., 2006; Lee H. et al., 2014) or the impactor with three-partitioned horizontal inlet (Zahir M.Z. et al., 2018). The virtual impactor with an ultrafine cutoff diameter at a moderate pressure drop was developed by using a very small round nozzle and at a low flow rate (Sioutas C. et al., 1994b) or slit nozzles to operate at a high flow rate (Sioutas C. et al., 1994a).

Since it is hard to control both minor and major flows, the virtual impactor is usually designed as a single-stage virtual impactor. The multi-stage virtual impactor to collect particles in different size ranges simultaneously was studied (Marple V.A. et al., 2013, 2014a; Wada M. et al., 2017). To increase the flow rate to 1000 L/min, the use of multi-nozzle virtual impactors was also designed to reduce the pressure drop (Szymanski W.W. and Liu B.Y., 1989). It is noticed that the multi-nozzle virtual impactor may have multiple jet interaction problem leading to the degradation of the impactor's performance (Fang C. et al., 1991). The virtual impactor with the rectangular nozzle can increase the flow rate without changing the cut-size as compared to the single round-nozzle virtual impactor (Masuda H. and Nakasita S., 1988). A slit-shaped nozzle virtual impactor in which the width of the slit is the same with the diameter of the round nozzle was developed to overcome the crossflow interaction problems of the multiple jets at a high flow rate (Ding Y. and Koutrakis P., 2000).

3. Application of inertial impactors

The development of the inertial impactor is in line with the need to develop PM measurement devices. PM measurement serves various purpose such as (i) the determination of PM_{10} or $PM_{2.5}$ concentrations to determine the compliance with the national ambient air quality standard (NAAQS), (ii) the determination of particle mass distribution, (iii) the determination of physical and chemical properties of particles, and (iv) the exposure assessment of PMs. Many studies were carried out by our group for ambient mass measurement of $PM_{2.5}$ and ultrafine particles using commercial inertial impactors for $PM_{2.5}$ mass concentration measurement and the evaluation of the performance of $PM_{2.5}$ monitors (Liu C.N. et al., 2013a), the measurement of mass concentration and chemical composition of $PM_{2.5}$ (Liu C.N. et al., 2014; Liu C.N. et al., 2015) and ultrafine particles (Chen S.C. et al., 2010a; Chen S.C. et al., 2010b), long-term measurement for $PM_{2.5}$ and ultrafine particles mass concentrations (Lin G.Y. et al., 2015), and the measurement of PM_{10} , $PM_{2.5}$ and $PM_{0.1}$ for source characterization and apportionment (Gugamsetty B. et al., 2012).

3.1 PM mass measurement

In order to measure the ambient PM mass concentration to determine the compliance with NAAQS for PM₁₀ and PM_{2.5}, respectively, the PM FRM (Federal Reference Method) samplers and FEM (Federal Equivalent Method) monitors are used (U.S.EPA, 2017a; Le T.C. et al., 2020). The FRM samplers and FEM monitors use size-selective inlets to classify the desired particle sizes for collecting on the filter for further analysis. Due to the sharp cutoff characteristics of the inertial impactors, they are widely deployed for the size-selective inlets. The PM₁₀ and PM_{2.5} size-selective inlets are designed based on the U.S. EPA requirements for the cutoff diameter, the sharpness of the collection efficiency curve, the flow rate, and the accuracy for long-term sampling. A list of PM₁₀ and PM_{2.5} sizeselective inlets including the conventional impactor and virtual impactor is shown in Table 26.1 in Watson J.G. and Chow J.C. (2011) and is not repeated here. U.S. EPA designated that the PM₁₀ size-selective inlets should have the cut-size of $10 \pm 0.5 \,\mu\text{m}$ and the sharpness of the sampling efficiency curve of 1.5 ± 0.1 (U.S.EPA, 2017a) and the PM2.5 size-selective inlets should have the cut-size of $2.5 \pm 0.2 \ \mu m$ but the curve sharpness is not specified. The sharpness curve of the PM_{2.5} inlet needs to agree with that of the WINS (GSD = 1.18) (Peters T.M. et al., 2001) and very sharp-cut cyclone (VSCC, GSD = 1.16) (Kenny L.C. et al., 2004), which are the standard inlets specified in U.S.EPA (2017a). Other countries specified the curve sharpness of 1.2 ± 0.1 (MEPC, 2013; ECS, 2014).

3.1.1 The inlet for a single size fraction

The conventional impactors are used extensively as an inlet to classify a single size fraction since they have sharper cutoff characteristics than that of the cyclone, which include AMI (Airmetrics) MiniVolTM impactors (AMI, 2020), Harvard sharp-cut impactors (Turner W.A. et al., 2000), Hi-vol PM₁₀ samplers (McFarland A.R. et al., 1984), Med-vol (Medium volume) PM₁₀ samplers (Olin J.G. and Bohn R.R., 1983), Flat Top Dichot PM₁₀ inlet (McFarland A.R. et al., 1978), BGI FRM Louvered PM₁₀ samplers (Tolocka M.P. et al., 2001), and EPA WINS PM_{2.5} inlet (Peters T.M. et al., 2001). These inlets are different in the sampling flow rate, cutoff diameter, and sampling curve sharpness. The Hi-vol PM₁₀ sampler is widely used for sample PM₁₀ with a high flow rate of 1133 L/min (Fujitani Y. et al., 2017). The impaction plate of the Hi-vol



PM₁₀ sampler was suggested to be grease-coated to eliminate the particle bounce and re-entrainment to avoid PM_{10} overestimation as compared to other samplers (Lee S.J. et al., 2005). A slight difference in the cutoff characteristic of the PM₁₀ inlet can cause a sensible difference in PM₁₀ measurements between different PM10 inlets since the mode of many ambient mass-size distributions is nearly 10 μm (Ranade M.B. et al., 1990). The Med-vol PM_{10} sampler is the one used for sampling PM₁₀ at the medium flow rate of 113 L/min (Gertler A.W. et al., 1993) but is not deployed widely. Some other impactors have been designed to operate at high flow rates that exceed hundreds of liters per minute (Misra C. et al., 2002) and even thousands of liters per minute (Fulghum M.R. et al., 2012; Staymates M. et al., 2013) to collect more mass of PM_{10} , $PM_{2.5}$, PM_1 or $PM_{0.1}$.

Nowadays, many FRM samplers and FEM monitors use low-volume flat-topped (McFarland A.R. et al., 1984) and louvered PM₁₀ inlets (Tolocka M.P. et al., 2001) to classify particles smaller than 10 µm at the low flow rate of 16.7 L/min (U.S.EPA, 2017b). However, several studies found that the low-volume PM₁₀ inlet has uncertainty in the measured sampling efficiency. These studies found that the sampling performance of PM₁₀ inlet is very sensitive to variation of particle sources (Wang L. et al., 2005), particle size distribution (Buser M.D. et al., 2008), and TSP/PM₁₀ ratio (Total suspended particulates) (Watson J.G. et al., 2011). The low-volume PM₁₀ sampler overestimated PM₁₀ when it was used to measure fly ash particles as compared to the Andersen cascade impactor (Park J.M. et al., 2009). When the particle source is dominant by particles larger than the cut-size, a small fraction of particles larger than the cut-size may cause the overestimation (Faulkner W.B. et al., 2014). In the previous study, we found that the distortion of the sampling performance of the low-volume PM₁₀ sampler could be due to particle bounce and re-entrainment from the uncoated surface of the PM₁₀ inlet, and particle overloading of the PM₁₀ impactor after a long sampling period, resulting in over-measurement and under-measurement, respectively. Thus, the PM₁₀ inlet was required to be cleaned every day to eliminate these effects. Similarly, most of FRM samplers and FEM monitors (16.7 L/min) using PM_{2.5} WINS as the PM2.5 inlet (U.S.EPA, 2017b), whose impaction well have to be replaced after 3-5 days sampling to eliminate the particle overloading problems (Le T.C. and Tsai C.J., 2017). The M-PM₁₀ inlet and PM_{2.5} M-WINS inlet developed by our group were tested for one month without frequent cleaning and maintenance. They can be used to replace the traditional PM₁₀ inlets and PM_{2.5} WINS inlet for PM sampling.

The MiniVol impactor with the flow rate of 5 L/min is also used to determine the mass and chemical composition of fine particles (Du W. et al., 2017; Fan Z.L. et al.,

calibration (Begum B.A. and Hopke P.K., 2019). However, the previous studies showed that the MiniVol data did not agree well with the other collocated samplers and monitors (Kingham S. et al., 2006). This could be due to the particle bounce and particle loading effect. The impaction plate of the MiniVol impactor needs to be cleaned and recoated grease after 5 sampling days or more often if overloading is observed to recovery the good performance (AMI, 2020). The mini-volume (4 L/min) or low-volume (10–20 L/min) Harvard sharp-cut impactors with different cut-sizes of 10, 2.5 and 1.0 µm, which use the oil-coated impaction substrate to eliminate the particle bounce effect, were mainly used for indoor measurement and outdoor field tests (Rovelli S. et al., 2017).
3.1.2 The inlet for two size fractions To determine the compliance with NAAOS it is often

2017; Thuy N.T.T. et al., 2018) or used as the reference for

To determine the compliance with NAAQS, it is often desirable to fractionate particles into two size fractions simultaneously, one corresponding to the coarse particle mode (> $2.5 \mu m$) and one corresponding to the fine particle mode ($\leq 2.5 \,\mu$ m). The virtual impactor is very suitable for this application (Lin G.Y. et al., 2015; Landis M.S. et al., 2017). The Andersen Dichotomous Virtual impactor (McFarland A.R. et al., 1978) is the most widely used for collecting coarse and fine particles at a low flow rate of 16.7 L/min (Gugamsetty B. et al., 2012). Other types of virtual impactors were developed and deployed for specific measurement purposes. For instance, the $PM_{1.0/2.5/10}$ trichotomous sampler (cascade virtual impactor) with the high sampling flow rate of 1133 L/min was developed to measure the mass and the ion concentrations of PM at Phoenix, Arizona, USA (Marple V.A. et al., 2013, 2014a).

3.2 Particle mass distribution measurement

The determination of the mass concentration of the particles less than a certain size is valuable but it is desirable to determine the mass distribution of entire aerosol particles. In this case, the cascade impactor can be deployed to cover a very wide particle size range from a few nanometers to tens of micrometers (Marple V.A. et al., 1991; Fernandez de la Mora J. and Schmidt-Ott A., 1993; Arffman A. et al., 2015). It is desirable to have a cascade impactor for particle mass distribution measurement with a wide range of flow rates, a large range of particle sizes, a good size resolution (or number of channels), low pressure drop, uniform particle collection, less inter-stage loss, no particle bounce, high loaded mass, and easy assembly and disassembly of the stages (Marple V.A., 2004). The list of the commercially available cascade impactors is shown in Table 8-1 in Marple V.A. and Olson B.A. (2011). Some commonly used cascade impactors are Andersen cascade impactor (Andersen A.A., 1966), Mer-



cer cascade impactor (Mercer T.T. et al., 1970), Quartz Crystal Microbalance (QCM) cascade impactor (Hering S.V., 1987), Pilat cascade impactor (Pilat M.J. et al., 1970), Berner low-pressure cascade impactor (Berner A., 1972), Low-Pressure Impactor (Berner A., 1972), Dekati[®] Low-Pressure Impactor (DLPI) (Durand T. et al., 2014), MOUDI (Marple V.A. et al., 1991; Marple V.A. et al., 2014b) and NMCI (Liu C.N. et al., 2013b; Chien C.L. et al., 2015).

The most widely used cascade impactor for determining particle mass distribution is MOUDI, which measures mass concentrations in ten size fractions down to nano-size particles with a moderate pressure drop $(D_{pa50} = 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and$ 0.056 µm) at the medium flow rate of 30 L/min (Marple V.A. et al., 2014b). In the MOUDI, particles with different size ranges are collected on the well-prepared substrates such as oil-coated aluminum foil or Teflon filter to determine the mass concentration distribution. An advantage of the MOUDI is that it can collect particles uniformly on the substrate by using multiple nozzles and rotating impaction plates and/or nozzle plates. The impaction substrates can either be Teflon filters for mass determination and chemical composition or grease-coated aluminum foil for mass concentration only without significant particle bounce effect. The MOUDI coupled with nano-MOUDI or 10 L/min MOUDI-II was further developed to have higher resolution for nanoparticles with three additional stages $(D_{pa50} = 0.010, 0.018 \text{ and } 0.032 \text{ }\mu\text{m})$ after the 10th stage $(D_{pa50} = 0.56 \,\mu\text{m})$ (Marple V.A. and Olson B.A., 1999). The MOUDI-II is used for size-fractionated measurement of mass concentration, chemical composition, and morphology of ambient ultrafine particles. The MOUDI-II needs a long sampling time to collect enough NP mass to measure their mass concentrations and chemical compositions accurately. Our group studied the performance of the MOUDI and found that the nozzles of 7th-10th stages of the MOUDI are clogged easily due to the stepwise structure with abrupt contractions. The nozzle plates are not suitable for ultrasonic cleaning to remove particle deposits due to their thin and fragile structure (Liu C.N. et al., 2013b). Therefore, the NMCI with a smooth nozzle shape was developed to eliminate the clogging problems (Liu C.N. et al., 2013b).

Due to the need for the automatic measurement of particle mass distribution, several cascade impactors have been developed and commercialized. The requirement of the real-time measurement is the sensitivity for low particle concentration detection and short response time. The ten-stage QCM cascade impactor, in which piezo-electric quartz crystals sensors are flush-mounted on the impaction plates, was developed earlier (Chuan R.L., 1970). In the QCM cascade impactor, the mass concentrations are calculated based on the difference in the frequencies of the QCMs before and after particle impaction on the piezoelectric crystal (Chen M. et al., 2016). The previous studies showed that the QCM cascade impactor has the particle bounce effect (Hering S.V., 1987), high particle loss of up to 50 %, low off-center sensitivity, and low sensitivity of nanoparticle concentrations (Keskinen J. et al., 1992). A novel QCM cascade impactor was developed to overcome these problems, in which the RH controller was used to control the RH of incoming aerosol to between 40 % and 65 % to eliminate the particle bounce effect and ensure particle coupling with the QCM, and the impedance measurement was used to achieve nanogram mass resolution (Chen M. et al., 2016).

The Electrical Low-Pressure Impactor (ELPI) developed by Keskinen J. et al. (1992) can be used to detect the number concentration distribution in real-time. The ELPI consists of a unipolar charger followed by a cascade impactor coupled with multichannel electrometers. Particles are first charged unipolarly when they pass through the charger and then collected on the electrically isolated impaction plates in the cascade impactor. The current of each stage is read by a corresponding electrometer channel and converted to particle number concentration. Numerous studies have been conducted to calibrate and improve the performance of the ELPI. The latest ELPI (Dekati[®] ELPI[®]+) was developed to measure particle number distribution with very high size resolution (13 channels), wide particle size range (from 6 nm to 10 µm), and fast response (seconds) (Järvinen A. et al., 2014). It should be noticed that the performance of the ELPI can be affected by the charging efficiency which depends on particle size and concentration and is influenced by the aging of the charger (Järvinen A. et al., 2014). The electrical low-pressure cascade impactor was developed further for achieving higher resolution with 100 or 500 size fractions (i.e. HR-ELPI+) (Saari S. et al., 2018) or measuring nanoparticle mass concentration using a wire-to-rode corona charger to eliminate the new particle formation which may occur in the pin-to-plate corona charger (Han J. et al., 2018).

3.3 Personal exposure measurement

Personal exposure measurement of PM is to assess the PM exposure of individual workers in workplaces or microenvironments where they spend most of their time daily (Marple V.A. and Olson B.A., 2011). The personal exposure measurement depends on the pollutant concentration and exposure time. Comparison to the inertial impactors used for PM sampling, the inertial impactors which are used for personal exposure measurement have specific requirements. The devices have to be light, small, portable, self-contained and battery-powered to move easily from one location to another and are placed near



the personal breathing zone, which is about 30 cm hemisphere around mouth and nose (Asbach C. et al., 2017). These devices need to collect an adequate amount of particle mass with a uniform deposit on the substrate for subsequent PM mass concentration, chemical composition, morphological, and crystallographic analyses manually. The personal exposure devices are listed in Volkwein J.C. et al. (2011) for workplaces and in Rodes C.E. (2011) for non-occupational microenvironments. Personal exposure impactors measure PM₁₀, PM_{2.5}, and PM_{1.0}, inhalable $(D_{pa50} = 100 \ \mu m$, thoracic $(D_{pa50} = 10 \ \mu m)$, and respirable $(D_{pa50} = 4 \ \mu m)$ particles regulated by the National Institute for Occupational Safety and Health (NIOSH), International Organization for Standardization (ISO), and Comite' European de Normalisation (CEN) (Volkwein J.C. et al., 2011).

To meet the respirable aerosol sampling criteria, the inertial impactors are designed to have a less sharp efficiency curve (Volkwein J.C. et al., 2011). Personal single-stage impactor (Tsai C.J. et al., 2012b), two-stage impactor (Demokritou P. et al., 2001), three-stage personal impactor (Tsai C.J. et al., 2008), and cascade impactor (Chen M. et al., 2018) and multipollutant samplers were developed for personal exposure measurement since 1970s and some which were widely used. These include Marple personal impactor, personal environmental monitor (PEM), mini-MOUDI, parallel particle impactor, personal modular impactor, Sioutas cascade impactor, personal PUF pesticide sampler, and personal impactor filter pack (Marple V.A. and Olson B.A., 2011). The Marple personal impactor with 8 stages at the flow rate of 2 L/min and Sioutas cascade impactor at the flow rate of 9 L/min are the most frequently used samplers for mass distribution measurement (Tsai C.J. et al., 1997b; Sharma R. and Balasubramanian R., 2018).

The personal exposure measurement for nanoparticles has drawn serious concern due to the adverse health effect of nanoparticles released from nanopowders and nanomaterial manufacturing processes. Nanopowders such as TiO_2 , SiO_2 , and ZnO are released to the workplaces depending on their dustiness or the property of a given material to generate dust (Tsai C.J. et al., 2009; Tsai C.J. et al., 2011). Some studies were carried out by our group (Tsai C.J. et al., 2011; Tsai C.J. et al., 2012a) to determine the generation and dispersion characteristics of nanoparticles.

Some commercialized personal cascade impactors can be used for the nanoparticle exposure measurement such as mini-MOUDI (13 stages with particle sizes ranging from 10 nm to 10 μ m) operating at the flow rate of 2 L/ min and Sioutas cascade impactor (4 stages with particle sizes ranging from 0.25 to 2.5 μ m) operating at the flow rate of 9 L/min (Asbach C. et al., 2017). Due to the high pressure drop that is needed to classify nanoparticles, only a few of personal exposure samplers were developed to collect nanoparticles. Besides, the nanoparticle samplers need to operate for a long sampling period to collect enough mass for further gravimetric analysis since nanoparticle mass is very small. The personal cascade impactors using inertial filters for nanoparticle collection were developed with a moderate pressure drop (< 5-10 kPa) (Kumsanlas N. et al., 2019) which is based on the design of inertial filter (Zhang T. et al., 2017).

Our group developed the PENS, which can be used to collect respirable particles and nanoparticles simultaneously by using a cyclone as a pre-separator to remove particles larger than 4 µm and a micro-orifice impactor with the D_{pa50} of 101.4 nm followed by the filter cassette (Tsai C.J. et al., 2012b). The PENS eliminated the particle bounce and overloading effects by using a rotating, silicone oil-coated Teflon filter as the substrate. The PENS operates at a low flow rate of 2 L/min and slightly high pressure drop (< 14-15 kPa), which is still acceptable for a personal sampling pump of 21 kPa (AirChek XR5000, USA). The PENS are used for NP mass concertation measurement in workplaces (Young L.H. et al., 2013; Asbach C. et al., 2017) and ambient air as well (Zhu C.S. et al., 2016; Zhu C.S. et al., 2017). The field comparison test of the PENS with the collocated SKC respirable dust aluminum cyclone (SKC Inc., PA, USA) and sequential mobility particle sizer (SMPS; GRIMM Aerosol Technik, Gmbh, Germany, Model 5.500) in metal working places showed that the PENS correlated well with the cyclone for PM₄ and SMPS for PN_{0.1} (Young L.H. et al., 2013). The aspiration efficiency of the PENS was good and agreed well with that of NIOSH two-stage personal bioaerosol samplers (Zhou Y. et al., 2014).

The PENS is currently being studied further to enhance its performance at a higher flow rate of 3-5 L/min and a lower pressure drop of < 15 kPa. To achieve the same cutsize of lower than 100 nm at the higher flow rate and lower pressure drop, the PENS can be re-designed with more nozzles with larger diameter and smaller *S/W*. The wetted GFF substrate can be used in the PENS to wash off deposited particles continuously to achieve a long sampling period without particle bounce and overloading effects (Le T.C. and Tsai C.J., 2017).

3.4 PM control

Control of PM emission is critical to reduce airborne PM concentration and health risks. Major particle control devices include wet scrubber, electrostatic precipitators (ESPs), cyclones, and baghouses, each of which has the advantages and disadvantages in the application. The wet scrubbers remove particles by using water spray or water film, which causes a very high operating pressure drop, metal corrosion, and water pollution (Huang C.H. et al.,



2007; Pui D.Y.H. et al., 2014). The ESPs which use electrostatic force to remove particles have the minimum removal efficiency for particles ranging from 0.1 to 1.0 μ m due to the minimum electrical mobility in this submicrometer range (Hinds W.C., 1999; Pui D.Y.H. et al., 2014). The cyclones are used extensively for PM control due to its simple structure, low pressure drop, and low cost but the collection efficiency for fine particles is low (Pui D.Y.H. et al., 2014). The baghouses use fabric filters to remove particles based on dust cake filtration with a high pressure drop (Hinds W.C., 1999; Pui D.Y.H. et al., 2014). Thus, the baghouses are required to be cleaned and regenerated frequently. Special materials such as electret filters can be used to enhance the efficiency of the depth filtration with a low pressure drop (Tien C.Y. et al., 2020).

Our group developed successfully some control devices overcoming some drawbacks to achieve high removal efficiency for fine and ultrafine particles including a wireon-plate ESP (Li Z. et al., 2015), an efficient single-stage wet ESP (Lin G.Y. et al., 2010), an efficient venturi scrubber system (Tsai C.J. et al., 2005; Huang C.H. et al., 2007), and a wet electrocyclone (Lin G.Y. et al., 2013). The efficient venturi scrubber system uses a condensation device to grow sub-micron particles to super-micron sizes before they are removed by a traditional venturi scrubber operating at a moderate pressure drop of 4.3 kPa (Huang C.H. et al., 2007). The wet electrocyclone combining the cyclone with an electrostatic precipitator with wall cleaning by water film was developed to enhance the collection efficiency for ultrafine particles for a long service period (Lin G.Y. et al., 2013). This combination technique was referred by other researchers (Titov A., 2015; Zhang X. et al., 2018).

The well-designed control devices can be used for PM and NP control in industries but they are not suitable for some circumstances such as the semiconductor industry with the coexisting residual gases and ultrafine particles (Tsai C.J. et al., 1997a). For instance, the ESPs may cause fire hazard or explosion. The inertial impactor is a potential device to replace the conventional control devices for removing NPs with a smaller footprint than the wet scrubber, a higher efficiency than the cyclone, less costly than the ESP, and a longer service time than the baghouse since it can be designed to have ultrafine cut-sizes and can use water/oil-wetted impaction substrate to eliminate overloading effect without frequent maintenance. However, the impactor requires a high operating pressure drop for NP control. This can be resolved by growing particles by condensation method. Recently, by coupling with particle condensation growth method, the inertial impactors were deployed to control ultrafine particles as a filterless control method to save the cost (Pyo J. et al., 2017). This condensation technique was used in the past to enlarge ultrafine particles to submicron particles to increase the collection efficiency of the impactor (Demokritou P. et al., 2002a). The combination of the inertial impactor with the particle growth device has the potential for ultrafine particle removal with a high removal efficiency, small footprint, moderate pressure drop and long-term use without frequent maintenance need.

3.5 Powder classification by inertial devices

Powder classification is different from PM sampling since powder sources generate high mass concentration and wide size range (0.01 to 1000 µm) (Lai W.H. et al., 2005). Powder classification is to separate powder smaller than a certain size from the source powder to obtain desired narrow powder distributions with high precision to use in bio-medicine, electronic information, fine ceramics, food industry, and coating industry (Guo L. et al., 2007; Wang D. et al., 2014). Powder classifiers can also be designed to classify coarse, fine, and nano-sized particles simultaneously with precise cutoff sizes and sharp cutoff characteristics to achieve high production rates (Liang S., 2010). Classification by inertial/centrifugal force such as cyclone is one of the popular methods since the cyclone has a simple structure and cheaper to make (Yoshida H. et al., 1991; Yoshida H. et al., 2008). It is found that large particles are repulsed or re-entrained if the inner wall of the cyclone is not oil-coated (Yoshida H. et al., 1991), and particles smaller than cut-size will be collected due to the turbulent eddies in hydrocyclone resulting in the so-called fishhook effect of the powder classification efficiency curve (i.e., the raise of curve in small particle size range) (Roldanvillasana E. et al., 1993; Lai W.H. et al., 2005). It is to be noted that the sharpness mentioned here refers to the ratio of $D_{\text{pa75}}/D_{\text{pa25}}$ (Morimoto H. and Shakouchi T., 2003; Lai W.H. et al., 2005).

Nowadays, powder classifiers are developed to separate nanopowder with a sharp classification efficiency (i.e., without contamination of coarse powders and fishhook effect) to have a uniform powder to use in ultra-conductor, optical, thermal, electromagnetic, and biomedical fields (Morimoto H. and Shakouchi T., 2003; Wang D. et al., 2014). In comparison to the cyclones, the inertial impactors, which have sharp cutoff characteristics and accurate cut-size, have a good potential to be used for powder classification with a narrow size range. The water/oil wetted inertial impactor in which the impaction substrate is washed clean by using water or oil can be used for powder classification at a high particle loading rate without particle loading effect. Further investigation to use the impactors for power classification is worthwhile.

4. Conclusions and future perspective

The study of the inertial devices has been an interesting topic since the 1860s when the first impactor was developed to observe the relationship between the particles and health effects due to its simple principle and structure, easy operation, and low cost. The design theory was also developed numerically based on the critical experimental and field tests by Marple and his co-workers. As a result, many inertial impactors were commercialized to serve as the size-fractionators and samplers for mass concentration measurement, mass and number distribution measurement, particle collection for chemical analysis, and health exposure measurement. Numerous studies were conducted to resolve the particle bounce, particle loading, and particle loss effects to improve the performance of the inertial impactors. Therefore, the inertial impactors are deployed widely to measure a wide size range of particles with a wide range of concentration and different particle types.

Inertial impaction technique still attracts researchers to work on it since the application of inertial devices is diverse. The impactors can be studied further to extend the cut-size to a very small size such as nano-size, provide real-time mass and number concentrations with very high sensitivity, fast response, and high resolution, and apply for specific applications in medical and pharmaceutical areas (Marple V.A., 2004). Besides sampling and measurement, the inertial impactors can potentially be used for PM control with a lower cut-size than the cyclone, a lower pressure drop than the baghouse and less costly than the electrostatic precipitator if they are coupled with condensation particle growth devices. The biggest challenge of the inertial impactors for the control and powder classifications is how to scale up and extend the lifetime. To meet these challenges, this article has reviewed and provided the design considerations and applications of the inertial impactors for the benefit of aerosol and powder communities.

Acknowledgments

The authors gratefully acknowledge financial support from the Taiwan Ministry of Science and Technology via the contracts MOST 108-2622-8-009-012-TE5, 107-3011-F-009-002- and 107-2221-E-009-004-MY3 and the Higher Education Sprout Project of the National Chiao Tung University and Ministry of Education (MOE), Taiwan.

Nomenclature

$C_{ m c}$	Slip correction factor
D	Collection probe diameter (m)
$D_{\rm p}$	Particle diameter (m)
D_{pa50}	Cutoff aerodynamic diameter (m)
GSD	Geometric standard deviation
μ	Dynamic air viscosity (kg·s/m ²)
$ ho_{\mathrm{a}}$	Air density (kg/m ³)
$ ho_{ m p}$	Particle density (kg/m ³)
$ ho_{ m p0}$	Unit density (1000 kg/m ³)
Q	Total flow rate (L/min)
$Q_{ m o}$	Major flow rate (L/min)
Q_1	Minor flow rate (L/min)
Re	Reynolds number
S	Jet-to-plate distance (m)
Stk	Stokes number
Stk_{50}	Stk for 50 % collection efficiency
Т	Throat length (m)
U_0	Air jet velocity (m/s)
W	Nozzle diameter/width (m)

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Reiew Paper

Drag Reduction in Turbulent Flows by Polymer and Fiber Additives[†]

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Abstract

This article provides a review of the recent progress in understanding and predicting additives-induced drag reduction (DR) in turbulent wall-bounded shear flows. We focus on the reduction in friction losses by the dilute addition of high-molecular weight polymers and/or fibers to flowing liquids. Although it has long been reasoned that the dynamical interactions between polymers/fibers and turbulence are responsible for DR, it was not until recently that progress was made in elucidating these interactions in detail. Advancements come largely from numerical simulations of viscoelastic turbulence and detailed measurements in turbulent flows of polymer/fiber solutions. Their impact on current understanding of the mechanics and prediction of DR is discussed, and perspectives for further advancement of knowledge are provided.

Keywords: turbulence, drag reduction, polymers, fibers

1. Introduction

Over the last decades, there has been a steady increase in the number of scientific events and publications dedicated to the phenomenon of Drag Reduction (DR) in turbulent wall-bounded flows. The reduction in turbulent friction losses by the dilute addition of high-molecular weight polymers, fibers or other types of additives (e.g. surfactants) to flowing liquids has been extensively studied since the phenomenon was first observed over 70 years ago. One of the reasons is the huge practical importance of turbulent DR in a wide range of process engineering applications that are commonly found in the food, pharmaceutical, and biomedical industries (Han et al., 2017; Bhambri et al., 2016; Jovanović et al., 2006). Indeed, almost all these applications, such as transport of crude oil in pipelines (Hart, 2014) or heat transfer and exchange (Tiong et al., 2015; Fsadni et al., 2016), involve the use of drag-reducing additives in gas-liquid/liquid-liquid flows.

It has long been argued that DR is determined by the dynamical interactions between additives and turbulence (see Lumley, 1969; Berman, 1978 for further details), yet it was not until recently that progress had been made in

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understanding these interactions and predicting DR in turbulent shear flows. Advancements have been granted by the possibility to perform high-fidelity simulations of viscoelastic turbulent flows and detailed measurements of turbulence in dilute/semi-dilute additive solutions, mostly via non-invasive optical techniques. Facing the applications quest for more quantitative information on DR mechanisms, numerical and experimental techniques characterized by unprecedented accuracy and access into the flow have been developed to disclose new features that are peculiar of additive-induced DR phenomena. In this review, we address precisely these phenomena, focusing on the case of polymer- and fiber-induced DR in turbulent wall-bounded shear flows. DR phenomena are discussed in connection with current physical understanding of how polymers and/or fibers interact with the various scales of turbulence: from the small scales resolving the flow in Lagrangian models to the large-scales of Euler-Euler models. Since the targeted field of research is extremely vast, we will cover only the issues relevant to the use of high-molecular weight polymers and fibers as Drag-Reducing Agents (DRA) in processes of industrial interest, leaving other types of additives (surfactants, micro-bubbles and compliant coatings) and applications out of the discussion.

2. Background: Phenomenology of DR

In this section, we will try to highlight current understanding of the microscopic interactions that occur



[†] Received 9 June 2019; Accepted 2 December 2019

J-STAGE Advance published online 29 April 2020

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between the coherent structures of the flow and the additive, which govern the macroscopic features of DR phenomena. The essential dynamical interactions were poorly understood and remained largely unknown until faithful direct numerical simulations (DNS) of polymer/fiberinduced DR in channel flows became feasible (Kim et al., 2008). We will discuss such interactions considering the review by White and Mungal (2008) as the starting point to provide an update on the advancements that have been achieved over the last decade through numerical and experimental evidence. In their review, White and Mungal (2008) already established that DR produced by polymer and/or fiber additives can be described phenomenologically as the outcome of dynamic interactions that take place between the additive and the turbulent flow. This interaction leads to a significant modification of the nearwall turbulence structure, as demonstrated, for instance, by the LDA measurements of viscoelastic polymer solutions of Escudier et al. (2009), thus altering the nature and strength of the coherent structures that populate this region of the flow and play a crucial role in the selfsustaining mechanism of wall turbulence. The reader is referred to Marchioli and Soldati (2002) and Picciotto et al. (2005), and references therein for further details on these mechanisms. A nice pictorial view of this process, as induced by rigid neutrally-buoyant fibers, was given by Paschkewitz et al. (2004, 2005), and is shown in Fig. 1.



Fig. 1 Instantaneous visualization of near-wall vortices and wallnormal velocity contours for (**a**) single-phase Newtonian and (**b**) fiberladen channel flow. Fiber parameters: Peclet number Pe = 1000, aspect ratio $\lambda = 100$, concentration $nL^3 = 18$. Velocity contours are equally spaced in the range $\pm 0.013U_c$ with U_c the centerline velocity. Panel (**c**): Mechanism for fiber-induced DR. *I*. Fibers align in intervortex regions. *II*. Fibers generate large stresses and body forces that oppose vortex motion. *III*. Vortex structures are dissipated and fibers realign in flow direction. *IV*. Vortices re-emerge and cycle repeats. Reproduced with permission from Paschkewitz et al. (2004).

Panels (a) and (b) of this figure show the effect of the fibres on the near-wall vortices, which are usually referred to as Quasi-Streamwise Vortices (QSV) and are visualized here using iso-surfaces of the second invariant of the velocity gradient tensor (Blackburn et al., 1996). In the fiber flow, QSVs are both larger and weaker, and the contours of the wall-normal velocity show an increase in spacing. The vortices are also spread out over a larger region in the wall-normal direction relative to the Newtonian flow. In the case of fibers, this happens because fibers that move through the high stress regions of the flow (phase I in Fig. 1), most pronounced in regions of intense vortex activity, generate large stresses and body forces that oppose to vortex motion (phase II). This interaction weakens the vortices and enhances fiber alignment in the flow direction (phase III). Upon fiber reorientation, the reduction in local fiber stress allows the vortices to reemerge and the turbulence is sustained in a weakened state (phase IV).

A similar phenomenology is observed in the case of polymer-induced DR, and is summarized in Fig. 2, taken from Graham (2014). This figure refers to situations in which the ratio of the elastic forces to the viscous forces within the flow, parameterized by the Weissenberg number Wi (defined more precisely in the next section), are low to moderate. In the case of Newtonian turbulence, the flow is characterized by active intervals, dominated by strong three-dimensional, coherent vortical motions (Marchioli and Soldati, 2002), for the majority of the time and only occasionally enters hibernation intervals. Once Wi exceeds an onset value, indicated as Wio in the figure, these flow structures start to stretch the polymer chains. Such stretching weakens the near-wall coherent structures, thus leading to reduction of the friction drag (regarded as the primary mechanism operating at low levels of DR). Specifically, the polymers are stretched within the low-speed streaks and relax as they get rolled into the



Fig. 2 Schematic of the stochastic cycle displayed by viscoelastic turbulent minimal channel flow at low Reynolds number ($Re \sim 3000$) and moderate Weissenberg number ($Wi \sim 25$). Reproduced with permission from Graham (2014).



streamwise vortices. The resulting polymer force works to loosen the vortices. As Wi further increases, polymer stretching by turbulence becomes persistent and stresses accumulated over time reach: The polymer chain is deformed more rapidly than it can relax, so a threshold value beyond which the active turbulence can no longer sustain itself is reached: Flow hibernation sets in and allows the polymer molecules to relax again. Once the turbulence becomes active again, the cycle repeats. Note that this scenario implies that DR is primarily a near-wall phenomenon. Under these circumstances, a limiting state may be reached, in which turbulence must be entirely suppressed near the wall (Graham, 2014; Wang et al., 2014). The scenario just described is in accordance with several studies (see Paschkewitz et al. (2004), Dubief et al. (2004, 2005) and Gillissen et al. (2008) among others) which revealed that the body forces due to polymeric stresses oppose the vortical motions of the QSV that populate the buffer layer that mediates momentum exchange between the near-wall region and core fluid in channels and pipes.

The similarity between the phenomenological interpretations of Paschkewitz et al. (2004, 2005) and of Graham (2014) highlights the fact that polymer and fiber stress tensors show the same characteristics, at least in the low drag reduction regime as noted by Boelens and Muthukumar (2016). In particular, because fibers cannot store turbulent kinetic energy in their backbone, this mechanism has to be explained by viscosity effects. The macroscopic manifestation of the mechanism just discussed is a reduced wall friction, namely a modified mean velocity profile, a redistribution of the shear stress inside the boundary layer and a reduction in the energy dissipation rate at length scales close to the lower end of the energy cascade yet still within the inertial range (de Chaumont Quitry and Ouellette, 2016; Xi et al., 2013; Ouellette et al., 2009).

Further evidence of the above-mentioned mechanisms has been provided by the analysis of the effect of elasticity on the coherent flow structures, which suggests that the self-sustaining process of wall turbulence becomes weaker because the additive is able to counteract both the biaxial and uniaxial extensional flow regions around QSVs (Roy and Larson, 2006). Above the buffer layer, however, hairpin vortices are more prevalent than QSV. In Newtonian flows, hairpins can regenerate to form hairpin packets that produce large amounts of streamwise kinetic energy, as well as multiple ejections resulting in turbulent bursts and formation of new QSVs (Adrian et al., 2000). Further, hairpin vortex packets significantly contribute to the mean Reynolds shear stress (Jodai and Elsinga, 2016; Ganapathisubramani et al., 2003), which has two parts: the coherent stress caused by non-linear interactions among individual vortices within the packet and incoherent stress originated from velocity fluctuations induced by each vortex (Lee and Sung, 2011; Adrian et al., 2000). In drag-reduced flows, the hairpins in the log layer are weakened by the counter torques produced by the additive (Kim et al., 2007), similarly to what happens to QSV in the buffer layer. Kim et al. (2008) have examined the time evolution of hairpin packets interacting with a polymer conformation field, showing that the non-linear threshold of initial vortex strength required to trigger auto-generation of new hairpins increases as the flow viscoelasticity increases, especially in the buffer layer. In other words, the generation of new vortices is suppressed by the polymer stresses, thereby decreasing the turbulent drag. Similar findings were obtained by Guan et al. (2013) and Fu et al. (2014). Guan et al. (2013) used time-resolved particle image velocimetry to investigate the effect of DRA on the spatial topological character of coherent vortices in wall-bounded turbulence. Although the (polymer) additive solution was not found to affect the spatial topological shape of these vortices, a drastic decrease of the associated fluctuating velocity and velocity derivatives in the solution was observed. The resulting reduction of the wall friction was ascribed to the suppression of vortex occurrence and intensity. Fu et al. (2014) used particle image velocimetry in combination with planar laser induced fluorescence to investigate DR in turbulent channel flow upon inhomogeneous injection of polymer solution from one channel wall. The focus of the study was polymer diffusion, which controls the local polymer concentration and was found to be suppressed due to turbulence inhibition compared to the diffusion of a passive scalar in unladen turbulence.

Very recently, Elsnab et al. (2019) have provided new experimental evidence of the effect of DR on the structure of turbulence in channel flow. These authors have shown that, for the DR between 6.5 % and 26 %, several fluid velocity statistics (e.g. the mean profile slope in the inertial sublayer or the peak value and peak position of the streamwise r.m.s.) tend to increase with DR in a continuous and essentially linear manner, whereas the relationship between the injected polymer concentration and the level of DR is nonlinear. According to Elsnab et al. (2019), a primary effect of polymer is that it limits near-wall vorticity stretching and reorientation, and thus attenuates/ delays the three-dimensionalization of the vorticity field. This scenario is corroborated by the observed onset of the inertial layer at large-enough wall distance, as well as an increase in the scale of the organized vortical motions, and, finally, a reduction in the overall scale separation in the inertial range.



3. Onset of DR, maximum DR and available theoretical frameworks

Two features of DR due to additives have been considered extensively in archival literature: the onset of DR and the so-called Maximum Drag Reduction (MDR) asymptote. In this section, we will recall these features showing how the physical mechanisms of DR and the underlying dynamical interactions between additives and turbulence have been incorporated in suitable criteria to predict DR.

Scaling arguments and experimental data have led to devise a time criterion for polymer-induced DR in wallbounded flows (Hershey and Zakin, 1967; Lumley and Kubo, 1985), which requires that for DR to occur, the polymer relaxation time must be longer than a representative time scale of the near-wall turbulence, i.e., $T_z > \frac{\mu_s}{\rho_s u_{\tau}^2}$, where T_z is the average time taken by a stretched polymer to return to a coiled configuration, μ_s and ρ_s are the viscosity and the density of the solution, and $u_{\tau} = \sqrt{\tau_{w}} / \rho_{s}$ is the wall friction velocity, with τ_w the wall shear stress. For a flexible linear polymer in solution, the relaxation time can be expressed as $T_z \sim \frac{\mu_{\rm s} \left(N^{3/5} a \right)^3}{k_B T}$, where N is the number of repeating monomers in the polymer molecule, a is length of a single monomer (the repeat unit from which a polymer is built), k_B is the Boltzmann constant, and T is the solution temperature (Flory, 1953). According to the classical formulation of the time criterion, onset of DR occurs when the ratio of the polymer timescale to the timescale of the near-wall turbulence, defined as the wallshear Weissenberg number $Wi_{\tau} = \frac{T_{z}\rho_{s}u_{\tau}^{2}}{\mu_{s}}$, is of order unity. Whenever this condition is met, the polymer molecule undergoes the so-called coil-stretch transition (Somani et al., 2010): Molecules become abruptly stretched and the elongational viscosity increases, up to several orders of magnitude. Elongational viscosity increases preferentially near the wall, where the extensional strain rates are the highest, and acts to suppress turbulent fluctuations, increase the buffer layer thickness and eventually reduce wall friction (Sher and Hetsroni, 2008). The flow-induced coil-stretch transition of high molecular weight polymers has generally been considered to be of first order (Ghosal and Cherayil, 2018). However, there is evidence of significant slowing down in the rate at which the polymers relax to equilibrium in the vicinity of the transition: This suggests that the transition may be more complex, since the slowing down effect is typical of a second-order transition, and characterized by a broad spectrum of conformational states (Ghosal and Cheravil, 2018).

A recent development of the time criterion for DR has been put forth by Boelens and Muthukumar (2016), who investigated numerically the drag-reducing mechanism in the onset regime for both flexible polymers and rigid fibers. Based on the similarity of the polymer and fiber stress tensors in turbulent flow, these authors infer that a common drag-reducing mechanism exists, and suggest that it must be associated with a viscous effect. In particular, they find that all terms in the stress tensor are negligible, except the off-diagonal terms associated with rotation: Therefore, DR arises from rotational motion of fibers and partially stretched flexible chains. Based on these observations, the rotational orientation time is proposed as the unifying time scale to characterize DR by both types of additive. This time scale can be defined as $\tau_r = K V_r \mu_s / k_B T$, where K is a proportionality constant including terms related to the shape and the volume of the rotating molecule, and $V_{\rm r}$ is the free space per molecule. The rotational orientation time of rod-like macromolecules can be obtained either directly by dielectric measurements or by relaxation of dichroism, or indirectly by viscoelastic measurements (Boelens and Muthukumar, 2016).

The time criterion for DR is generally confirmed by numerical and experimental data, yet the omission of polymer concentration represents a serious limit to the application of the criterion for predictive purposes. Indeed, several works in which mono-disperse polymers characterized by a single value of T_Z (instead of a distribution of T_Z as found for poly-disperse polymers) have demonstrated that the onset of DR depends systematically on polymer type and concentration (Campolo et al., 2015; Yang and Ding, 2013). The contribution of concentration in determining the onset of DR has been accounted for in the context of the so-called elastic theory developed by De Gennes and co-workers (Tabor and De Gennes, 1986; de Gennes, 1990) based on the elastic behaviour of stretched polymers. According to this theory, DR by coilstretch transition occurs when the elastic energy stored by the partially-stretched polymers, which increases with decreasing length scale of turbulence (i.e. increased stretching characteristic of turbulence dynamics), becomes comparable to the energy of the turbulent flow, which decreases with the scale size. When this situation occurs, the elastic energy interferes with the turbulent cascade mechanism preventing it to proceed all the way to the Kolmogorov scale (Xi et al., 2013). This can lead to buffer layer thickening and reduced drag. Experimental measurements by Ouellette et al. (Ouellette et al., 2009; de Chaumont Quitry and Ouellette, 2016), who studied the effect of long-chain polymers on the Eulerian structure functions in a turbulent von Kårman swirling flow, support this framework as they indicate that the introduction of polymers into the flow modifies the energy cascade by extracting turbulent kinetic energy from the flow and partially dissipating it directly (Valente et al., 2014). As a result, the rates of energy injection, transfer and dissipation for the turbulence are no longer all equal, as they must be in Newtonian turbulence where viscosity provides the





Fig. 3 Schematic representation of the elastic theory for the onset of DR. Panel (a) shows the time scales in homogeneous turbulence, including the onset length scale r^* . The 2/3 power law is valid for scales larger than the Kolmogorov scale η , *L* being the largest flow scale. Panel (b) sketches the condition for which the scale r^{**} can be determined, namely when the turbulent energy per unit volume, which scales as $r^{2/3}$, is equal to the elastic energy per unit volume, which begins to grow at r^* and scales as $[\lambda(r)]^{5/2}$, with $\lambda(r) = (r^*/r)^n$ the power law of polymer stretching for $r < r^*$. Reproduced with permission from Sreenivasan and White (2000).

only mechanism of energy dissipation.

When the elastic theory is applied to homogeneous isotropic turbulence, one might expect that, for a given combination of the polymer and the flow and using the same notation as in Sreenivasan and White (2000), a turbulent length scale r^* exists, whose corresponding time scale τ_r^* matches T_{Z} , as sketched in Fig. 3(a). This length scale can be expressed as $r^* = u_{r^*}T_Z$, with u_{r^*} the velocity scale characteristic of the scale r*. Following Kolmogorov 41 theory, such velocity scale can be expressed as u_{r^*} = $(r^*\langle\epsilon\rangle)^{1/3}$. Polymer molecules are expected to undergo stretching by all scales smaller than r^* and to affect the flow only at scales smaller than r^{**} . The scale r^{**} is smaller than r^* and can be determined assuming that the elastic energy per unit volume stored by the polymer equals the turbulent energy per unit volume that can be associated to that scale, as sketched in Fig. 3(b). Another crucial result of the elastic theory is the relation that connects the elastic energy with the power law scaling of polymer stretching, which reads as $G[\lambda(r^{**})]^{5/2} = \rho_s u_{r^{**}}^2 =$ $\rho_{\rm s}(\epsilon_T r^{**})^{2/3}$ (Sreenivasan and White, 2000), where G = ckT/N is the elastic energy (c being the polymer concentration in units of monomers per unit volume) and the quantity on the right-end side is the turbulent kinetic energy at scale r^{**} , which can be expressed via the energy transfer rate per unit mass through the inertial range, ϵ_T . Note that, in non-Newtonian turbulence, ϵ_T differs from the energy injection rate through the cascade and from the energy dissipation rate due to viscosity, since polymers can provide a non-viscous mechanism for draining energy from the cascade (de Chaumont Quitry and Ouellette, 2016). When concentration is very small, the scale r^{**} will be smaller than the Kolmogorov scale η and the turbulence will be unaffected by the polymer. A minimum concentration exists for which $r^{**} = \eta$, and onset of DR occurs. Following the onset, for a fixed value of the flow Reynolds number Re, DR initially increases with polymer concentration but saturates beyond a certain value. This threshold value for concentration corresponds to the so-called Maximum Drag Reduction (MDR), which is generally attributed to the dynamics being reduced to a marginal yet persistent state of subdued turbulent motion (Virk, 1975; Li et al., 2015; Choueiri et al., 2018). In the literature, the MDR asymptote is found to be identical for different types of polymer-solvent combinations (Calzetta, 2010). For a fixed value of polymer concentration, DR initially increases with increasing Re, following a unique concentration-dependent trajectory up to a certain Re after which an abrupt change of trajectory is observed. Such change indicates the location at which the DR curve merges with the MDR asymptote.

One scenario is that MDR occurs when the concentration of the polymer is high enough to allow for unstretched coils to overlap. This implies (see also Sreenivasan and White (2000) for experimental validation) that $G_m = \rho_s u_\tau^2 \cdot Wi^{-1}$ where G_m is the elastic energy when concentration is equal to the value c_m at which DR data cross over the MDR asymptote. Since this expression for G_m neglects the dependence on the scale r^{**} , the following additional expression for the energy can be derived (Sreenivasan and White, 2000):

$$\left[\frac{G_{\rm m}}{\rho_{\rm s}u_{\tau}^2}\right]^{1/3}Wi^{5/6} = Re_{\tau}^{\beta} , \qquad (1)$$

where $Re_{\tau} = u_{\tau}R/v$ is the shear Reynolds number of the flow (*R* being the characteristic size of the flow domain, e.g. the pipe radius in pipe flow) and β is a constant that can be determined upon comparison with experiments. For pipe flow, the best agreement with available data is obtained for $\beta \simeq 1$, which implies that r^{**} near the MDR asymptote scales with *R*. The interpretation of this scaling is that, at the MDR asymptote, a small amount of stretching (characteristic of length scales of order *R*) will be enough to make the elastic energy of the polymer comparable to the turbulent kinetic energy of the fluid. When this condition is met, polymers cause the growth of the buffer layer thickness across the entire boundary layer.

In spite of the apparently sound theoretical ground on

which the theory is based, and despite the agreement with several experimental datasets, the phenomenological explanation just discussed is not able to provide a unique bounding mechanism of MDR. First off, the theory is not self-consistent since it assumes that, whenever stretched, polymers can drain energy from the flow but also that they can affect the flow only at scales $r < r^{**} < r^*$. This inconsistency was addressed by Xi et al. (2013), who proposed to modify the original elastic theory framework by balancing the rate of energy transfer rather than the energy itself. By doing so, these authors were able to identify the scale at which the additive is expected to affect the energy cascade and use this scale to collapse their experimental DR data on a single master curve. The same model, referred to as energy flux-balance model, has been assessed by de Chaumont Quirty and Ouellette (2016), who focused on the characterization of concentration effects on the Eulerian and Lagrangian structure functions. One example of their results is provided in Fig. 4, which shows the compensated velocity transverse structure



Fig. 4 Panel (**a**): Compensated transverse velocity structure function as a function of r/η^w , with η^w the Kolmogorov scale in flow of pure water. Panel (**b**): same data as in panel (**a**) with length rescaled by a factor $\phi^{2/5}$, derived from the energy flux-balance model. Reproduced with permission from de Chaumont Quitry and Ouellette (2016).

function, $D_{\rm NN}$, expressed as:

$$\left[\frac{3}{4}\frac{D_{\rm NN}(r)}{C_2 r^{2/3}}\right]^{3/2} = \epsilon_T , \qquad (2)$$

where C_2 is a known scaling constant. The figure compares the compensated structure function for pure water with that obtained for polymer solution at varying concentration ϕ , expressed in ppm, at high *Re* but moderate Wi. As ϕ increases, the structure function reaches a plateau at larger length scales and the value of this plateau is different from that measured in pure water. The important points, however, are that (1) data for different polymer concentrations are found to collapse when curves are rescaled by the factor $\phi^{2/5}$ (see Xi et al. (2013) for further details), and (2) data collapse on two distinct curves: One for concentrations below 5 ppm and one for concentrations above 10 ppm. Such different ϕ -dependent behaviour was ascribed to the possible onset of interactions between individual polymer chains, which are favoured at higher concentrations and are more likely at small Wi (e.g. below the range for which a sharp coil-stretch transition is observed). Based on these findings, which were observed to hold also for structure functions in the time domain, de Chaumont Quitry and Ouellette (2016) concluded that the energy flux-balance model seems to be able to capture the essential effect of polymer concentration on turbulence, even if its application should be limited to dilute solutions.

In addition, there is evidence of situations in which MDR occurs when the Reynolds stresses are due primarily to the fluctuating stresses of the additive (see White and Mungal, 2008 for further details) and situations in which the polymer concentration field is inhomogeneous, e.g. in injection experiments: The theory does not take such inhomogeneities into account. Most importantly, however, the difficulty in predicting MDR comes from the fact that the flow, at the onset of MDR, does not reach a purely laminar state: Rather, turbulence is reduced (either via elastic or viscous effects or both) to a marginal state at the edge between laminar and turbulent motion. This may suggest the existence of a peculiar self-sustaining transitional flow regime in which the stresses produced by the additive play a key role and promote DR mechanisms that are inherently different from those known for Newtonian fluids. Indeed, very recent results from Choueiri et al. (2018) provide evidence of a dynamical disconnection of the asymptotic state from ordinary turbulence: These authors show that, for an appropriate choice of parameters, additives can reduce the drag beyond the MDR limit, eliminating turbulence and giving way to laminar flow. At higher polymer concentrations, however, the laminar state becomes unstable, resulting in a fluctuating flow with the characteristic drag of the MDR



asymptote. At sufficiently high Reynolds numbers, such flows are observed to be structurally different from Newtonian turbulence albeit being characterized by streak patterns that are similar to those resulting from elastoinertial turbulence at Reynolds numbers well below the threshold for Newtonian turbulence. This type of behaviour has brought to a new interpretation of MDR, which is based on the idea that the dynamics of the flow upon onset of MDR are driven by the elastoinertial instability for high-enough polymer concentrations (Choueiri et al., 2018; Samanta et al. 2013). In other words, the MDR limit and the characteristic approach towards it may be seen as the result of two states of turbulence: Newtonian turbulence and elastoinertial turbulence. When these two turbulent states coexist, a transition from one to the other is observed. Based on such observations, Choueiri et al. (2018) have proposed a state map for Reynolds number versus polymer concentration, in which the different manifestations of turbulent flow observed for a specific type of additive (polyacrylamide) are summarised. This map is reported in Fig. 5 and shows a number of interesting features. First, the onset of turbulence (the left lower branch in Fig. 5) is delayed by the action of polymers. Second, as Re is increased, turbulence sets in as localized turbulent puffs and, subsequently, to growing turbulent slugs provided that polymer concentration remains below a certain threshold of concentration (C < 20 ppm in Fig. 5). The onset of puffs and slugs is delayed compared to Newtonian fluids, and leads to mixed state which then eventually approaches MDR instead of allowing for complete relaminarization of the flow. Third, above the threshold for concentration, fluctuations set in more uniformly in space and lack the spatial intermittent character of the Newtonian transition scenario. For a further increase in concentration (C > 90 ppm in **Fig. 5**), this insta-



Fig. 5 State map for Reynolds number versus polymer concentration. While Newtonian turbulence is controlled by the Reynolds number, elastoinertial turbulence and its instabilities are controlled by the relation between shear rate $\dot{\gamma}$ and concentration. Iso- $\dot{\gamma}$ lines are shown in the portion of the map where elastoinertial instabilities are observed. Reproduced with permission from Choueiri et al. (2018).

bility occurs at *Re* significantly smaller than the lowest value for which Newtonian turbulence would be observed. The important finding here is that, at intermediate concentrations, elastoinertial instability sets in before MDR is reached.

The discussion made so far highlights that drag reduction may be characterized by relatively few dimensionless groups, notably the flow Reynolds number and the Weissenberg number. Such parameter space has been nicely summarized by Graham (2014), and the schematic proposed by this author is shown in Fig. 6. In this figure, *Ex* is the extensibility number, representing the maximum value of the ratio between the extensional stress due to the polymer and the extensional stress due to the solvent, $\beta = \mu_s / (\mu_s + \mu_p)$ with μ_s the solvent viscosity and μ_p the additive viscosity, while El = Wi/Re is the elasticity number (El = 0 for Newtonian flow). For a given set of experiments, Ex and β have constant value the schematic provides the DR map as a function of Re and Wi only. Each oblique line in the figure is characterized by constant El and represents a series of experiments at increasing flow rate. As Re increases, transition from laminar to turbulent flow occurs. The lowest oblique line, labeled "A", corresponds to small El. As flow rate increases, transition to turbulence occurs first, then at some higher flow rate, Wi becomes sufficiently large for the polymers to stretch and DR to set in. This onset Weissenberg number, denoted as Wi_{o} in the figure, is around 10–20. The MDR regime is eventually reached at Re much higher than those considered in the plot. The line labeled "B" corresponds to larger El, and refers to a situation in which transition occurs at a sufficiently high Wi to prevent Newtonian turbulence: Polymer relaxation is slow enough to leave the turbulence unaffected by viscoelasticity, yet the flow rate must still increase beyond transition to reach MDR. The line labeled "C" corresponds to values of El large enough to let the flow enter the MDR regime directly upon transi-



Fig. 6 Parameter space of turbulence and DR in dilute polymer solutions. Boundaries are in general fuzzy and oblique. The linear stability limit Re = 5772 is also shown but is not relevant for the present discussion. Reproduced with permission from Graham (2014).



tion to turbulence. Finally, the line labeled "D" corresponds to the case of elastoinertial turbulence (referred to as early turbulence): In this case, transition can occur at significantly lower *Re* than in Newtonian flow. As mentioned by Graham (2014), the detailed correspondence between this regime and the MDR regime is still poorly understood. Experiments suggest the existence of a continuous transition from the laminar flow curve to the MDR curve, driven by the occurrence of some kind of linear instability of the laminar state at sufficiently high *Re* and *El*: To the best of our knowledge, however, no simulation data obtained from available viscoelastic constitutive models has provided evidence of such linear instability yet.

4. Recent analyses of DR onset and MDR in wall-bounded turbulence

In this section, we provide a survey of both numerical and experimental analyses of DR onset and MDR in wallbounded flows, with a twist towards viscoelastic effects, to highlight current trends and research pathlines in the study of turbulence-additives interaction. Shahmardi et al. (2019) investigated the turbulent flow of a polymer solution in non-axisymmetric square ducts, using the FENE-P model to simulate the presence of polymers. The main macroscopic effect associated to the presence of the polymers is to modify the secondary flow by increasing the circulation of the streamwise main vortices and moving the location of the maximum vorticity towards the centre of the duct. In addition, the low- and high-speed streaks that characterize the fluid velocity distribution near the wall are found to grow in size and coherence. As far as the viscoelastic behaviour of the flow is concerned, the Weissenberg number is found to influence strongly the flow (as also shown in Zhou and Schroeder, 2016): The cross-stream vortical structures grow in size and the in-plane velocity fluctuations are reduced as flow elasticity increases. Overall, the viscoelastic flow is less uniform than its Newtonian counterpart, even if the direct contribution of the polymer stress term in the energy budget is found to be small in amplitude. The same type of numerical approach, namely direct numerical simulation of an incompressible FENE-P fluid, was employed by Li et al. (2015) and Teng et al. (2018) to study DR in both turbulent Poiseuille and Couette flow in a plane channel. Focus of the analysis was the additive-induced modification of the near-wall flow structures. In Poiseuille flow, the ratio of polymer relaxation time to the time scale of vorticity fluctuations in the mean flow direction is found to remain close to unity in the near-wall region, from the onset of DR to MDR. Moreover, the average axial energetic vortex convection time is observed to increase with increasing

DR while its rotation speed decreases. Since the rate of decrease in the rotation speed is found to exceed the increase of the vortex convective time, MDR is achieved when these two time scales become nearly equal. A similar DR mechanism is observed in Couette flow only in the near-wall region. In the core region of the flow, differences are found, the most intriguing being the significant polymer stretching that arises from a more intense mutual exchange between the elastic potential energy and the turbulent kinetic energy of the flow (Teng et al., 2018). Also, the spanwise and wall-normal components of the conformation tensor are found to reach their peak value: Such finding is in contrast with that observed in Poiseuille flow, where polymer stretching and elastic/kinetic energy exchanges in the core region are negligible and peak values of the conformation tensor components occur near the wall (Teng et al., 2018).

White et al. (2018) also investigated polymer dragreduced flow in a wall-bounded domain, focusing on the redistribution of mean momentum and the mechanisms underlying the redistribution processes in channel flow. From a mechanistic perspective, the experimental observations of White et al. (2018) indicate that polymers reduce the intensity of near-wall vorticity stretching, thus leading to an outward migration of the peak in the Reynolds shear stress and its gradient. In turn, such migration leads to a reduced mean velocity gradient at the wall, a more gradual decay of the mean vorticity, and causes the wall-normal position where inertially dominated mean dynamics occurs to move outward from the wall. At high enough DR, the inertial sublayer runs out of physical space and ceases to exist: This implies that the state of MDR is attained only upon annihilation of the inertial sublayer.

Owolabi et al. (2017) investigated experimentally the turbulent DR mechanism in flow through ducts of circular, rectangular and square cross-sections using two grades of polyacrylamide (a flexible linear polymer) in aqueous solution having different molecular weights and various semi-dilute concentrations. The authors explored the relationship between DR and fluid elasticity, exploiting the polymer mechanical degradation¹ to vary the rheological properties of the solution. Under controlled degradation conditions, streamwise velocity profiles at various levels of DR indicated a thickening of the buffer layer, up to the entire cross-section at MDR, in agreement with previous studies (Gillissen and Hoving, 2012; Paschkewitz et al., 2004). Based on their measurements, Owolabi et a. (2017) were able to derive a quantitative prediction of DR from the knowledge of polymer relaxation time, flow rate and geometric length scale (using ei-

 $^{^1\!}Mechanical$ degradation and its effects on DR will be discussed in Sections 5 and 6.

ther the Newtonian pressure drop combined with rheology data, or the average shear rate as an initial guess to determine *Wi*, combined with an iterative procedure). This prediction reads as:

$$DR\% = 2C_{\infty} \left(\frac{1}{1 + \exp(Wi_{\rm c} - Wi)} - Wi_{\rm c} \right)$$
(3)

with C_{∞} the approximate limiting value of *DR* % as $Wi \rightarrow \infty$ and Wi_c the critical Weissenberg number for the onset of drag reduction (set to be $Wi_c = 0.5$, in agreement



Fig. 7 Fanning friction factors at different flow rates and pumping times for (a) pipe, (b) rectangular channel and (c) square duct. Dotted lines represent the appropriate laminar flow equations for Fanning friction factor; dot-dashed lines represent the correlations of Blasius for pipe and square duct and of Dean for rectangular channel; solid lines represent the correlations of Virk (1975) for pipe and rectangular channel and of Hartnett et al. (1986) for square duct at MDR; the shaded regions represent $f = \pm 10$ % of MDR. Reproduced with permission from Owolabi et al. (2017).



Fig. 8 (a) Combined *f-Re* data for cylindrical pipe, rectangular channel and square duct (symbols and colours as in **Fig. 7**). (b) Variation of *DR* % with Weissenberg number. The solid black line represents Eq. 3. Reproduced with permission from Owolabi et al. (2017).



with the theory of Lumley, 1973). In observing a working functional dependence of DR % on Wi alone, the dependence on the ratio β of solvent to total viscosity, on inertia (i.e. on the flow Reynolds number) and on other viscometric functions, e.g. first or second normal-stress differences, is neglected. In spite of these approximations, the prediction fits reasonably well with the data, as shown in Figs. 7 and 8. It must be noted that, in the MDR limit, some weak Reynolds number dependence remains, as DR % scales roughly as $Re^{0.1}$ in this limit, and there is a spread in the literature for data nominally at MDR (Graham, 2014), highlighted by the grey region in Fig. 8(b). Given the quality of the data collapse illustrated in **Fig. 8(b)**, however, the authors concluded that both β and Re should be regarded as second-order effects, at least for the concentrations and range of Re investigated.

Another correlation to predict the upper limit of DR using polymers as DRA has been proposed recently by Zhang et al. (2018), for the case of turbulent pipe flow. The main equation of the model computes the average drag reduction as:

$$DR\% = (1 - \beta) \left(1 + \frac{1}{12Wi^2} \right) \cdot \mathcal{H}$$
⁽⁴⁾

where β is the ratio of the solvent viscosity to the liquid viscosity after the polymer is added at the zero shear rate, and $\mathcal{H} = \frac{1 - c - c/l^2}{\left(1 - c/l^2\right)^3}$, with *c* the trace of the conformation tensor and l the dimensionless maximum length of the polymer in the solution. Since c and l cannot be measured, the above equation must be used assuming c = 0 to make it useful for practical engineering applications. The model assumes that all vortex structures disappear in the turbulent flow, i.e. complete laminarization is achieved. A slightly older work on DR in dilute polymer solutions was carried out by Xi and Bai (2016). These authors investigated the laminar-turbulent transition of the solution showing its connection with MDR. The idea of the study comes from the speculation (prompted by the universality of MDR) that the MDR asymptote might be associated with a class of weak or marginal turbulent states that already exist in Newtonian flows but only become unmasked at high levels of polymer elasticity. As fluid elasticity increases, the transition to hibernating states becomes much more frequent, resulting in them taking up a larger proportion of the overall statistics or a flow more dominated by features of MDR. This idea clearly hints to the already-mentioned DNS results (Graham, 2014; Xi and Graham, 2012) on the intermittent transitions between strong active turbulence and weak hibernating turbulence. Xi and Bai (2016) identified the marginal state associated to the weakest form of turbulence that can be sustained as a dynamical edge state consisting of traveling waves and relative periodic orbits. The dynamics of such state are characterized by low-frequency fluctuations and exhibit regular bursts of turbulent activities separated by extended quiescent periods. The flow field is dominated by elongated vortices and streaks, with weak extensional and rotational motions. Flow structures and ES kinematics match hibernating turbulence and, according to Xi and Bai (2016), offer explanations for the existence and universality of MDR. Yet, the quantitative magnitude of MDR still remains unsolved.

Fujimura et al. (2017) studied numerically the influence of the polymer aggregation length on turbulent DR in channel flow. Polymer aggregation was modeled using a bead-spring chain model. The authors find that the local polymer relaxation time increases as the natural length of the polymer increases and the spring constant decreases, and observe that DR increases logarithmically with the relaxation time. Based on this logarithmic dependency, the authors speculate that the drag-reducing effect of the polymer occurs when it is longer than the diameter of turbulent vortical structures: Longer polymers are found to induce higher energy dissipation upon interacting with the flow structures and tend to suppress turbulent fluctuations. The role of polymer length was also examined by Yang and Dou (2010) in connection with wall roughness effects. These authors proposed and validated a theoretical formula to describe the flow resistance in laminar, transitional and turbulent flows from the hydraulically smooth regime to the fully rough one. This formula was developed based on the findings that, while polymers in smooth pipe flow increase the viscous sublayer thickness (thus leading to DR), polymers in rough pipes also increase the near-wall velocity when compared to Newtonian flow conditions, implying that roughness has a negative effect on DR. Indeed, larger roughness tends to narrow the gap between the resistance in viscoelastic flows and that in unladen flows.

As far as analysis of fiber-induced DR is concerned, Moosaie and Manhart (2011, 2013) used a sophisticated rheological model based on direct Monte-Carlo solver to compute fiber orientation dynamics and study the effect of Brownian diffusivity and fiber aspect ratio on the non-Newtonian stress generated by the fibers. The model enables stochastic simulation of the Fokker-Planck equation, in contrast to the moment approximation simulation approach used by Paschkewitz et al. (2004), which requires a closure model. Application of the model to turbulent channel flow shows a shift of the logarithmic law region of the mean velocity profile, indicating a thickening of the viscous sublayer. The streamwise velocity fluctuations are enhanced, while the spanwise and wallnormal ones are attenuated. However, there are discrepancies with the results of the moment approximation approach. The closure model required by the moment approximation approach provides wrong estimates of the



mean non-Newtonian shear stress at the wall: This has a direct effect on the wall stress deficit and hence on the amount of DR (Moosaie and Manhart, 2013).

Fiber-induced DR has been investigated also by Gillissen and Hoving (2012). These authors performed pipe flow experiments showing that turbulent DR in plugflow of concentrated suspensions of macroscopic fibers is a self-similar function of the wall shear stress over the fiber network yield stress. This behaviour was modelled in terms of a central fiber network plug, whose radius is determined by the yield stress. The pipe cross section can then be divided into a solid plug for $r < r_c$, with r_c the radial coordinate at which the surface of the plug is located (corresponding to the point in the pipe where the shear stress of the fluid equals the fiber network yield stress), and a Newtonian annulus for $r > r_c$. The plug constrains the size of the turbulent eddies in the surrounding annulus, thus reducing the friction factor as compared to Newtonian flow. Note that, if the notion that a large aspect ratio is key for DR, then one should expect polymers and fibers to reduce the drag by similar mechanisms. The experiments by Gillissen and Hoving (2012), however, showed marked differences, e.g. in the profiles of the mean flow. Polymers act in the near-wall, buffer layer, effectively thickening the viscous sublayer, while leaving the momentum transfer in the turbulent core unaffected. Macroscopic fibers, on the other hand, act in the turbulent core, and have little effect in the near-wall region. This difference stems from the different lengths of polymers and fibers. Polymers are usually of sub-Kolmogorov length scale and, on the scale of the near-wall vortices, can be regarded as a continuum that induces an additional viscosity and acts to reduce the momentum transfer of the near-wall vortices (Voth and Soldati, 2017). Fibers, on the other hand, are rarely below the Kolmogorov scale. Rather, they are usually orders of magnitude larger than the near-wall vortices and, instead of inducing internal friction, tend to impose external constraints on the nearwall vortices, which are thus forced to restructure themselves.

5. Predictive correlations for DR in wallbounded flows

In the previous sections, we focused on the phenomenology of polymer/fiber-induced turbulent DR and on the theoretical frameworks that have been developed to explain the underlying physics. In this section, we focus on one aspect of practical relevance for the design of industrial systems exploiting DRA, namely the predictive correlations that are available to determine amount of DR expected for a given DRA concentration in a specific solvent. The amount of DR can be predicted using two types of correlations: those that simply fit the experimental data (typically collected in small-scale pipes), whose predictability for industrial scale applications is however rather limited (Campolo et al., 2015), or those developed based on physics of the DR phenomena which appear more promising in the industrial practice (Dubief et al., 2005). Given the wealth of correlations for drag-reducing flows that are available in the literature, we will purposely focus only on those providing the friction factor. Specifically, we will discuss results from unpublished experimental tests made with polymers (polyethylene oxide, PEO) in pipes of different diameter, equipped with centrifugal pumps to assess the predictive capability of some widely-used correlations, discussing the efficacy of the tested additives as DRA. Tests were performed under controlled conditions: A pre-mixed homogeneous mixture of additive and solvent was introduced in the test rig and pumped along the loop using a low-shear pumping system in order to avoid peaks of shear stress, which could prematurely degrade the additive (Elbing et al., 2009; Choi et al., 2000). Details on the experimental facility are provided in Campolo et al. (2015).

The theoretical variation of friction factor expected in the polymeric regime when polymer degradation is negligible reads as (Shetty and Solomon, 2009; Virk, 1975):

$$\frac{1}{\sqrt{f}} = (4+\delta)\log_{10}\left(Re\sqrt{f}\right) - 0.4 - \delta\log_{10}\left(Re\sqrt{f}\right)^*$$
(5)

where δ is the slope increment and $\left(Re\sqrt{f}\right)^*$ is the onset Reynolds number, defined as:

$$\left(Re\sqrt{f}\right)^* = \frac{\sqrt{2\tau_{\rm w}/\rho} \cdot D}{v_{\rm s}} \propto \tau_{\rm w}^{0.5} \propto \gamma_{\rm w}^{0.5} \tag{6}$$

where D is the pipe diameter, v_s is the kinematic viscosity of the solvent, τ_w is the wall shear stress and γ_w is the wall shear rate. Fig. 9 shows the results of tests performed in the pipes using PEO (Polyox WSR-301 by Dow Chemicals), and hydrolized Polyacrylammide (HPAM, Magnafloc 1011 by Basf) as water-soluble polymer. Each panel in the figure shows the variation of friction factor, $1/\sqrt{f}$, for a given polymer concentration (symbol) as a function of wall Reynolds number, $Re\sqrt{f} = Re_{\tau}\sqrt{2}$, in Prandtl Karman coordinates. The black line represents the Prandtl-Karman friction factor (P-K) for pure water and smooth pipe; the gray line in the top left corner represents Virk's MDR asymptote. Dashed lines shown together with the experimental points represent the theoretical variation of friction factor given by Eq. (5). The experimental data follow the polymeric regime up to a threshold value of $(Re\sqrt{f})^*$ above which they depart from theory due to mechanical degradation. The latter can be ascribed to two different phenomena: the mechanical degradation due to turbulence and the mechanical degradation due to the injection system. Mechanical deg-





Fig. 9 Prandtl-Karman plot of friction factor variation produced by polymer injection: different symbols refer to different polymer concentrations; each row shows the effect of polymer type: WSR-301 (top row) and Magnafloc 1011 (bottom row); each column shows the effect of pipe diameter (D = 30 mm, left column; D = 100 mm, right column); colours represent concentration (0.25 ppm, red; 0.50 ppm, blue, 1.00 ppm violet; 2.50 ppm, green; 5.00 ppm, brown; 10.00 ppm, purple). Results from the Authors.

radation due to turbulence is associated to breakage of the monomers of the polymer chain produced when the shear rate exceeds the threshold value γ_w^* which is a function of polymer molecular weight, $M_{\rm w}$: $\gamma_{\rm w}^* = A \cdot M_{\rm w}^B$, with A and B coefficients that depend on polymer type (Elbing et al., 2009). For PEO: $A = 3.4 \cdot 10^{18}$ and B = -2.20; for HPAM: $A = 1.16 \cdot 10^{23}$ and B = -2.73. We remark here that, following Tabor and De Gennes (1986), the onset condition identifies a value of the fluid time scale, usually equal to $1/\gamma_{\rm w}$, matching the relaxation time scale of the polymer, which depends on the polymer molecular weight. This vields $\gamma_w \propto M_w^{-1}$. The use of such relation assumes that the onset of drag reduction is independent of polymer concentration. This assumption has been widely used since Virk (1975) showed a negligible influence over a wide range of polymer concentrations. However, other studies (see Elbing et al. (2009) and references therein) have shown that weak concentration dependence may be observed under certain conditions. Winkel et al. (2009) and Vanapalli et al. (2006) found that $\gamma_{\rm w} = a \cdot M_{\rm w}^{-1}$ with $a = 3.35 \cdot 10^9$ for PEO, as derived from the experimental data reported by Campolo et al. (2015). Elbing et al. (2009) report $\tau_w = 1.68 \pm 0.60 Pa$ for HPAM having $M_{\rm w} = 5.5 \cdot 10^6$ from which one can calculate $a = 9.25 \cdot 10^9$. The slope increment δ depends on molecular weight and concentration, whereas it should not depend on pipe diameter (Campolo et al., 2015) and a specific slope increment $\delta/C^{0.5}$ can be defined to characterize the drag reducing ability of a polymer-solvent pair and an intrinsic slope increment $\Pi = \delta/(C/M_w)^{0.5}$ can be defined which depends only on the species skeletal structure. Based on these assumptions, one can use experimental data to identify the value of onset Reynolds number and slope increments.

The second mechanism for polymer chain degradation is due to the injection system, characterized by locallylarge values of strain rate, $\dot{\epsilon}_D = u_{\rm ss} / d$, with $u_{\rm ss}$ and d the velocity of polymer master solution and the injection pipe diameter, respectively. Recent experimental evidence (Elbing et al., 2011) has demonstrated that individual polymer chains are stretched and fractured on a relatively short time scale (order of milliseconds in the cited experiments), whereas changes in the mean molecular weight occur on a significantly longer time scale (order of tenths of seconds). This large time scale separation is ascribed to the fact that, at any instant in time, a relatively low percentage of polymer chains are significantly stretched. According to Vanapalli et al. (2006), polymer chain deg-





Fig. 10 Reference curves for DR prediction in industrial loop. TC (red line) is the theoretical line corresponding to the polymeric regime; OP (green line) is the curve corresponding to one-pass scission; SS (blue line) and INJ (purple line, visible only in the largest pipe) correspond to steady state scission and degradation due to the injection system, respectively. Symbols correspond to WSR-301 solution at the reference concentration of 1 ppm. Results from the Authors.

radation under elongational flow is triggered by strain rates exceeding a threshold given by: $\dot{\epsilon_D} = D \cdot M_w^E$, where D and E are also coefficients, e.g. $E = 4.2651 \cdot 10^{10}$ and D = -1.23 for PEO; $D = 1.64737 \cdot 10^{11}$ and E = -1.27 for HPAM (Vanapalli et al., 2006). These data on polymer mechanical degradation can be used to identify and plot in P-K coordinates the limiting value of shear stress and elongational stress the polymer can be exposed to before being degraded by the flow. Fig. 10 shows these curves together with the experimental data collected for PEO (WSR-301) at 1 ppm concentration in the three different pipes. TC (red line) is the theoretical line corresponding to the polymeric regime (Eq. 5); OP (green line) is the curve corresponding to one-pass scission; SS (blue line) corresponds to steady state scission and INJ (purple line, visible only in the largest pipe) corresponds to degradation produced by the injection system. The agreement between experimental data (red symbols) and reference curves for degradation is quite good and indicates that drag reduction in real systems can be predicted with some confidence also for situations in which $Re\sqrt{f} \ge (Re\sqrt{f})^{-1}$. Mechanical degradation leads to the alteration of the molecular weight (Yang and Ding, 2013). To determine the local molecular weight of the injected polymer, Elbing et al. (2011) proposed the following scaling:

$$\frac{M_{\rm w} - M_{\rm ws}}{M_{\rm wo}} = \exp\left[-8.6 \cdot 10^{-5} (t_{\rm f} \cdot \gamma_{\rm w})\right]$$
(7)

where M_w is the local molecular weight, M_{ws} is the steadystate molecular weight (defined as the minimum M_w that can be obtained at a given γ_w), M_{wo} is the non-degraded value of M_w at the point of injection, and $t_f = (X - X_{inj})/U_\infty$ is the polymer residence time in the flow, $(X - X_{inj})$ being the distance travelled by the polymer, and U_∞ the convection velocity. **Fig. 11** shows the accuracy of this scaling for different characteristics of polymer degradation within



Fig. 11 Normalized difference between measured and steady-state molecular weights scaled with the product of residence time and wall shear rate. Results refer to rough (solid symbols) and smooth (open symbols) surfaces. The solid curve is the fit to the data and is provided by Eq. 7, namely Eq. (3.12) in Elbing et al. (2011). The error bars were determined from standard error propagation analysis. Reproduced with permission from Elbing et al. (2011).

a turbulent boundary layer. Changes in mean molecular weight occur on a time scale proportional to the polymer residence time. In addition, M_w tends to a finite level with increased residence time and shear rate, and the key parameters that control the degradation process appear to be the shear rate, polymer residence time in the TBL flow, M_{wo} and M_{ws} (Elbing et al., 2011).

6. Additive DR from a physico-chemical perspective

As mentioned in the previous section, mechanical degradation represents an important aspect of DR phenomena because of its practical implications for the design of ac-



curate experiments (Wyatt et al., 2011). Mechanical degradation pertains the physico-chemical aspects of DR, which are in strong connection with the rheological and fluid mechanics aspects already covered. We believe that discussing physico-chemical aspects is thus important to provide a coherent picture of the intrinsic complexity of DR phenomena.

Regarding mechanical degradation, a crucial issue is the polymer resistance to chain scission, which poses an upper bound to the level of DR that can be achieved by the additive as well as the time/distance over which the additive is effective as drag reducer (see Choi et al., 2000; Elbing et al., 2009; Soares et al., 2015). When polymers are added to the flow as a homogeneous mixture in a wall-bounded flow, protocols (e.g. batch mixing by low shear impeller or tumble blenders, in line mixing by recirculation using low shear pumps, as in Campolo et al., 2015; Japper-Jaafar et al., 2009) are typically enforced during polymer mixture preparation to avoid mechanical degradation. When polymers are injected at the wall, small information is generally given on details of the injection system used which, per se, might induce degradation. Whichever the origin of mechanical degradation, the limiting value of the shear rate able to produce chain scission can be measured by experiments. Scaling relationships have been derived to link the limiting shear rate to the polymer molecular weight and to the strength of chemical bonds (Vanapalli et al., 2006). As demonstrated by Vanapalli et al. (2006), in a system properly designed to avoid any local degradation, the local stress at the Kolmogorov scale able to generate the molecular tension leading to polymer covalent bond breakage inside the pipe can be evaluated and the effect of polymer mechanical degradation can be accounted for. The loss of efficiency of the additive as the mechanical degradation proceeds has been analysed by Choi et al. (2000) in a rotating apparatus and by Soares et al. (2015) in pipe flow. Whichever the flow configuration, the physical mechanism governing degradation is independent of geometry. Kalashnikov (2002) found that for low enough additive concentration, the initial value of the friction coefficient and its variations in the course of degradation are also independent of the Weissenberg number. A half-degradation time can be defined from theoretical considerations and measured in connection with the flow hydrodynamics and network characteristics to estimate the span over which periodic polymer injection should be performed to maintain a desired level of DR.

A recent investigation focusing on the deformation of polymer molecules is reported in Shaban et al. (2018), who used planar PIV to gather detailed measurements of the turbulent flow field in a channel when polymers (PAM) are exploited as DRA. Their data, together with the rheological characterization (shear and elongational viscosity) of the polymeric solution allowed to characterize the interaction between the polymer molecules and turbulence. Measurements of mean flow, second-order turbulence statistics, and local strain-rate and rotation rate obtained using time-resolved 2D-PIV, showed that the extent of polymer deformation strongly depends on the wall-normal location, and is caused mainly by the streamwise strain rates. In the log-layer, polymer molecules do not exhibit significant stretching, since they were found to sample regions of strong rotation more often than regions of strong shear. At a high polymer concentration, rotation and shear were found to be in balance both in the buffer layer and in the log layer.

Another important physico-chemical aspect of DR is represented by the polymer microstructure, which nowadays can be designed ad-hoc to support the synthesis of well-defined macromolecules able to achieve desired supramolecular characteristics (D'hooge, 2015). Wever et al. (2013) used controlled synthesis to produce high molecular weight branched polyacrylamides, PAM, to be used as drag reducing agents. The equilibrium conformation of polymers having the same molecular weight but different microstructure were analysed using Dynamic Light Scattering (DLS) to measure their hydrodynamic volume; their intrinsic viscosity in solution was measured by viscosity tests. Results showed that the molecular architecture of more branched (13 and 17-arm PAMs) polymers was more extended in solution than that of their linear (4 and 8-arm analogues) counterpart; as a consequence, the elastic response of polymers solutions was enhanced, leading to an improved thickening efficiency that supported the use of branched PAMs for application in Enhanced Oil Recovery and DR. Controlling the microstructure of the polymer may also allow controlling its extensional viscosity, which according to many authors, can become much higher than the intrinsic viscosity (see Housiadas and Beris (2004) and references therein). An abrupt increase in the extensional viscosity that depends on the extensional strain rate is therefore deemed to be a key factor in turbulent DR (Hidema et al., 2013). Polymerinduced DR under different extensional strain rates have been analyzed by image processing calculating the curvature histogram of the interference pattern, which is related to the distribution of the velocity fluctuation. Results indicate that different processes of energy transfer reduction are activated depending on the polymer type (flexible/rigid). Flexible polymers are stretched and oriented parallel to the streamwise direction, whereas rigid rod-like polymers are only re-oriented parallel to the streamwise direction without extension. In the normal direction, the energy transfers are prohibited by orientated polymers. The stretching process of flexible polymers (PEO) increased the extensional viscosity, which also prohibits energy transfer in the streamwise direction (Shaban





→ Increase of PEO concentration

Fig. 12 Interference images of turbulence in flowing soap films of PEO solution at different extensional rates. Images refer to increasing PEO solution ($C = 0.5 \cdot 10^{-3}$ wt %, $1 \cdot 10^{-3}$ wt % and $2 \cdot 10^{-3}$ wt % from left to right) and increasing extensional rates ($\dot{\epsilon} = 250$ s⁻¹ and 350 s⁻¹ from top to bottom). Reproduced with permission from Hidema et al. (2013).

et al., 2018). Hidema et al. (2013) developed ad-hoc tests in two-dimensional turbulence made by flowing soap films to investigate DR by flexible polymers (e.g. PEO) and rod-like polymers (e.g. HPC, hydroxypropyl cellulose) in the absence of shear flow. Using a grid to generate extensional strain in a flowing solution containing polymers, Hidema et al. (2013) recorded the interference pattern of soap films with a video camera to observe the effect of polymer stretching and polymer re-orientation on 2D turbulence. **Fig. 12** shows the corresponding interference images of the turbulence in flowing soap films of PEO-added solution at different extensional rate.

7. Conclusions and future perspectives

The discussion proposed in this review highlights a number of crucial challenges for future research. Many experimental and numerical results indicate that the structure of a turbulent flow laden with polymers and/or fibers can be modified over a wide range of length scales even for very small concentrations of the additives. Additionally, effects due to additives depend strongly and not straightforwardly on the concentration: While the flow statistics in the dissipation range of turbulence change smoothly as a function of additive concentration, there is evidence that the inertial-range values of the structure functions are modified only when the concentration exceeds a specific threshold (which is flow and polymer-type dependent). Open issues are therefore related to the lack of a clearcut explanation of the qualitative change in the effect of the additive above the critical concentration, and to the need for a better understanding of the exact ways in which the additives affect the energy cascade. Considering that the time criterion for the onset of DR does not hold in the bulk of the flow, a physical mechanism by which the polymers can affect scales much larger than

their size has yet to be identified. A promising route to achieve this goal seems to be represented by the possibility to describe the effect of the polymer/fiber additive through models derived from viscoelastic turbulence theory. In terms of available scaling laws, it appears that more comprehensive datasets (both experimental and numerical) are needed to develop truly universal relations. Datasets need to be expanded by including a wider range of polymer types, molecular weights, injection conditions (for processes involving polymer degradation) and flow parameters to properly assess the universality of the scaling. This would lead to further improvement of existing correlations, which aim to predict mechanical degradation and the resulting loss of efficiency of drag reducers induced either by turbulence or by the injection system.

Acknowledgments

We are very grateful to Professor Soldati for the useful discussions.

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Authors' Short Biographies



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Cristian Marchioli is Associate Professor of Fluid Mechanics at the University of Udine, Editor of Acta Mechanica and former chairman of the COST Action "Fiber suspension flow modeling". Currently, Prof. Marchioli sits in the scientific council of the International Center of Mechanical Sciences, where he coordinated several advanced schools on particles in turbulence. His research interests involve multiphase flow modeling, from small-scale particle-turbulence interactions to large-scale modeling of gassolid/gas-liquid flows. Prof. Marchioli has published 50+ papers and 100+ conference proceedings. He has also delivered several invited and keynote lectures at international conferences.



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Marina Campolo is Associate Professor in Chemical Engineering at the University of Udine. She received her Laurea (M.S. - B.S.) in Industrial Engineering and got her Ph.D. in 1999 in Chemical Engineering from the University of Udine. Her research interests are in the area of process and environmental engineering with an emphasis on multiphase systems. Prof. Campolo has published 30+ papers and 50+ conference proceedings. Together with A. Soldati and A. Cremese, she received the 2007 Knapp award from the American Society of Mechanical Engineers.

Agglomeration and Dispersion Related to Particle Charging in Electric Fields[†]

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Abstract

Electrostatic forces cause spontaneous movement of charged particles; subsequently, electrostatic technology is attracting attention because of its application in powder handling processes, such as separation, classification, dispersion, and collection. Dielectric and conductive particles are charged by induction in a strong electric field and moved by Coulomb forces. The magnitude and polarity of the transferred charges are controlled by the strength and direction of the electric field. The dielectric particles are also polarized in the electric field, and dipole interactions occur between particles or in the particle layers, complicating the particle behavior. This review paper presents induction charging, agglomeration, levitation, and other behaviors resulting from particle layers in electric fields. A series of particle phenomena occur in parallel electrode systems, which consist of a lower plate electrode and an upper mesh electrode. Charged agglomerates are formed on the particle layers, levitated by the Coulomb forces, and disintegrated with rotation when approaching the mesh electrode. The mechanisms of agglomeration and disintegration have been elucidated in multiple studies, including microscopic observations and theoretical analyses of particle motion, based on numerical calculations of the electric field. Furthermore, a new system is proposed for continuous feeding of dispersed particles using electric fields and vibration.

Keywords: particle, electric field, charging, agglomeration, levitation, dispersion

1. Introduction

In powder handling processes, the deposition of charged particles is a common phenomenon. The accumulation of charged particles on surfaces reduces operability and leads to lower productivity; thus, charged particles must be removed from the surfaces. Fluid flow (Masuda et al., 1994; Gotoh et al., 2015) and vibration (Kobayakawa et al., 2015; Adachi et al., 2017) are effective for removing particles. Another effective method is the application of external electric fields, which enables remote control of the motion of charged particles (Masuda et al., 1972; Calle et al., 2009; Kawamoto et al., 2011). Dielectric particles and conductive particles can be charged by induction in a strong electric field and moved by Coulomb forces. The magnitude and polarity of the transferred charge are controlled by the strength and direction of the electric field. The dielectric particles are also polarized in the electric field, and dipole interactions act between the particles or in the particle layers; thereby, the particle behavior becomes

more complicated.

The induction charging, agglomeration, levitation, and other behaviors resulting from particle layers in electric fields have been studied in detail (Shoyama and Matsusaka, 2017, 2019; Shoyama et al., 2019). Furthermore, a new system has been proposed for the continuous feeding of dispersed particles using electric fields and vibration (Shoyama et al., 2018). Based on previous studies, this review paper summarizes the mechanisms of induction charging, the control of particle behavior, and the concept of its application.

2. Induction charging of single particles

When a conductive particle comes into contact with an inside wall of a parallel electrode with a different polarity, the particle is charged to the same polarity as the electrode. This phenomenon is called induction charging (Blanchard, 1958; Cho, 1964). Charges cannot pass through ideal dielectric materials; however, dielectric materials have a low degree of conductivity on the surface or in the body. Thus, various types of particles can be charged by induction.

The equilibrium charge of a conductive particle by induction is represented by (Cho, 1964)



Received 13 June 2020; Accepted 28 July 2020
 J-STAGE Advance published online 5 September 2020

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$$q_{\infty} = 1.65\pi\varepsilon_{\rm rf}\varepsilon_0 D_{\rm p}^2 E_{\rm ex} \tag{1}$$

where $\varepsilon_{\rm rf}$ is the relative permittivity of the fluid, ε_0 is the vacuum permittivity, $D_{\rm p}$ is the particle diameter, and $E_{\rm ex}$ is the external electric field strength.

The equilibrium charge of a dielectric particle is represented by (Wu et al., 2003)

$$q_{\infty} = 0.55 p \pi \varepsilon_{\rm rf} \varepsilon_0 D_{\rm p}^2 E_{\rm ex} \tag{2}$$

and

$$p = \frac{3\varepsilon_{\rm rp}}{\varepsilon_{\rm rp} + 2} \tag{3}$$

where ε_{rp} is the relative permittivity of the particle. The particle charge as a function of time is expressed as

$$q_{\rm p}(t) = q_{\rm pe}[1 - \exp(-t/\tau)]$$
 (4)

and

$$\tau = \rho_{\rm v} \varepsilon_0 \varepsilon_{\rm rp} \tag{5}$$

where $\rho_{\rm v}$ is the volume resistivity of the particle.

3. Motion of charged particles between parallel electrodes and other applications

Particles sufficiently charged by induction can be made to levitate from the electrode by Coulomb forces, and then move toward the counter electrode. When the particles come into contact with the counter electrode, their polarity is inverted. Consequently, the particles move back to the first electrode and then oscillate between the electrodes (Cho, 1964). Highly conductive particles are charged immediately after contact with the electrodes. For low conductivity particles, charging takes time (Ohkubo and Takahashi, 1996a, 1996b; Wu et al., 2003; Nader et al., 2009). However, if electrical resistance is extremely high, induction charging will not occur. Instead, contact charging will dominate (Matsusaka et al., 2010; Matsusaka, 2011). As the quantity of charge transferred by one contact charging event is rather small, particles involved in contact charging cannot be levitated.

In the above system, there can be both positively and negatively charged particles between electrodes. To extract unipolar charged particles, openings may be required in one of the parallel electrodes. Replacing the upper plate electrode with a mesh electrode allows the passage of unipolar charged particles through the openings (Tada et al., 2004). When charged particles with the same polarity are extracted from the revised system, these particles are dispersed by their mutual electrostatic repulsion (Masuda, 2009).

There are many electrostatic applications for the control of particle position (Matsusaka et al., 2008), separation (Dwari et al., 2015), classification (Kawamoto, 2008), and surface cleaning (Mazumder et al., 2007; Kawamoto et al., 2011). In addition, there are reports regarding particle levitation using various configurations of electrodes (Adachi et al., 2016; Blajan et al., 2017). These electric fields allow particles to move even in the absence of mechanical and/or pneumatic systems. Thus, electrostatic techniques are expected to be used in various fields such as space exploration (Kawamoto et al., 2011; Adachi et al., 2016), and under atmospheric pressure.

4. Agglomeration and levitation in electric fields

Dielectric particles are polarized in an electric field and tend to form chain agglomerates along the direction of the electric field because of the interactions between polarized particles (Hollmann, 1950; Pearce, 1954; Nakajima and Matsuyama, 2002). The interaction between dipoles is illustrated in **Fig. 1**. A typical example of the application of this interaction is an electrorheological fluid (ERF), which is a suspension of dielectric particles dispersed in an insulating liquid. The ERF changes apparent viscosity by forming chain-like structures of particles (Parthasarathy and Klingenberg, 1996).

Shoyama and Matsusaka (2017) conducted experiments on the behavior of particles (glass beads: $D_{p50} = 100 \,\mu\text{m}$) in gases using parallel electrodes at a distance of 10 mm. **Fig. 2** schematically shows the experimental setup. Particle layers with a thickness of 1 mm are placed on the lower electrode, which is connected to a power supply, and the upper electrode is grounded. The behavior of the particles in the external electric field is recorded by a high-speed camera with a zoom lens.

When the voltage of the lower electrode is set to $V_{\rm L} = 5$ kV, single particles and chain agglomerates levitate from the particle layers, as shown in **Fig. 3**. These phenomena can be explained as follows. (1) The dielectric particles



Fig. 1 Interaction between dipoles.



(glass beads) are polarized in the upward electric field. (2) As mutual electrostatic interactions act between the particles, chain agglomerates are formed. (3) As the particle surfaces have a relatively low conductivity, the electrons move downward due to induction; consequently, the particles on the top surface of the particle layers are positively charged. (4) The charged particles experience upward Coulomb forces in the electric field. (5) As the Coulomb forces overcome the downward forces, the particles levitate.

Fig. 4a shows a simulation model for electric field calculation using FEM (COMSOL Multiphysics, COMSOL, Inc.). A chain agglomerate is placed on the top surface of 1-mm-thick particle layers in a 3D Cartesian coordinate system (x, y, z). The calculation domain is set to $5 D_p \times 3\sqrt{3} D_p$ for the horizontal cross section and 10 mm for the height, which is the same as the distance between the electrodes in the experimental setup. The top and bottom boundaries are set to zero and a given voltage, respectively. Periodic boundary conditions are applied at the side



Fig. 2 A parallel electrode system.



Fig. 3 Snapshots: (a) levitation of single particles and chain agglomerates and (b) formation of large agglomerates (glass beads: $D_{p50} = 100 \,\mu\text{m}, \rho_p = 2300 \,\text{kg/m}^3, \varepsilon_{rp} = 7$).

boundaries. The charges of the agglomerate and the top particle layer are given based on the experimental result. The relative permittivity of the particles is also given for the calculation.

Fig. 4b shows the calculated electric field strength $E_{\rm exz}$ in the *z*-direction. The $E_{\rm exz}$ value in the region of z < 1 mm is almost zero in an electrostatic equilibrium state, although there are small fluctuations caused by particle arrangements. In contrast, the $E_{\rm exz}$ values within the agglomerate (z = 1 - 1.18 mm) are relatively high and fluctuate significantly at the particle contact points and on the top of the agglomerate.

Fig. 5 shows a series of images of a levitated particle at intervals of 2 ms. The particle moves upward, accelerating in the electric field. **Fig. 6** shows a series of images of agglomeration and levitation at intervals of 10 ms. The polarized particles form a straight-chain agglomerate by mutual electrostatic interactions, and the agglomerate levitates at 60 ms.

Particle charge can be calculated based on the motion analysis of levitated particles. A straight-chain agglomerate moving in an electric field experiences a drag force $F_{\rm d}$, a gravitational force $F_{\rm g}$, and an electrostatic force $F_{\rm e}$. The equation of motion of the agglomerate is expressed as



Fig. 4 Electric field calculation using FEM: (a) simulation model and (b) calculated values along the axis of the chain agglomerate.



Fig. 5 Levitation of a single particle (glass beads: $D_{p50} = 100 \ \mu m$).





Fig. 6 Agglomeration and levitation (glass beads: $D_{p50} = 100 \ \mu m$).

$$nm_{\rm p}\frac{\mathrm{d}\boldsymbol{v}_{\rm a}}{\mathrm{d}t} = \boldsymbol{F}_{\rm d} + \boldsymbol{F}_{\rm g} + \boldsymbol{F}_{\rm e} \tag{6}$$

where *n* is the number of the primary particles constituting the agglomerate, m_p is the mass of each primary particle, v_a is the velocity of the agglomerate, and *t* is time. The mass of each particle is defined as

$$m_{\rm p} = \frac{\pi D_{\rm p} \,^3 \rho_{\rm p}}{6} \tag{7}$$

where $\rho_{\rm p}$ is particle density. For a stationary fluid, $F_{\rm d}$ is given by (Kasper et al., 1985; Niida and Ohtsuka, 1997)

$$\boldsymbol{F}_{\mathrm{d}} = 3\pi\mu D_{\mathrm{a}}\boldsymbol{v}_{\mathrm{a}}\boldsymbol{\kappa} \tag{8}$$

where μ is the viscosity of the fluid and D_a is the volume equivalent diameter of the agglomerate, which is defined as

$$D_{\rm a} = n^{\frac{1}{3}} D_{\rm p} \tag{9}$$

 κ is the dynamic shape factor given by

$$\frac{1}{\kappa} = \frac{1}{\kappa_{\perp}} + \left(\frac{1}{\kappa_{\parallel}} - \frac{1}{\kappa_{\perp}}\right) \cos^2 \theta_{\rm m} \tag{10}$$

where $\theta_{\rm m}$ is the angle between the agglomerate axis and the moving direction. κ_{\perp} and κ_{\parallel} are the dynamic shape factors perpendicular and parallel to the moving direction, respectively. That is,

$$\kappa_{\perp} = \begin{cases} 1.00 & (n=1) \\ 1.16 & (n=2) \\ 1.26 & (n=3) \end{cases}$$
(11)

and

$$\kappa_{\parallel} = \begin{cases} 1.00 & (n=1) \\ 1.03 & (n=2) \\ 1.07 & (n=3) \end{cases}$$
(12)

The gravitational force of the agglomerate is defined as

$$\boldsymbol{F}_{g} = n \, \boldsymbol{m}_{p} \, \boldsymbol{g} \tag{13}$$

where g is gravitational acceleration. When the agglomerate is close to an object, such as the surface of the particle

layers, the electrostatic force $F_{\rm e}$ consists of the Coulomb force $F_{\rm ex}$ in the external electric field, the image force $F_{\rm i}$, the interaction force $F_{\rm p}$ between polarized particles, and the gradient force $F_{\rm grad}$ in a non-uniform electric field (Morgan and Green, 1997). That is,

$$\boldsymbol{F}_{e} = \boldsymbol{F}_{ex} + \boldsymbol{F}_{i} + \boldsymbol{F}_{p} + \boldsymbol{F}_{grad}$$
(14)

Here, F_{ex} is expressed as

$$\boldsymbol{F}_{\text{ex}} = \sum_{i=1}^{n} \boldsymbol{F}_{qi}$$
(15)

where F_{qi} is the Coulomb force acting on the *i*-th particle in the agglomerate, which is defined as

$$\boldsymbol{F}_{qi} = \boldsymbol{q}_i \boldsymbol{E}_{ex} \tag{16}$$

where q_i is the charge of the *i*-th particle, and E_{ex} is the external electric field. F_i is expressed as (Weber, 1950)

$$\boldsymbol{F}_{i} = \frac{1}{16\pi\varepsilon_{rf}\varepsilon_{0}} \cdot \frac{\varepsilon_{rs} - \varepsilon_{rf}}{\varepsilon_{rs} + \varepsilon_{rf}} \sum_{i=1}^{n} \frac{q_{i}^{2}}{z_{pi}^{2}}$$
(17)

where ε_{rs} is the relative permittivity of the particle layers, and z_{pi} is the position of the *i*-th particle on the top surface of the particle layers in the *z*-direction. When the axis of the chain agglomerate is parallel to the external electric field, F_{p} is expressed as (Parthasarathy and Klingenberg, 1996)

$$\boldsymbol{F}_{\rm p} = \frac{3}{8} \pi \varepsilon_0 \varepsilon_{\rm rf} \left(\frac{\varepsilon_{\rm rp} - 1}{\varepsilon_{\rm rp} + 2} \right)^2 \left(\frac{D_{\rm p}}{d} \right)^4 D_{\rm p}^2 \boldsymbol{E}_{\rm ex}^2$$
(18)

where ε_{rp} is the relative permittivity of the particle. F_{grad} is expressed as (Hywel and Green, 1997)

$$\boldsymbol{F}_{\text{grad}} = \frac{1}{4} \pi \varepsilon_0 \varepsilon_{\text{rf}} \frac{\varepsilon_{\text{rp}} - 1}{\varepsilon_{\text{rp}} + 2} D_a^3 \operatorname{grad} \boldsymbol{E}_{\text{ex}}^2$$
(19)

Fig. 7 shows the experimental data (circles) regarding the position of the levitated particle in the vertical direction z shown in **Fig. 5**. The solid lines in this figure are particle trajectories calculated using Eq. (6). The experimental data agree well with the solid line calculated with a charge of



Fig. 7 Particle position as a function of elapsed time with a parameter of particle charge (glass beads: $D_{p50} = 100 \ \mu m$).





Fig. 8 Relationship between specific charge and the number of primary particles in levitating agglomerate (glass beads: $D_{p50} = 100 \ \mu m$).

0.134 pC, which is 58 % of the value calculated using Eq. (1) and 75 % of the value calculated using Eq. (2). The charge of a particle levitated from particle layers is generally smaller than the charge of a particle levitated from an electrode because of the difference of $\varepsilon_{\rm rs}$ in Eq. (17).

Fig. 8 shows the relationship between specific charge, $q_m (= q/m_p)$, and the number of primary particles constituting a levitated agglomerate $(n \ge 2)$ or a single particle (n = 1). The q_m value decreases with an increase in *n*. When the charge of the single particle is small, that is, the Coulomb force is small, the particle cannot be levitated. However, when the magnitude of the total Coulomb force of the constituent primary particles is large, the agglomerate can be levitated from the particle layers.

5. Effects of particle characteristics on agglomeration and levitation

Fig. 9 shows the images of particles levitated from different types of particle layers. The applied electric voltage is $V_{\rm L} = 5$ kV. For the glass beads (Fig. 9a) and alumina particles (Fig. 9b), large numbers of both single particles and chain agglomerates are levitated. In contrast, for the ferrite particles (Fig. 9c), very few chain agglomerates are levitated. This difference is mainly caused by the electrical resistances of the particles. In cases of low electrical resistance (ferrite particles: $\rho_v = 0.8 \ \Omega \cdot m$), particles are immediately charged up by induction before forming agglomerates, resulting in single-particle levitation. However, when there is high electrical resistance (glass beads: $\rho_v = 1.1 \times 10^7 \,\Omega \cdot m$; alumina particles: $\rho_v = 0.3 \times 10^6 \,\Omega \cdot m$), particles take time to be charged; in the meantime, chain agglomerates are formed on the particle layers. Although the relative permittivity also affects the relaxation time of charge transfer, as shown in Eqs. (4) and (5), the difference in materials is small (glass beads: $\varepsilon_{\rm rp} = 7$; alumina particles: $\varepsilon_{rp} = 8.5$; ferrite particles: $\varepsilon_{rp} = 2.2$). The effect of the applied voltage on the agglomeration is also small, fitting within a range of $V_{\rm L} = 4 - 6$ kV.



Fig. 9 Images of particles levitated from particle layers at $V_{\rm L}$ = 5 kV.



Fig. 10 Forces acting on a charged agglomerate just prior to its separation from particle layers.

To analyze the condition of levitation, the forces acting on agglomerates on the top surface of the particle layers should be studied. **Fig. 10** shows the forces calculated from the experimental values of particle diameter, particle charge, and other physical properties for n = 3. Although the polarization force F_p , image force F_i , and gradient force F_{grad} are small, the Coulomb force F_{ex} and gravitational force F_g are significantly large. That is, the dominant upward and downward forces are F_{ex} and F_g , which increase as a function of particle diameter. These analytical results indicate that the concept of force balance is valid within a permissible error.



6. Disintegration of agglomerates in nonuniform electric fields

The motion of charged particles is changed in a non-uniform electric field. **Fig. 11a** shows an electric field generated by parallel electrodes, which consist of the plate electrode and mesh electrode. The electrode configuration for the simulation is the same as those used in the experiment (see **Fig. 2**). The lines and arrows in this figure indicate the electric potential and electric field direction, respectively. The electric field is uniform in the lower area but non-uniform in the upper area. **Fig. 11b** shows the details of the upper area, indicating that the non-uniform electric field is directed to the center of the wire of the mesh electrode.

Fig. 12a shows a series of images of a chain agglomerate passing through the mesh electrode. The agglomerate consisting of three primary particles moves upward, but its velocity decreases with an increase in height. During this movement, the agglomerate changes its state. **Fig. 12b** shows enlarged images of the same agglomerate. The agglomerate is in a straight-chain structural state at the beginning. From top to bottom, the three primary particles are denoted as P1, P2, and P3, respectively. After the agglomerate begins to rotate counterclockwise, P3 separates from it and moves upward and to the right. The agglomerate consisting of the two primary particles continue to rotate counterclockwise; finally, P1 separates from P2. The prob-



Fig. 11 Calculated electric field: (a) overview and (b) enlarged view.

ability of disintegration generally increases as a function of the number of constituent primary particles.

When the forces acting on each primary particle in the agglomerate are not the same, the agglomerate experiences the forces in the circumferential as well as in the radial direction. **Fig. 13** illustrates the rotation models in an electric field E_{ex} for n = 2 and 3, respectively. θ is the angle of the agglomerate axis relative to the vertical, and φ is the angle between the agglomerate axis and the electric field direction. That is,

$$\varphi = \theta - \theta_{\rm ex} \tag{20}$$

where θ_{ex} is the angle of the external electric field direction at the position of the agglomerate relative to the vertical.

Fig. 14 illustrates the torques acting on chain agglomerates with different values of φ . Here, it is assumed that the charge q_1 for the upper particle is larger than the charge q_2 for the lower particle at $\varphi = 0$. The larger charge generates a stronger Coulomb force; thus, the agglomerate experiences a torque (T_q) around the centroid. The agglomerate also experiences a torque (T_p) caused by the dipole interactions



Fig. 12 Disintegration of a chain agglomerate passing through the mesh electrode: (a) fixed-point images and (b) enlarged images of the agglomerate (glass beads: $D_{p50} = 100 \ \mu m$).



Fig. 13 Rotation model of chain agglomerates in an electric field (a) n = 2 and (b) n = 3.





Fig. 14 Torques acting on chain agglomerates (n = 2).

in the electric field. T_{p} allows the particle axis to align with the electric field direction.

Furthermore, an agglomerate consisting of *n* primary particles experiences a torque (T_d) caused by the drag forces during rotation; therefore, the equation for rotational motion is expressed as

$$I\frac{d\boldsymbol{\omega}}{dt} = \boldsymbol{T}_{q} + \boldsymbol{T}_{p} + \boldsymbol{T}_{d}$$
(21)

where I is the moment of inertia given by

$$I = \sum_{i=1}^{n} m_{\rm p} r_i^{\ 2} \tag{22}$$

where r_i is the particle position relative to the axis of rotation, and ω is the angular velocity. The magnitude of ω is given by

$$\omega = \frac{\mathrm{d}\theta}{\mathrm{d}t} \tag{23}$$

The torque T_q around the centroid caused by Coulomb forces is given by

$$\boldsymbol{T}_{q} = \sum_{i=1}^{n} \left(\boldsymbol{F}_{qi} \times \boldsymbol{r}_{i} \right)$$
(24)

The interaction force F_{pij} between particles polarized in the electric field was defined by Klingenberg et al. (1989) and Washizu and Jones (1994). They considered an induced field caused by the existence of the particles in the electric field. A simple model was also presented by Klingenberg et al. (1989) and Parthasarathy and Klingenberg (1996). Using this simple model, the electrostatic interaction force F_{pij} between the *i*-th and *j*-th particles is determined as

$$\boldsymbol{F}_{\mathrm{p}ij} = F_0 \left(\frac{D_{\mathrm{p}}}{r_{ij}}\right)^4 \left\{ \left(3\cos^2\varphi - 1\right)\boldsymbol{e}_r + \sin 2\varphi \boldsymbol{e}_{\varphi} \right\}$$
(25)

where r_{ij} is the distance between the two particle centroids. e_r and e_{φ} are unit vectors in the radial and circumferential directions, respectively. F_0 is expressed as

$$F_0 = \frac{3}{16} \pi \varepsilon_0 \varepsilon_{\rm rf} D_{\rm p}^2 \left(\frac{\varepsilon_{\rm rp} - 1}{\varepsilon_{\rm rp} + 2}\right)^2 E_{\rm ex}^2$$
(26)

The first and second terms on the right-hand side of Eq. (25) represent the electrostatic interaction forces in the radial and circumferential directions, respectively. Therefore, the force acting on the *i*-th particle due to the other particles F_{poi} in the circumferential direction is given by

$$\boldsymbol{F}_{\mathrm{p}\varphi i} = \sum_{j=1}^{n} F_0 \left(\frac{D_{\mathrm{p}}}{r_{ij}}\right)^4 \sin 2\varphi \, \boldsymbol{e}_{\varphi} \qquad (j \neq i)$$
(27)

Torque T_{p} caused by dipole interactions in the electric field is given by

$$\boldsymbol{T}_{\mathrm{p}} = \sum_{i=1}^{n} \left(\boldsymbol{F}_{\mathrm{p}\phi i} \times \boldsymbol{r}_{i} \right)$$
(28)

In the same manner, torque $T_{\rm d}$ caused by the drag forces is given by

$$\boldsymbol{T}_{d} = \sum_{i=1}^{n} \left(\boldsymbol{F}_{di} \times \boldsymbol{r}_{i} \right)$$
(29)

where F_{di} is the drag force of the *i*-th primary particle as a function of the velocity \mathbf{v}_{p} . That is,

$$\boldsymbol{F}_{di} = 3\pi\mu D_{p}\boldsymbol{v}_{pi} \tag{30}$$

The rotation of the agglomerate can be calculated using Eq. (21). The angular velocity increases as a function of the spread of charge distribution in the agglomerate. Charge distribution is generally caused by electrostatic induction during levitation in the external electric field. The rotation generates centrifugal force, which can cause the disintegration of the agglomerate. The centrifugal force $|F_c|$ acting on a constituent primary particle is given by

$$|F_{\rm c}| = m_{\rm p} r \,\omega^2 \tag{31}$$

Fig. 15 shows the temporal variation of the adhesion force $|F_a|$ and centrifugal force $|F_c|$ based on the actual particle behavior (see **Fig. 12**). The values of $|F_a|$ and $|F_c|$ are calculated using the first term on the right-hand side of Eq. (25) and Eq. (31), respectively. $|F_a|$ is initially high but decreases with time, whereas $|F_c|$ increases with time for both n = 3 and n = 2. Particle separation is initiated at 10 and 15 ms when $|F_c| > |F_a|$ is satisfied. This implies that the centrifugal force plays a significant role in agglomerate disintegration in the non-uniform electric field.



7. Continuous feeding of dispersed particles

In powder handling processes, continuous feeding and the control of particle motion are essential for stable operation and the quality control of products. To realize these operations, a conceptual system using electric fields and vibration has been proposed (Matsusaka et al., 2013; Kawamoto et al., 2016). This system can also be applied to the electrostatic characterization of particles, where the particles are charged by the contact potential difference (Mizutani et al., 2015). Shoyama et al. (2018) have developed a new system for continuous particle feeding and dispersion using both parallel electrodes and a vibrator. The experimental setup is schematically shown in Fig. 16. A mesh electrode is placed at a distance of 20 mm from the plate electrode, which is attached to an inclined acrylic base. One of the electrodes is connected to a DC power supply, and the other electrode is grounded. Particles are fed at a constant flow rate and transported on the lower electrode, which is vibrated to improve particle flowability.

Fig. 17 shows images of particle behaviors observed at different applied voltages. The particles are levitated from the lower electrode and widely dispersed. When voltage is applied to the upper electrode, the particles are more widely spread than when a voltage is applied to the lower electrode. The spread area of the particles increases as a function of the absolute value of the applied voltage.



Fig. 15 Comparison between centrifugal force and adhesion force (glass beads: $D_{p50} = 100 \ \mu m$).



Fig. 16 Experimental setup for continuous feeding of dispersed particles.

Fig. 18 shows the quantitative analysis of particle dispersion for different applied voltages. For $V_{\rm U} = 0$ and $V_{\rm L} > 0$ (**Fig. 18a**), the range of particle position increases as a function of the value of $V_{\rm L}$, and the distributions are monomodal. As for $V_{\rm L} = 0$ and $V_{\rm U} < 0$ (**Fig. 18b**), the distributions are bimodal, and the range is obviously wider.

Fig. 19 illustrates the concept of the charging and the motion of particles in this system. The upper virtual boundary is assumed to be zero. For $V_{\rm U} = 0$ and $V_{\rm L} > 0$ (**Fig. 19a**), the electric field below the upper electrode is directed upward. Particles that are positively charged on the lower electrode experience upward Coulomb forces. The levitated



Fig. 17 Effect of applied voltage on particle dispersion (alumina particles: $D_{p50} = 48 \ \mu m, \rho_p = 3800 \ \text{kg/m}^3$).



Fig. 18 Quantitative analysis of particle dispersion in the *z*-direction (alumina: $D_{p50} = 48 \ \mu\text{m}$): (a) $V_U = 0$ and $V_L > 0$; and (b) $V_L = 0$ and $V_U < 0$.



particles can pass through the mesh electrode due to particle inertia. However, there are limits to the maximum heights of the particles under the effect of the gravitational forces; thus, these particles are attracted to the upper electrode. After adhesion, their polarity is changed by induction charging. The negatively charged particles levitate from the upper electrode. However, the Coulomb forces above the upper electrode drastically decrease with increasing height; therefore, the particles cannot reach higher positions. The polarities in **Fig. 19b** are opposite to those in **Fig. 19a**; however, the motions of the particles are the same.

When $V_{\rm U} < 0$ (Fig. 19c), two electric fields are formed; one is directed upward below the upper electrode, and the



Fig. 19 Concept of the charging and the motion of particles in this system: (a) $V_{\rm U} = 0$ and $V_{\rm L} > 0$; (b) $V_{\rm U} = 0$ and $V_{\rm L} < 0$; (c) $V_{\rm L} = 0$ and $V_{\rm U} < 0$; (d) $V_{\rm L} = 0$ and $V_{\rm U} > 0$.



Fig. 20 A series of a particle's motions on the lower electrode and the specific charge of the particle (alumina: $D_{p50} = 48 \ \mu m$, $V_L = +8 \ kV$ and $V_U = 0$).

other is directed downward above this electrode. Once the particles adhere to the upper electrode, their polarity changes. As the Coulomb forces above the upper electrode are directed upward, the particles can reach higher positions. Consequently, the polarity of the charged particles at the higher position is opposite to that of the particles levitated from the lower electrode. The polarities in **Fig. 19d** are opposite to those in **Fig. 19c**; however, the motions of the particles are the same.

The polarity of charged particles is changed by the conditions; thus, some particles repeatedly collide with the electrodes. Fig. 20 shows a series of a particle's motions on the lower electrode and the specific charge of the particle $q_{\rm m}$. The upper figure indicates the particle position in the z-direction as a function of time. The experimental results (solid lines) agree well with the calculated results based on the equation of motion (broken lines). The lower figure indicates the variation of the specific charge estimated from the motion analysis. The particle motion can be classified into three categories, namely, collision, adhesion, and levitation. In the collision process, the charged particle is attracted to the lower electrode by the Coulomb force and repeatedly collides with decreasing rebound height. The absolute value of the negative charge of the particle decreases with the number of collisions because the particle acquires some positive charge during each collision. After losing its kinetic energy, the particle adheres to the lower electrode. As the particle acquires a larger positive charge by induction charging for a period of 15 ms, the polarity of the particle is changed to positive. When the Coulomb force becomes sufficiently large, the particle is levitated again. Here, it is worth noting that the transferred charge depends on the contact time.

8. Conclusions

This review paper presents a series of particle phenomena occurring in parallel electrode systems consisting of a lower plate electrode and an upper mesh electrode. Particle layers are placed on the plate electrode. The mechanisms of induction charging, the control of particle behavior, and the concept of its application are summarized as follows:

(1) Particles on the top surface of the particle layers are charged by induction in a strong electric field even though the particles are dielectric. These particles are also polarized and form a straight-chain agglomerate on the particle layers by mutual electrostatic interactions.

(2) Single particles and agglomerates can be levitated from the particle layers by Coulomb forces. When the charge of single particles is relatively small, the particles are not levitated. However, when the magnitude of the total Coulomb force of the constituent primary particles is large, the agglomerates can be levitated. The charge of the



primary particles decreases with an increase in the number of primary particles in the agglomerate.

(3) In situations of low electrical resistance, particles are immediately charged up by induction. When there is high electrical resistance, particles take time to be charged. Therefore, in the former, single particles are easily levitated because of excessive charges on the surfaces. As for the latter, agglomerates tend to be levitated.

(4) Levitated agglomerates disintegrate with rotation when approaching the mesh electrode. The rotation is controlled by the torque, which is caused by the charge distribution in the agglomerates. The rotation generates a centrifugal force, which acts as a separation force.

(5) A new system is proposed for the continuous feeding of dispersed particles using electric fields and vibration. Particle charge depends on the contact time of the electrode. When voltage is applied to the upper electrode, particles are more widely spread above the electrode than when a voltage is applied to the lower electrode. The spread area of the particles increases as a function of the absolute value of the applied voltage.

Nomenclature

$D_{\rm a}$	volume equivalent diameter of agglomerate (m)
$D_{\rm p}$	particle diameter (m)
$D_{\rm p50}$	mass median diameter (m)
$\boldsymbol{E}_{\mathrm{ex}}$	external electric field (V/m)
$E_{\rm exz}$	external electric field strength in the <i>z</i> -direction (V/m)
e	unit vector (–)
$ F_{a} $	magnitude of adhesion force (N)
$ F_{\rm c} $	magnitude of centrifugal force (N)
\boldsymbol{F}_{d}	drag force (N)
F _e	electrostatic force (N)
F _{ex}	Coulomb force in external electric field (N)
\pmb{F}_{g}	gravitational force (N)
\pmb{F}_{grad}	gradient force (N)
$\boldsymbol{F}_{\mathrm{i}}$	image force (N)
F _p	interaction force between polarized particles (N)
$m{F}_{\mathrm pij}$	interaction force between <i>i</i> -th and <i>j</i> -th particles polarized in electric field (N)
F_{q}	Coulomb force acting on primary particle (N)
$F(z_p)$	cumulative distribution of particle positions in the z -direction (–)

- *g* gravitational acceleration (m/s²)
- I moment of inertia $(kg \cdot m^2)$

mass of primary particle (kg) $m_{\rm p}$ number of primary particles constituting an agglomerate п or single particle (-) specific charge (charge to mass ratio) (C/kg) $q_{\rm m}$ charge of primary particle (C) qequilibrium charge of primary particle (C) q_{∞} particle position relative to its axis of rotation (m) r distance between centroids of *i*-th and *j*-th particles (m) r_{ij} torque caused by rotational drag force (N·m) $T_{\rm d}$ $T_{\rm p}$ torque caused by the interaction between polarized primary particles (N·m) torque caused by the difference in Coulomb force of each T_{q} primary particle (N·m) time (s) t $V_{\rm L}$ voltage applied to the lower electrode (V) voltage applied to the upper electrode (V) $V_{\rm U}$ velocity of agglomerate (m/s) **v**_a velocity of particle (m/s) $v_{\rm p}$ horizontal or longitudinal direction х transverse direction perpendicular to the xz plane v direction perpendicular to the xy plane Ζ. particle position in the *z*-direction (m) $Z_{\rm p}$ vacuum permittivity = 8.85×10^{-12} (F/m) ε_0 relative permittivity of fluid (-) $\varepsilon_{\rm rf}$ $\varepsilon_{\rm rp}$ relative permittivity of particle (-) relative permittivity of solid (or particle layers) (-) $\varepsilon_{\rm rs}$ θ angle of the agglomerate axis from the vertical (rad) θ_{ex} angle between external electric field direction and the vertical (rad) angle between the agglomerate axis and moving direc- $\theta_{\rm m}$ tion (rad) dynamic shape factor (-) κ dynamic shape factor perpendicular to moving direction κ_{\perp} (-) κ dynamic shape factor parallel to moving direction (-) viscosity of fluid (Pa·s) μ $\rho_{\rm p}$ particle density (kg/m³) volume resistivity of particle ($\Omega \cdot m$) $\rho_{\rm v}$ relaxation time (s) τ

- φ angle between the agglomerate axis and electric field direction (rad)
- ω angular velocity of agglomerate (rad/s)

subscripts

- *i* index for primary particle
- r radial direction
- φ circumferential direction

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Recent Progress in Efficient Gas–Solid Cyclone Separators with a High Solids Loading for Large-scale Fluidized Beds[†]

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Abstract

Circulating fluidized beds (CFB)s are important technical equipment to treat gas–solid systems for fluid catalytic cracking, combustion, gasification, and high-temperature heat receiving because their mass and heat transfer rates are large. Cyclones are important devices to control the performance of CFBs and ensure their stable operation; heat-carrying and/or solid catalyst particles being circulated in a CFB should be efficiently separated from gas at a reduced pressure loss during separation. In commercial CFBs, a large amount of solids (> 1 kg-solid (m³-gas)⁻¹ or > 1 kg-solid (kg-gas)⁻¹) is circulated and should be treated. Thus, gas–solid cyclones with a high solids loading should be developed. A large number of reports have been published on gas–solid separators, including cyclones. In addition, computational fluid dynamics (CFD) technology has rapidly developed in the past decade. Based on these observations, in this review, we summarize the recent progress in experimental and CFD studies on gas–solid cyclones. The modified pressure drop model, scale-up methodology, and criteria for a single large cyclone vs. multiple cyclones are explained. Future research perspectives are also discussed.

Keywords: gas-solid cyclone, circulating fluidized bed, high solids loading, design

1. Introduction

Circulating fluidized beds (CFB)s are commercially used for fluid catalytic cracking (FCC), and combustion and gasification of coal, biomass, and waste material because their heat and mass transfer rates are very large (Basu P., 2015; Grace J.R. et al., 1997; Gräbner M., 2015; Lettieri P. and Macrì D., 2016; Li C.-Y. et al., 2017; Pecate S. et al., 2019; Scala F., 2013; Stolten D. and Scherer V., 2011). Recently, novel CFB solar receivers have been developed for concentrated solar power generation (Ansart R. et al., 2017; García-Triñanes P. et al., 2016, 2018). In a CFB, because heat-carrying and/or catalyst particles are circulated to transfer heat between each reactor, fast and efficient gas-solid separation is extremely important for a stable operation and reducing particle loss due to entrainment. Cocco R et al. (2017) investigated particle entrainment and clustering in a fluidized bed. Cyclones are widely used as primary gas-solid separators owing to their simple configuration and ease of operation. A stable operation of cyclones is important to reduce load in secondary gas-solid separators, makeup of the heat-carrying and/or catalyst particles, and pressure loss. Thus, much attention has been paid to the research and development of cyclones over the past several decades (Hoffmann A.C. and Stein L.E., 2010).

In commercial CFB boilers where carbonaceous solids are combusted to generate heat, a high solids-loading gas $(C_T > 10 \text{ kg-solid (kg-gas)}^{-1}$ as defined in Eq (1)) should be treated in the primary gas–solid separator in order to efficiently separate solids from the gas (Van de Velden M. et al., 2007; Dewil R. et al., 2008).

$$C_{\rm T} = \frac{\text{total mass flow rate of solid to cyclones } \left[\frac{\text{kg}}{\text{s}}\right]}{\text{total mass flow rate of gas to cyclones } \left[\frac{\text{kg}}{\text{s}}\right]} (1)$$

Cortés C. and Gil A. (2007) extensively reviewed the models developed for the flow behavior, velocity profiles, pressure drop and collection efficiency in inverse-flow cyclones under the conditions of $C_{\rm T} < 0.23$ kg-solid (kg-gas)⁻¹. Huard M. et al. (2010) comprehensively reviewed gas–solid separators including cyclones, impact separators, and other separators with a riser top and downer



 [†] Received 8 August 2019; Accepted 23 September 2019
 J-STAGE Advance published online 2 November 2019

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bottom configuration. They summarized the solidsseparation mechanism and separation efficiency of each separator and reported that recent research on reverseflow cyclones is directed toward the influence of high solids loadings on cyclone performance and computational fluid dynamics (CFD) simulations. However, in the past, CFD calculations were not highly reliable for large solidsloading cyclones and fast separators due to limitations on computational power.

On the basis of such reviews and reports, in the current review, we summarized progress in the past decade in terms of experimental and numerical studies on high solids-loading gas-solid separators (mainly cyclones) in fast solids-circulation systems in CFBs.

2. High solids-loading cyclones

2.1 Pressure-drop model

Chen J. and Shi M. (2007) analyzed pressure drop in a reverse-flow cyclone with a tangential inlet by dividing the total pressure loss into the four components, namely (1) expansion loss at the cyclone inlet, (2) contraction loss at the entrance of the outlet tube, (3) swirling loss due to gas flow and cyclone walls, and (4) dissipation loss of gas dynamic energy in the outlet tube. They reported that component (2) has limited effect on the total pressure loss and can be omitted. Based on this result, they proposed the Chen-Shi (C-S) model to predict pressure drop in cyclones operating with (i.e., an inlet solid concentration (C_s) of 0.002 to 2 kg-solid (m³-gas)⁻¹) or without dust gas at ambient and high temperatures. Li S. et al. (2011) investigated cyclone pressure drop at a very high C_s (0.125– 4.42 kg-solid $(m^3-gas)^{-1}$ and inlet gas velocities (v_i) of 13.2, 17.5, and 21 m s⁻¹. They improved the C-S model to predict cyclone pressure drop more accurately and reported that component (4) in the C-S model should not be included; further, they suggested that the swirl exponent may be zero for high solids-loading conditions.

The improved C-S model can be described as follows to estimate pressure loss in a cyclone (Li S. et al., 2011; Chen J. and Shi M., 2007).

$$v_{\rm ze} = \frac{4Q}{\pi (D_{\rm e}^2 - D_{\rm c}^2)} = \frac{v_{\rm i}}{K_{\rm A} (\tilde{D}_{\rm e}^2 - \tilde{r}_{\rm c}^2)}$$
(2)

$$\overline{v}_{\theta} = \sqrt{v_{\theta c} v_{\theta e}} = \widetilde{v}_{\theta w} \left(\widetilde{r}_{c} \widetilde{D}_{e} \right)^{0.5n} v_{i}$$
(3)

$$\Delta p_{\rm x} = \frac{\rho_{\rm g}}{2} v_{\rm ze}^2 = \frac{1}{K_{\rm A}^2 \left(\tilde{D}_{\rm e}^2 - \tilde{r}_{\rm c}^2\right)^2} \frac{\rho_{\rm g} v_{\rm i}^2}{2} \tag{4}$$

or

$$\Delta p_{\rm x} = \frac{\rho_{\rm g}}{2} \left(\overline{v_{\theta}^2} + v_{\rm ze}^2 \right) = \left[\frac{\tilde{v}_{\theta \rm w}^2}{\left(\tilde{r}_{\rm c} \tilde{D}_{\rm e} \right)^n} + \frac{1}{K_{\rm A}^2 \left(\tilde{D}_{\rm e}^2 - \tilde{r}_{\rm c}^2 \right)^2} \right] \frac{\rho_{\rm g} v_{\rm i}^2}{2}$$
(4)

$$\Delta p_{1} = \left(1 + \frac{C_{s}}{\rho_{g}}\right) \times \left(1 - \frac{2k_{i}\tilde{b}}{1 + 2(1 - \tilde{c})\tilde{b} - \tilde{D}_{e}}\right)^{2} \frac{\rho_{g}v_{i}^{2}}{2}$$
(5)

$$\Delta p_{\rm b} = \frac{fA_{\rm s}\rho_{\rm g} \left(v_{\rm \theta w} v_{\rm \theta CS}\right)^{1.5}}{2 \times 0.9Q} 1.11 fK_{\rm A} \tilde{A}_{\rm S} \tilde{v}_{\rm \theta w}^{\prime3} \tilde{D}_{\rm e}^{-1.5n} \frac{\rho_{\rm g} v_{\rm i}^2}{2}$$
(6)

$$f = f_{\rm air} (1 + 3\sqrt{C_{\rm s} / \rho_{\rm g}}) \tag{7}$$

$$K_{\rm A} = \frac{\pi D_{\rm b}^{\ 2}}{4ab} \tag{8}$$

$$\tilde{A}_{s} = \frac{4A_{s}}{\pi D_{b}^{2}} = (1 - \tilde{D}_{e}^{2}) + 4\tilde{D}_{e}\tilde{l} + 4\tilde{H}_{b} + (1 + \tilde{B})\sqrt{4(\tilde{H} - \tilde{H}_{b})^{2} + (1 - \tilde{B})^{2}} + 4\tilde{D}_{h}\tilde{H}_{h}$$
(9)

$$\tilde{\nu}_{\theta w} = \frac{1.11 K_{\rm A}^{-0.21} \tilde{D}_{\rm e}^{0.16} R e^{0.06}}{1 + f_{\rm air} \tilde{A}_{\rm s} \sqrt{K_{\rm A} \tilde{D}_{\rm e}}}$$
(10)

$$Re = \frac{\nu_{\rm x} \rho_{\rm g} D_{\rm e}}{\mu_{\rm g}} \tag{11}$$

$$\tilde{\nu}_{\theta w} = \frac{\tilde{\nu}_{\theta w}}{1 + 0.35 (C_{\rm s} / \rho_{\rm g})^{0.27}}$$
(12)

$$n = 0 \tag{13}$$

$$\tilde{r}_{\rm c} = 0.38\tilde{D}_{\rm e} + 0.5\tilde{D}_{\rm e}^2 \tag{14}$$



Fig. 1 Comparison between model-predicted and experimental data ($v_i = 17.5 \text{ m s}^{-1}$). Reprinted with permission from Ref. (Li S. et al., 2011). Copyright: (2011) WILEY-VCH Verlag Gmbh & Co. KGaA, Weinheim.



In the improved C-S model, geometric and velocity variables were normalized with respect to cyclone diameter. As shown in **Fig. 1**, the performance predicted by the improved C-S model agrees well with experimental data when $C_{\rm s} = 1-5$ kg-solid (m³-gas)⁻¹, thus effectively amending the overprediction of the original C-S model.

2.2 Multi-cyclone and non-uniform distribution of particles

In large-scale industrial reactors with high gas-solid flow rates, small parallel cyclones are often preferred to achieve a high separation efficiency when the distribution of gas-solid flow at each cyclone inlet is uniform. However, it is difficult to place a refractory in such small cyclones (Nowak W. and Mirek P., 2013) and there is strong evidence that gas-solid flow in parallel cyclones is non-uniform, which reduces the total separation efficiency (Zhang C. et al., 2016).

Masnadi M.S. et al. (2010) examined gas-solid flow distribution across two parallel and identical cyclones based on an analytical model and compared flow distribution through parallel pipes. They confirmed the consistency of their analytical model by comparing the experimental data of two identical cyclones (barrel diameter D = 101.6 mm). They reported that a non-uniform (or maldistribution) gas-solid flow is unavoidable for a high solids loading (upstream solids hold up > 0.01 %) and that fouling can significantly affect maldistribution of gassolid flow through the identical cyclones. Zhang N. et al. (2010) calculated a three-dimensional full-loop CFB boiler model with two parallel cyclones using an Eulerian granular multiphase model. In their study, they found minor differences in the average solids mass flux (G_s) in the two cyclones (5.74 and 6.05 kg $m^{-2} s^{-1}$) and pointed out that the maximum G_s alternates between these two cyclones. Zhou X. et al. (2012) investigated gas-solid flow through six parallel cyclones located asymmetrically on the left and right walls of the riser (i.e., three cyclones on the left and three cyclones on the right) in a CFB cost test apparatus. They observed that the distribution of gassolid flow was non-uniform across three cyclones on one side and that the middle cyclone on each side exhibited higher particle velocities while their G_s was lower than that of other cyclones. Jiang Y. et al. (2014) conducted numerical calculations on gas-solid flow hydrodynamics at a CFB boiler test facility with six parallel cyclones using an Eulerian-Lagrangian model and computational particle fluid dynamics (CPFD). They validated simulation data using experimental data obtained by electrical capacitance tomography (ECT) in cold model tests (at ambient temperature and atmospheric pressure). The geometry of the six cyclones was either axis-symmetric or point-symmetric, as shown in Fig. 2.

They also observed that the solids concentrations of the four cyclones located at the corners of the chamber were greater than those of others and stated that an "axis-symmetric" arrangement (case A) for cyclones is better than a "point-symmetric" arrangement (case B) from the view point of uniform distribution of solids (**Fig. 3**).

Wang S. et al. (2017) investigated the hydrodynamics of gases and solids in six parallel cyclones with central symmetry and axial symmetry arrangements combined with a full-loop CFB by CFD and a discrete elemental method (CFD-DEM, **Fig. 4**). They reported that for a uniform distribution of solid mass flux in parallel cyclones, axial symmetry is better than central symmetry. The middle







Fig. 3 Time-averaged particle mass flow rate distribution in cyclones according to CPFD simulations. Reprinted with permission from ref. (Jiang Y. et al., 2014). Copyright (2014) Elsevier B.V.



cyclones on both sides have higher solid velocity and solid holdup than other corner cyclones (**Fig. 5**).

Shuai D. et al. (2017) also investigated the flow behavior of gas and solids in six cyclones in parallel in an annular furnace. They observed a non-uniform distribution of G_s and cyclone pressure drop (Δp_c) in the six cyclones. However, no regularity could be observed. The relative deviation of G_s in the six cyclones was 8.0 % under typical operating conditions.

2.3 Design principles of multi-cyclones

The design principles of small multi-cyclones and a large single cyclone were analyzed. Mo X. et al. (2015) investigated the influence of wall friction and solid acceleration on the non-uniform distribution of gas-solid flow in two parallel cyclones. They reported that pressure drop in cyclones has an inflection point with respect to the



Fig. 4 Schematic of 6 cyclones in CFD calculation (a) Front view of simulation geometry (b) Central symmetry (c) Axial symmetry arrangements (units: mm). Reprinted with permission from ref. (Wang S. et al., 2017). Copyright (2017) Elsevier B.V.

mass flow rate ratio between solids and the gas $(C_{\text{T,inf}}, \text{Eq.}(1))$, which is around 0.5–3.33 kg-solid (kg-gas)⁻¹, as calculated from the reported values. They also suggested that the inflection point increases with an increase in the wall friction but decreases with an increase in solid acceleration. The inflection point has a large effect on non-uniform gas–solid distribution in the two parallel cyclones. As summarized in **Table 1**, the solid flow distribution is non-uniform when C_{T} approaches $C_{\text{T,inf}}$.

Zhang C. et al. (2016) analyzed multi-phase interactions and investigated instabilities in uniformity in two parallel cyclones installed after a fluidized bed reactor. They provided a novel design principle to avoid nonuniform distribution of solids using $C_{\rm T}$ and dimensionless vortex finder diameter ($d_{\rm r}$) defined in Eq. (15). Fig. 6 shows a phase diagram of uniformity of the two parallel cyclones as a function of fraction of solid flow to cyclone 1 (i.e. path 1) and $C_{\rm T}$. They reported that under the condition that inlet velocity of air is 15 m s⁻¹, Reynolds number is 3.08×10^5 and glass beads are used at 20 °C and 101.3 kPa, a low solids loading ($C_{\rm T} < 1.35$), the uniform distribution is stable but at $C_{\rm T} = 1.35$, there occurs a turning point from uniform to non-uniform distribution. When $C_{\rm T} > 1.35$, the maldistribution of solids is stable.



Fig. 5 Time-averaged solid flux distribution in cyclones. Reprinted with permission from ref. (Wang S. et al. 2017). Copyright (2017) Elsevier B.V.

 Table 1
 Summary of the three phases in two parallel cyclones. Reprinted with permission from ref. (Mo. X. et al. 2015). Copyright (2015) Elsevier B.V.

	Dilute phase	Transition phase	Dense phase
$C_{\mathrm{T,inf}}$	$C_{\mathrm{T}} \ll C_{\mathrm{T,inf}}$	$C_{\rm T} \sim C_{\rm T,inf}$	$C_{\rm T} >> C_{\rm T,inf}$
Main contributor	Wall friction	Both greatly influence the pressure drop	Solid acceleration
Gas fraction in cyclone 1 (ψ) and solids fraction in cyclone 1 (γ)	$\psi > 0.5$ and $\gamma > 0.5$ or $\psi < 0.5$ and $\gamma < 0.5$	$\psi \sim 0.5$ and highly uneven solid distribution at certain flow perturbation	$\psi > 0.5$ and $\gamma < 0.5$ or $\psi < 0.5$ and $\gamma > 0.5$

They found that d_r should be less than 0.32 and that d_r strengthens the swirl in a cyclone for enhancing the stability of uniformity and cyclone efficiency under this condition.

Fig. 7 shows a phase diagram of stability based on the data in literature (Zhang C. et al., 2016). For parallel cyclones that treat high solids loading, d_r should be small enough to ensure the stable operation. These criteria are very useful in the selection of single large cyclones or multi-cyclones for uniform and steady operation.



Fig. 6 Phase diagram of stability of uniformity at different mass flow rate ratios (C_T) when inlet velocity of air is 15 m s⁻¹, Reynolds number is 3.08×10^5 and glass beads are used at 20 °C and 101.3 kPa. Reprinted with permission from ref. (Zhang C. et al., 2016). Copyright (2016) John Wiley and Sons.



Fig. 7 Stability phase graph of the relationship between the stability of uniform distribution/maldistribution and dimensionless vortex finder diameter d_r and mass flow rate ratio C_T . Ref. A: Jiang Y. et al. (2014)

- Ref. B: Liao L. et al. (2011)
- Ref. C: Zhou X. et al. (2012)
- Ref. D: Zhang N. et al. (2010)
- Ref. E: Wang F.J. et al. (2014)
- Ref. F: Liu F. et al. (2014)
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$$d_{\rm r} = \frac{vortex finder \ diameter \ [m]}{cyclone \ barrel \ diameter \ [m]} \tag{15}$$

2.4 Cyclones in series

Wu X. et al. (2011) experimentally measured and calculated the pressure drop of two scroll-type cyclones connected in series for a wide range of solids loading $(C_{\rm T} = 0-30 \text{ kg-solids (kg-gas)}^{-1})$ and cyclone inlet velocity $(v_i = 16-24 \text{ m s}^{-1})$. The experimental data showed that the cyclone pressure drop decreased dramatically as $C_{\rm T}$ increased to 7.5 kg-solids (kg-gas)⁻¹ after which it remained almost constant.

Fushimi C. and Guan G. et al. developed a triple bedcombined CFB for coal gasifiers (Fushimi C. et al., 2011, 2014; Guan G. et al., 2010, 2011) and experimentally investigated the hydrodynamics of silica sand (average particle diameter of 126 μ m) at a high flux (G_s in the range of 200–546 kg m⁻² s⁻¹) in cold model tests. In these experiments, three cyclones were connected in series to separate solids from air. Separation efficiency at the outlet of the third cyclone was 99.998 % when G_s was



Fig. 8 Schematic diagram of the proposed iG-CLC system Reprinted with permission from ref. (Wang X. et al., 2015). Copyright (2015) The American Chemical Society.





Fig. 9 (a) Schematic diagram of the experimental setup of a fluidized bed, a riser, and a dipleg connected with a cyclone, (b) the photograph of the fluidized bed and dipleg (non-operating status). Reprinted with permission from ref. (Wei Z.G. et al., 2016) under the terms of the CC-BY 4.0 license. Copyright: (2016) The Authors, published by Springer Nature.

490–510 kg m⁻² s⁻¹. Meanwhile, Hoffmann A.C. and Stein L.E. (2010) recommended that the underflow pipes of series-connected cyclones should be independently sealed.

2.5 Combination of an inertial separator and a cyclone for a high-flux CFB

Wang X. et al. (2015) developed a high-flux CFB reactor, comprising of a fuel reactor, an air reactor, a J-valve, a downcomer, and solid separation systems, for in situ gasification chemical looping combustion (iG-CLC). They optimized the iG-CLC system by developing an inertial separator for primary gas-solids separation and a cyclone for secondary gas-char and remaining solids separation to improve operation stability and solid separation efficiency. They reported that the selective separation efficiency of coal particles in the first-stage inertial separator was 77.7 % when the mass flow rate of the solid was 1021 kg h⁻¹ and the overall separation efficiency after the second-stage cyclone reached 99.5 % when the mass flow rate to cyclone was 35 kg h⁻¹ in their cold model tests.

In their subsequent work (Shao Y. et al., 2017), they carried out three-dimensional full loop CFD calculation using an Eulerian-Eulerian two-fluid model combined with the standard *k*- ε turbulence model for the gas phase and the kinetic theory of granular flow for the solid phase to investigate the hydrodynamics of coal and iron ore particles on the basis of the experimental results of cold model tests. They reported continuous and stable solid circulation in the iG-CLC model when $G_{\rm s}$ was around 400 kg m⁻² s⁻¹.

2.6 Design principles of the cyclone inlet and body for high solids-loading multi-cyclones

Hoffmann A.C. and Stein L.E. (2010) recommended



Fig. 10 Diagram of fluidization regimes in a dipleg with the increase of solid mass flux (G_s) (a) and (b) the dilutedense coexisting falling flow, (c) the dense conveying flow, (d) dense conveying flow with a high particle concentration. Reprinted with permission from ref. (Wei Z.G. et al., 2016) under the terms of the CC-BY 4.0 license. Copyright: (2016) The Authors, published by Springer Nature.

that 1) bends should be located at a distance of ten pipe diameters or its equivalent before cyclone inlets to avoid non-uniform distribution of gases and solids in the cyclone inlet piping and 2) a scroll or wrap-around type of inlet should be used. At high solids or liquid loadings (> ~10 vol%), care must be taken not to restrict the discharge opening or the annular space around a vortex stabilizer.

2.7 Flow behavior of gas and solids in a dipleg below cyclone

Wei Z.G. et al. (2016) examined the pressure of a catalyst powder (Sauter mean particle diameter of $63.6 \,\mu$ m)



flow in a dipleg (150 mm inner diameter and 9 m height) when G_s was in the range of 50.0 to 385.0 kg m⁻² s⁻¹. Fig. 9 shows the experimental apparatus consisting of setup of a fluidized bed (600 mm i.d. and 8 m height), a riser (200 mm i.d. and 12.5 m height), and a dipleg (150 mm i.d. and 9 m height) connected with a cyclone (400 mm i.d.). The bottom of the dipleg was immersed into the fluidized bed. Fig. 10 shows the observed fluidization pattern in the dipleg. At small G_s (G_s < 50.0 kg m⁻² s⁻¹) (cf. **Fig. 3a, b**), a dilute-dense coexisting falling flow. The swirl flow (just below the cyclone), the dilute particle falling flow (in the middle) and the dense flow (bottom) were observed. In the dense flow, some ascending gas bubbles were observed like a bubbling fluidized bed. When $G_s = 200.0 - 250.0 \text{ kg m}^{-2} \text{ s}^{-1}$ (cf. Fig. 3c), no interface between the dilute particle falling flow and the dense flow was observed. Pressure fluctuation intensity reached a maximum in the fluidization pattern being transformed. Further increase in G_s ($G_s > 350.0 \text{ kg m}^{-2} \text{ s}^{-1}$) (cf. Fig. 3d), the fluidization regimes developed the dense conveying flow with a high particle concentration.

3. Scale-up methodology and grade efficiency

The scale-up of cyclones is important for reactor design and estimating separation efficiency. Mirek P. (2016, 2018) investigated the scaling rules of cyclones in CFB boilers and estimated the separation efficiency of cyclones by setting up the following model (Eqs. (16)–(21)). In this model, the total separation efficiency of a cyclone η_{tot} is the sum of the efficiency at the wall (η_{wall}) and in the inner vortex (η_{vtx}) (Eq. (16)). A portion of the incoming solids not collected by the wall is collected by the inner vortex, which is based on the Muschelknautz model (Muschelknautz E., 1972),

$$\eta_{\text{tot}} = \eta_{\text{wall}} + \eta_{\text{vtx}} = 1 - \frac{\mu_{\text{lim}}}{\mu_{\text{e}}} + \frac{\mu_{\text{lim}}}{\mu_{\text{e}}} \sum_{j=1}^{m} \eta_{\text{F}}(d_j) \Delta R_{\text{Ai}}(d_j)$$
(16)

where μ_{lim} is the limited loading ratio defined by Eq. (17).

$$\mu_{\rm lim} = K_{\rm lim} \cdot \left(\frac{d_{\rm e}}{d_{50,\rm A}}\right) \cdot \left(10\mu_{\rm e}\right)^{\gamma} \tag{17}$$

Here, the constant $K_{\text{lim}} = 0.02$ for fine particles and 0.03 for coarse particles. For initial load, $\mu_{\text{e}} < 2.2 \times 10^{-5}$, the exponent *y* has a value of 0.81 and for $\mu_{\text{e}} > 0.1$, y = 0.15. The value of d_{e} is calculated using Eq. 18 (Mirek P., 2018).

$$d_{\rm e} = \sqrt{\frac{0.5(0.9V)}{A_{\rm W}} \cdot \frac{18\mu_{\rm g}}{(\rho_{\rm p} - \rho_{\rm g})\overline{z_{\rm e}}}}$$
(18)

Wang J. et al. (2019) reported that when the solids loading is higher than the limit loading ($\mu_e > \mu_{lim}$), dense particles cannot flow through the rotating/swirling stream because of their high inertia; in this case, these particles hit the outside wall of the cyclone and descend to the bottom.

Mirek P. also described the particle size distribution of the carryover, $R_{\rm F}(d)$, and it can be determined using Eq. (19).

$$\Delta R_{\rm F}(d) = \frac{\mu_{\rm lim}}{\mu_{\rm e}} \cdot \frac{(1 - \eta_{\rm F}(d))}{(1 - \eta_{\rm tot})} \cdot \Delta R_{\rm A}(d) \tag{19}$$

The total separation efficiency is determined by Eq. (20).

$$\eta_{\rm F}(d) = 1 - (1 - \eta_{\rm tot}) \frac{\Delta R_{\rm F}(d)}{\Delta R_{\rm A}(d)} \tag{20}$$

The same researcher summarized the scaling relationship using five dimensionless parameters sets shown in **Table 2**. They compared estimation curves based on the

 Table 2
 Scaling relationships and parameters used for the analysis of the cyclone performance in cold model tests (cf. Fig. 11).

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Scaling relationships	Parameters chosen independently	Notation
$\frac{U_0}{u_{\rm T}}, \frac{G_{\rm s}}{\rho_{\rm p}U_0}, PSD$	$d_{32}, ho_{ m p}, ho_{ m g}, D_{ m r}, \mu_{ m g}, g$	Set (1)
$Re_{\rm p}, \frac{U_0}{u_{\rm T}}, Ar, PSD$	$ ho_{ m p}, ho_{ m g},D_{ m r},\mu_{ m g},g$	Set (2)
$\frac{U_0}{u_{\rm T}}, \frac{G_{\rm s}}{\rho_{\rm p}U_0}, Fr, PSD$	$ ho_{ m p}, ho_{ m g},D_{ m r},\mu_{ m g},g$	Set (3)
$\frac{U_0}{u_{\rm T}}, \frac{G_{\rm s}}{\rho_{\rm p}U_0}, Fr, \frac{\rho_{\rm p}}{\rho_{\rm g}}, PSD$	$ ho_{ m g}, D_{ m r}, \mu_{ m g}, g$	Set (4)
$Fr, Re_{\rm p}, \frac{\rho_{\rm p}}{\rho_{\rm g}}, \frac{G_{\rm s}}{\rho_{\rm p}U_0}, \frac{d}{D_{\rm r}}, PSD$	$ ho_{ m g}, \mu_{ m g}, g$	Set (5)


Fig. 11 Influence of a set of scaling relationships on the total grade efficiency curve based on the parameter sets shown in **Table 2** and the Stokes equation. Reprinted with permission from ref. (Mirek P., 2018). Copyright (2018) Elsevier B.V.

five dimensionless parameter sets and the Stokes equation (Eq. (21)).

$$Stk_{\rm in, i} = \frac{(\rho_{\rm p} - \rho_{\rm g})d_{50}^2 v_{\rm i}}{18\mu_{\rm g}D_{\rm b}}$$
(21)

Fig. 11 shows the result. All the proposed scaling relationships resulted in a very high separation efficiency (> 99.4 %). However, the results strongly depended on the selected scaling relationships set (Mirek P., 2018).

Wang J. et al. (2019) recently conducted experiments extensively and introduced sophisticated models to improve the prediction of grade efficiency of cyclone separators. They constructed generalized linear mixed-effects (GLME) models that are functions of the parameters (*St*, $\frac{d}{d_{50}}$, σ_{ξ} , $\frac{d_{50}}{D_{b}}$, *Re*, *Fr*_{,H}) to understand and control grade efficiency (*n*(*d*)) variation. Note σ is the size deviation in

efficiency ($\eta_F(d)$) variation. Note σ_{ξ} is the size deviation in particle diameter at the inlet.

In their GLME models, the observed grade efficiency vector (η) is considered to be a summation of the expected grade efficiency vector (μ) and the noise vector (e), which is assumed to follow a normal distribution with mean 0 (Eq. (22)).

$$\boldsymbol{\eta} = \boldsymbol{\mu} + \boldsymbol{e} \tag{22}$$

The expected grade efficiency (μ) is represented by the Gaussian regression model shown in Eq. (23),

$$g(\boldsymbol{\mu}) = \beta_{0} + (\beta_{1} + \phi_{1})\ln(St) + (\beta_{2} + \phi_{2})\ln\left(\frac{d}{d_{50}}\right) \\ + \beta_{3}\ln(\sigma_{\zeta}) + \beta_{4}\ln\left(\frac{d_{50}}{D_{b}}\right) + (\beta_{6} + \phi_{6})\ln(Re) \quad (23) \\ + \beta_{7}\ln(Fr)$$

where ϕ_i is a random effect corresponding to the *i*th com-

Table 3GLME model estimation parameters. Reprinted with
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Estimate	Std. Error	P-value
64.952	4.7019	1.7896e-38
-6.8608	0.64062	7.4357e-25
14.721	1.2805	4.303e-28
23.673	3.2352	7.0839e-13
14.794	0.98611	3.2965e-44
1.6486	0.40073	4.3607e-05
-2.2869	0.36419	6.0287e-10
Estimate	Lower	Upper
0.0011382	0.00035134	0.0036874
0.16095	0.13411	0.19315
0.038589	0.028213	0.052781
	Estimate 64.952 -6.8608 14.721 23.673 14.794 1.6486 -2.2869 Estimate 0.0011382 0.16095 0.038589	EstimateStd. Error64.9524.7019-6.86080.6406214.7211.280523.6733.235214.7940.986111.64860.40073-2.28690.36419EstimateLower0.00113820.00351340.160950.134110.0385890.028213



Fig. 12 The parity plot of fitted values based on the GLME model and experimental results of the grade efficiency. Reprinted with permission from ref. (Wang J. et al., 2019). Copyright (2019) Elsevier B.V.

ponent and has a normal distribution with a variance σ_i^2 . The g(μ) and the expected grade efficiency (μ) are linked in the following equations ((24), (25)).

$$g(\boldsymbol{\mu}) = -\ln(-\ln(\boldsymbol{\mu})) \tag{24}$$

$$\boldsymbol{\mu} = \exp[-\exp(-g(\boldsymbol{\mu}))] \tag{25}$$

Table 3 lists the values estimated for the parameters $(\beta_{0.7}, \sigma_1, \sigma_2, \sigma_6)$ in Eq. (23), including a 95 % confidence interval for random effects. **Fig. 12** shows the parity plot of experimental results and fitted values predicted by using the GLME model. It can be seen that the GLME modeling predicts the experimental grade efficiency accurately. It is considered that the GLME model can provide setting conditions for cyclone separators (Wang J. et al., 2019).

Table 4 Summ	ary of recent research on gas	-solid cyclones. (co	ntinued on next	page)					
Method	References	Barrel diameter, D [m]	Inlet gas velocity, $v_i [m s^{-1}]$	Particle size, d _p [μm]	Solid loading, C _T [kg-solid (kg-gas) ⁻¹]	Solid concentration, $C_{\rm s} [kg \text{-solid} (m^3 \text{-}gas)^{-1}]$	Particle recovery ratio [%]	Inlet type	CFD method Above: Fluid Below: Solid
Experimental	Mirek P. (2018)	0.6			1.87, 7.87			Tangential	I
	Demir S. (2014)	0.29	10-18					Tangential	I
	Lee H. and Yook S.J. (2014)	0.133 (Single) 0.094 (Dual)	4.4–12.5 3.1–8.9	100-500			95	Tangential	
	Haig C.W. et al. (2014)	0.04	15-45	0.2–5.5		0.00009-0.0003		Tangential	Ι
	Oh J. et al. (2014)	0.15	5.2-13.0			(< 1.5 vol%)	99.5	Tangential	
	Xiong Z. et al. (2014)	0.168	19–39	9.26	0.0001 - 0.0005	0.0002	66	Axial	
	Avci A. et al. (2013)	0.04	2.4–37.2					Tangential	
	Yoshida H. et al. (2010)	0.072	2.7-19.1	1.8					
	Ahuja S.M. (2010)	0.3	6.63–15.11	35 (Fly ash) 7 (Talc)			86.02– 95.72	Tangential	
	Wang W. et al. (2010)	0.148 - 0.428	12–16	10.2		0.0015	82–96	Tangential	I
	Zhang P. et al. (2019)	0.24	17-36.5	2.4		0.002 - 0.010	97	Tangential	
	Karagoz I. et al. (2013)	0.19	10–25	14			80-90	Tangential	
	Hsiao T.C. et al. (2015)	0.025		26				Tangential	
	Mazyan W.I. et al. (2017)	0.19	14	4-150	0.008		90-95	Tangential	I
	Wu X. et al. (2011)	0.15	16-24	55, 128	0-30			Tangential	
	Li S. et al. (2011)	0.282	13.2–21	263		0.125-4.42			Ι
	Wei Z.G. et al. (2016)			63.6		$(G_{\rm s}:50.0-$ 385 kg m ⁻² s ⁻¹)		Tangential	
Experimental	Prabhansu et al. (2017)	0.100	7–30	100-1000			86–98	Tangential	
and simulational	Song J. et al. (2017)	0.5	16-29	2-120		0.04	> 90	Tangential	Euler Lagrange
	Huang A.N. et al. (2018b)	0.0723	15	2.1			80.7		
	Huang A.N. et al. (2017a)	0.072	11–21	2.1	0.00149 - 0.00078	0.00179-0.000936		Tangential	
	Huang A.N. et al. (2017b)	0.547	13.6–18.8	16.9		0.00025-0.00059		Tangential with slits	
	Gao Z. et al. (2019)	0.14	12–18						RSM—
	Wei J. et al. (2017)	0.3	4-12	2000	0.72-8.64			Tangential	
	Yu X. et al. (2018)		1.33 - 4.64	300, 600				Tangential	

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Table 4 Sumn	nary of recent research on gas-soli	d cyclones. (continued	l from previous p;	ıge)					
Method	References	Barrel diameter, D [m]	Inlet gas velocity, v_i [m s ⁻¹]	Particle size, $d_{\rm p}$ [μ m]	Solid loading, $C_{\rm T}$ [kg-solid (kg-gas) ⁻¹]	Solid concentration, C_{s} [kg-solid $(m^{3}-gas)^{-1}$]	Particle recovery ratio [%]	Inlet type	CFD method Above: Fluid Below: Solid
Simulational	Su Y. et al. (2011)	0.200 × 0.200 (square)	17.98, 20.21			0.0084, 0.0088			
	Surmen A. et al. (2011)	2–20 (L/D)							
	Qiu Y. et al. (2012)	0.33	8-22	12.8			> 92		
	Winfield D. et al. (2013)	0.0066	16.70, 16.74			(< 1.5 vol%)	99.5		
	Shi B. et al. (2013)	0.04	30				66		
	Bogodage S.G. and Leung A.Y.T. (2015)	0.3302	10	0-18		0.001		Tangential	
	Hsiao T.C. et al. (2015)	0.025	0.0025 - 0.01	2–6				Tangential	
	Misiulia D. et al. (2015)	4.21–5.07 (H/D)	3.5	0.2–30		0.003		Tangential	
	De Souza F.J. et al. (2015a,b)	0.031	10.67	0.5-6.0				Tangential, axial	
	Yang J. et al. (2015)	0.3, 1.2, 0.9, 0.6, 0.186						Tangential	
	Xu W. et al. (2016)	0.25	23	10			88		
	Schneiderbauer S. et al. (2016)	2.5	13.4	0.6–400	0.224		93	Tangential	Lagrange-Euler hybrid
	Kozołub P. et al. (2017)	0.2	5.55-9.49	40-80	1.0-2.7			Tangential	Euler Lagrange
	Mazyan W.I. et al. (2017)	0.19	14					Tangential	
	Siadaty M. et al. (2017)	0.3	16.04	2-6		(3 vol%)	> 91.11	Tangential	
	Sun X. et al. (2017)	0.29	16.34	1-5				Tangential	
	Wang S. et al. (2017)	0.07		1600		(< 0.03 vol%)			
	Wasilewski M. and Brar L.S. (2017)	3.35	8.84				80.4– 82.4	Tangential	
	Huang A.N. et al. (2018a)	0.0723	15, 18	0.339–11.565		0.0016-0.153	> 99 % (> 3 µm)		
	Safikhani H. and Mehrabian P. (2016)	1, 1.7, 2.3 (L/D)	17	20, 21, 23, 19, 13				Axial	
	Safikhani H. et al. (2018)	1.7 (L/D)	8.75, 17.5, 35	20, 21, 23, 19, 13			60-62	Axial	
	Zhang N. et al. (2010)	8.08		200		$(G_{\rm s}; 4-8.5 \text{ kg m}^{-2} \text{ s}^{-1})$		Tangential	Euler
	Chu K.W. et al. (2011)	0.2	20	2000	0-2.5			Tangential	
	Chu K.W. et al. (2017)	1,000	3.9	200-600000	5–11 Medium to Coal			Tangential	
	Jang K. et al. (2018)		10-30	0.4–10			57–75	Tangential	





4. Recent studies on other gas-solid cyclones

Table 4 summarizes the experimental and numerical studies on gas-solid cyclones conducted in the last decade. Recently, a number of numerical studies using CFD simulations have been conducted to investigate the velocities and volume fractions of gases and solids and pressure drop in cyclones by varying their configurations. Most of these experimental and numerical studies were conducted under dilute conditions (C_s or $C_T \sim 0.001$). Huang A.N. et al. (2018a) investigated the effect of particle mass loading on the hydrodynamics of solids and separation efficiency using the Eulerian-Lagrangian approach with a two-way coupling method for CFD and compared with the experimental results of laboratory-scale cyclones at C_s of 0.0016–0.153 kg-solid (m³-gas)⁻¹ and $v_i = 15$ and 18 m s⁻¹. They reported that the overall separation efficiency increased from 74.5 % for a conventional cyclone to 80.7 % for a cyclone with a lower cone slit. More detailed experimental and numerical studies under high solids loading conditions on gas-solid cyclones are expected in the future.

5. Conclusions and future prospects

In this review, recent progress in high solids-loading gas–solid cyclones has been summarized. The improved C-S model proposed by Li S. et al. (2011) is highly useful for predicting pressure drop in cyclones. For commercial-scale CFBs, 2 to 6 multi-cyclones are often used in parallel. However, the non-uniform distribution of solids in the parallel section is a problem. Mo et al. investigated the effect of wall friction and solid acceleration on the non-uniform distribution of gas–solids flow and found that the inflection point has a significant influence on the maldistribution of gas–solids in two cyclones in parallel. Zhang C. et al. (2016) found that the phase graph of the stability of uniform distribution/maldistribution of solids in two parallel cyclones as functions of $C_{\rm T}$ (kg-solid (kg-gas)⁻¹) and $d_{\rm r}$.

To improve the scale-up methodology, Mirek P. (2018) summarized and modified the Muschelknautz model by applying five sets of scaling relationships and found that all the employed sets of scaling relationships resulted in a very high separation efficiency (> 99.7 %). The GLME model developed by Wang J. et al. (2019) can predict grade efficiency with a large prediction variability.

It is expected that CFB boilers will be used for biomass co-combustion to reduce CO_2 emissions due to power generation. In waste-treatment plants, CFB incinerators may be used in the future because of their high thermal efficiency and operability. In CFB boilers used for power generation, non-steady-state operations (rapid changes in load) are required. In these operations, a high solids separation efficiency and control over the cut-off diameter are required. We expect for future research, flow behaviours of gas and solids, and separation efficiency of solids in cyclones under non-steady state or transient operation conditions should be investigated.

Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research B (Kakenhi Kiban B, 17H03451) and the Takuma research grant.

Nomenclature

- A_s : Total area of the contact surfaces between gas flow and the cyclone wall, $A_s = \tilde{A}_s \pi D_b^{-2/4} \text{ [m}^2 \text{]}$
- $A_{\rm w}$: Sedimentation area of the cyclone wall [m²]
- a: Cyclone inlet height [m]
- *b*: Cyclone inlet width, $b = \tilde{b} D_{b}$ [m]
- *B*: Diameter of the cyclone dust exit, $B = \tilde{B}D_{\rm b}$ [m]
- c: Width of the inlet cutting into the cyclone body, $c = \tilde{c}b$ [m]
- $C_{\rm s}$: Inlet solid concentration [kg-solid (m³-gas)⁻¹]
- $C_{\rm T}$: Mass flow rate ratio between solids and gas [kg-solid (kg-gas)⁻¹]
- $C_{\text{T,inf}}$: Solids loading at the inflection point [kg-solid (kg-gas)⁻¹]
- d: Feed particle diameter [m]
- $d_{\rm e}$: Cut size for separation at wall [m]
- d_r : Dimensionless vortex finder diameter [-]
- d_{32} : Sauter mean particle diameter [m]
- d_{50} : Mass mean particle diameter in feed [m]
- $d_{50,A}$: Median particle diameter in feed [m]
- D_b: Cyclone barrel diameter [m]
- $D_{\rm h}$: Cyclone hopper diameter, $D_{\rm h} = \tilde{D}_{\rm h} D_{\rm b}$ [m]
- $D_{\rm c}$: Diameter of core flow, $D_{\rm c} = 2r_{\rm c}$ [m]
- $D_{\rm e}$: Cyclone outlet diameter, $D_{\rm e} = \tilde{D}_{\rm e} D_{\rm b}$ [m]
- *D*_r: Riser hydraulic mean diameter, 4A(cross-sectional area of the flow)/P(wetted perimeter of the cross-section) [m]
- e: Noise vector [-]
- f: Friction coefficient [-]
- f_{air} : Friction coefficient for dust-free gas flow [-]
- *Fr*: Froude number based on D_r , (U_0^2/gD_r) [–]
- $Fr_{,H}$: Froude number based on H, (v_i^2/gH) [–]
- g: Gravitational acceleration $[m s^{-2}]$
- $G_{\rm s}$: Solids mass flux [kg m⁻² s⁻¹]
- $H_{\rm b}$: Cyclone barrel height, $H_{\rm b} = \tilde{H}_{\rm b} D_{\rm b} [{\rm m}]$
- *H*: Cyclone body height, $H = \tilde{H} D_{\rm b} [\rm m]$



 $H_{\rm h}$: Cyclone hopper height, $H_{\rm h} = \tilde{H}_{\rm h} D_{\rm b}$ [m] k_i : Correction coefficient of expansion loss [-] K_{lim} : Constant for calculating the limited load ratio [-] *l*: Insert depth of the cyclone outlet, $l = \tilde{l} D_{\rm b}$ [m] *n*: Swirl exponent [-] Δp_1 : Expansion loss at the cyclone inlet [Pa] $\Delta p_{\rm b}$: Cyclone body pressure drop [Pa] $\Delta p_{\rm c}$: Cyclone pressure drop [Pa] Δp_x : Outlet pressure drop [Pa] *Q*: Cyclone inlet gas flow rate $[m^3 s^{-1}]$ r: Radius of cyclone barrel [m] $r_{\rm c}$: Radius of core flow, $r_{\rm c} = \tilde{r}_{\rm c} r [{\rm m}]$ $R_{Ai}(d)$: Residue of the inner feed [-] *Re*: Reynolds number, $v_i D_b \rho_g / \mu_g$ [-] Re_{p} : Particle Reynolds number, $U_{0}d_{32}\rho_{g}/\mu_{g}$ [-] $R_{\rm F}(d)$: Residue of the emitted dust [-] Stk_{in i}: Stokes number [-] $u_{\rm T}$: Terminal velocity of particles [m s⁻¹] U_0 : Superficial gas velocity [m s⁻¹] \dot{V} : Gas flow rate [m³ s⁻¹]

- v_i : Gas velocity at the cyclone inlet [m s⁻¹]
- v_z : Axial gas velocity [m s⁻¹]
- v_{ze} : Axial gas velocity in the outlet annular region [m s⁻¹]
- v_{zw} : Axial gas velocity near the outlet wall [m s⁻¹]
- v_{θ} : Tangential gas velocity, $v_{\theta} = \tilde{v}_{\theta} v_{i} [m s^{-1}]$
- \overline{v}_{θ} : mean tangential velocity in the outlet tube [m s⁻¹]
- $v_{\theta c}$: Tangential gas velocity at the radius [m s⁻¹]
- $\nu_{\theta CS} {:}$ Tangential gas velocity at the imagined control surface $[m \; s^{-1}]$
- $v_{\theta e}$: Tangential gas velocity in outlet annular region [m s⁻¹]
- $\nu_{\theta w}$: Tangential gas velocity near the cyclone wall, $\nu_{\theta w} = \tilde{\nu}_{\theta w} \nu_i$ [m s^-1]
- $\nu'_{\theta w}\!\!:\!$ Tangential gas velocity near the cyclone wall for dust-laden gases $[m \; s^{-1}]$
- y: Exponent for calculating the limited load ratio [-]

 $\overline{z_e}$: Mean centrifugal acceleration at the reference radius [m s⁻²]

Greek alphabets

- *µ*: Expected grade-efficiency vector [–]
- $\mu_{\rm e}$: Initial load [kg kg⁻¹]
- μ_{g} : Gas viscosity [Pa s]
- μ_{lim} : Limited load ratio [kg kg⁻¹]
- $\rho_{\rm g}$: Gas density [kg m⁻³]
- $\rho_{\rm p}$: Particle density [kg m⁻³]
- η : Observed grade-efficiency vector [-]
- $\eta_{\rm F}(d)$: Grade efficiency [–]

 η_{tot} : Total separation efficiency [-] η_{vtx} : Separation efficiency in cyclone vortex [-] η_{wall} : Separation efficiency at wall [-] ϕ_i : Random effect of the *i*th component [-] σ_i : Standard deviation of ϕ_i [-] σ_{ξ} : Size deviation of particle diameter at inlet [-] ψ : Gas fraction in cyclone 1 [-] γ : Solids fraction in cyclone 1 [-]

Abbreviations

CFB: Circulating fluidized bed

- CFD: Computational fluid dynamics
- CPFD: Computational particle fluid dynamics
- C-S: Chen and Shi
- DEM: Discrete elemental method
- ECT: Electrical capacitance tomography
- FCC: Fluid catalytic cracking
- GLME: Generalized linear mixed-effects
- iG-CLC: In situ gasification chemical looping combustion
- PSD: Particle size distribution

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Screening of Ternary Intermetallic Catalysts Is Possible Using Metallurgical Synthesis: Demonstration on Heusler Alloys[†]

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Abstract

Intermetallic compounds are becoming hot materials as catalysts because they show unique catalytic properties that originate from a unique electronic structure and an atomic ordered surface. Ternary intermetallic catalysts have rarely been reported, which is likely due to the difficulty in synthesizing their supported nanoparticles, the typical form for catalysis research; however, there could be novel catalysts in ternary systems because they have much more elemental combinations than binary systems. They are expected to exhibit novel properties due to the synergy between three elements. Metallurgical methods, such as arc-melting, can easily synthesize intermetallic compounds even in ternary (or more) systems if they are thermodynamically stable. Thus, only metallurgical synthesis enables screening for ternary intermetallic catalysts. The catalyst screening of Heusler alloys, which are a group of ternary intermetallic compounds popular in other research fields, such as magnetics, has been conducted using metallurgical synthesis. The screening revealed fundamental catalytic properties of Heusler alloys for several reactions and identified good catalysts for the selective hydrogenation of alkynes. The systematic control of catalysis was also demonstrated by the substitution of fourth elements using a feature of Heusler alloys. This paper describes the importance of ternary intermetallic catalysts with practical examples of Heusler alloy catalysts and discusses future prospects.

Keywords: intermetallic catalyst, Heusler catalyst, intermetallic compound catalyst, Heusler alloy catalyst, ternary intermetallic compound, Heusler alloy

1. Introduction

A "catalyst" is defined as a material that promotes a chemical reaction but is not consumed and not irreversibly modified during the reaction. The mechanism of reaction promotion occurs when a reaction pathway changes into another pathway with a lower activation barrier, as illustrated in **Fig. 1**. The change in the pathway sometimes changes the product species, as shown in **Fig. 1(b,c)**. Thus, catalysts are necessary to make a massive amount of products with a lower energy cost and fewer waste materials (unfavorable byproducts) and to remove harmful species. A chemical reaction, including elementary steps of a catalytic reaction, proceeds through an exchange of electrons. Therefore, an electronic structure of catalysts dominates a

catalytic reaction. Obviously, a surface is also important for solid-state catalysts because the reaction proceeds on the surface.

Intermetallic compounds have a unique electronic structure completely different from a mixed state of component metals (Tsai A.P. et al., 2004; 2017) and have an atomic ordered structure even at the surface (Furukawa S. and Komatsu T., 2017). Thus, they are becoming hot materials for catalytic applications (Armbrüster M., 2014; Tsai A.P. et al., 2017; Furukawa S. and Komatsu T., 2017). Although almost all reports on intermetallic catalysts have discussed binary systems, there could be novel catalysts in ternary systems because there are much more potential elemental sets: 85,320 ternary and 3,240 binary systems are possible among 81 elements, and 13,026 ternary and 6,441 binary compounds have been validated according to Dshemuchadse J. and Steurer W. (2015). Ternary intermetallic catalysts are also expected to exhibit novel properties due to the synergy between three elements. Catalyst research is mostly conducted by chemists, typically using nanoparticles supported by oxide fine particles; however, the synthesis of ternary intermetallic nanoparticles requires considerable efforts to identify the appropriate conditions.



 [†] Received 3 March 2020; Accepted 16 March 2020
 J-STAGE Advance published online 29 April 2020

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Fig. 1 Schematic illustration of a binding reaction between A and B atoms (a) without a catalyst, (b) with a catalyst, and (c) with another catalyst. Blue Gaussian-like lines schematically represent the height of the activation energy for each elementary step. The activation barriers in all elementary steps in (b) and (c) are lower than that in (a). The AB molecule desorbs from the surface easily in (b) but hardly in (c). The ABA molecule forms more easily than AB in (c).

The use of nanoparticles is impossible for the screening of ternary intermetallic catalysts with changing component elements. This is the reason for the lack of studies on ternary systems.

On the other hand, metallurgical methods, such as arc-melting, can easily synthesize most intermetallic compounds even in ternary (or more) systems if they are thermodynamically stable. Intermetallic compounds are usually brittle, being easily crushed into powder. Thus, the screening of ternary intermetallic catalysts is possible. We have investigated Heusler alloys as new catalysts using metallurgically synthesized samples (Kojima T. et al., 2017, 2018, 2019a, 2019b). Heusler alloys are a group of ternary intermetallic compounds described as X_2YZ with L2₁ structure (body-centered cubic basis, called "full-Heusler" in a narrow sense), as shown in Fig. 2 (Kojima T. et al., 2018) (there are also other types, including XYZ with C1_b structure, which lacks one of two X sites in the L21 structure, called "half-Heusler") (Kojima T. et al., 2019a). They are popular as magnetic (spintronic) (Graf T. et al., 2016), thermoelectric (Nishino Y. et al., 2001), and shape memory materials (Planes A. et al., 2009), and they have been studied as topological materials nowadays (Manna et al., 2018). Although their catalytic properties were unknown, we hypothesized that there are novel catalysts in the numerous elemental sets (Fig. 2). The abundant choice of elements also enables the substitution of various elements in a wide composition range (e.g. $X_2 Y Z_{1-x} Z'_x$), by which electronic structures can be fine-tuned. This tuning is a common practice in the aforementioned fields but is also applicable for the precise control of catalytic properties (called the ligand effect, Fig. 2). Obviously, the fourth element substitution changes the type of surface element, by which catalytic properties can be controlled (called the ensemble effect, Fig. 2). Considering these advantages of Heusler alloys, we have conducted the screening for various reactions to reveal their fundamental catalytic properties and to identify novel catalysts.

2. Sample preparation and characterization

Heusler alloy (X = Fe, Co, Ni, or Cu; Y = Ti, Mn, or Fe;



Fig. 2 Crystal structure of Heusler alloys (L2₁ type), schematic illustration of elemental substitution effects, and typical components of *X*, *Y*, and *Z*. DOS means electron density of states. Components are not restricted to the periodic table in the figure; for example, Fe and Mn sometimes occupy *Y* and *X* sites, respectively, and lanthanoids, alkali metals, and alkaline earth metals can be components (Yin M. et al., 2016). The figure was excerpted from Ref. (Kojima T. et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).

Z = AI, Si, Ga, Ge, or Sn) ingots were prepared from pure metal pieces (purity: > 99.9 %) by arc-melting and were annealed in Ar atmosphere. For the annealing, the ingot was put on (into) an alumina piece (tube) or wrapped by a Ta or Mo foil in a quartz tube that was then sealed using a hydrogen gas burner after a cycle of evacuation and Ar purge. Although an annealing condition depends on alloys, we currently adopt 1000 °C 48 h for homogenizing followed by 600 °C 72 h for atomic ordering in many cases. The condition for each sample used in previous works has been described in Kojima T. et al. (2017) and (2018). The ingot was crushed using a pestle and mortar into powder that was then sieved to 20–63 µm for a catalytic reaction and < 20 µm for a structural evaluation using X-ray diffraction (XRD).

Before the XRD, a sample powder was annealed at 600 °C for 1 h to remove the strain. The XRD revealed that all the samples used in the published works (Kojima T. et



al., 2017, 2018, 2019a, 2019b) were (almost) single phase with a highly ordered L2₁ structure, although few samples had a tiny amount of second phases, as shown in Fig. 3. Some Heusler alloys disorder their atomic arrangements by heating, transforming the phase from L2₁ to B2 (disordering between Y and Z atoms) followed by A2 (disordering between all atoms), which is referred to as "ordered alloys" rather than "intermetallic compounds" (Kojima T. et al., 2019a). Thus, a degree of ordering should be evaluated. A long-range order parameter is typically used for the evaluation, which is estimated from an XRD intensity ratio of a superlattice and fundamental peaks (Warren B.E., 1990). Webster's model using parameters of S and α is easily usable for Heusler alloys, where a high S means a high ordering of X atoms and a low α means a high ordering of Y and Z atoms (Webster P.J. and Ziebeck K.R.A., 1973). All the samples had high S and low α (Kojima T. et al., 2017). Note that the superlattice peaks, such as 111 and 200 peaks, are essentially weak when the atomic numbers of the components are close, such as Co₂FeGe (Fig. 3), because an intensity in the superlattice peaks is proportional to the square of the difference of the atomic numbers.

A specific surface area of catalysts was estimated using the Brunauer-Emmett-Teller method for Kr adsorption isotherms at 77 K, which is a typical method for surface area estimation. Although the values per weight distributed from 0.047 to 0.13 m² g⁻¹ depending on atomic weights, the values per volume were similar (4.0–8.3 × 10⁵ m⁻¹) due to the sieving into 20–63 µm, as shown in **Table 1**.

Catalytic tests were conducted using a flow reactor, as shown in **Fig. 4**. An appropriate amount of catalyst pow-



Fig. 3 XRD patterns for Ni_2TiAl (red) and Co_2FeGe (blue) powders. Intensity was normalized by the height of a 220 peak. Co_2FeGe showed a peak of a second phase, which was likely CoGe.

ders was set on quartz wool in a quartz tube. Before the reactions, the catalyst was heated at 600 °C for 1 h under H_2 gas flow to remove surface oxides and strain. A gaseous reactant was introduced from a mass flow controller with an inert carrier gas. A liquidous reactant was introduced using a plunger pump with the carrier gas, followed by evaporated using an electric furnace surrounding the quartz tube so that the reaction took place in the gas phase. Unreacted and produced gaseous species and their concentrations were analyzed using a gas chromatograph. When the amount of gas products was large (e.g. > 10 % of carrier gas), a flow meter was used for analysis along with

Table 1 Specific surface area of catalyst

Catalyst	Surface area per weight $[10^{-2} \text{ m}^2 \cdot \text{g}^{-1}]$	Surface area per volume [10 ⁵ m ⁻¹]
Fe ₂ TiSn	7.1	6.0
Co ₂ TiAl	11	7.3
Co ₂ TiGe	8.4	6.8
Co ₂ TiSn	7.0	5.9
Co ₂ MnSi	8.8	6.5
Co ₂ MnGa	6.1	5.1
Co ₂ MnGe	6.7	5.7
Co ₂ MnSn	5.6	5.1
Co ₂ FeGa	4.7	4.0
Co ₂ FeGe	5.4	4.7
Ni ₂ TiAl	13	8.3
Ni ₂ TiSn	9.5	7.9
Ni ₂ MnSn	8.9	7.7
Cu ₂ TiAl	12	7.4



Fig. 4 Schematic illustration of a catalytic reaction system. The illustration is highly simplified.



the gas chromatograph (used in **section 5**). The details of the reaction conditions have been described in the original papers (Kojima et al., 2017; 2018; 2019b).

3. Oxidation of carbon monoxide

As a simple oxidation reaction, the oxidation of carbon monoxide $(CO + 1/2O_2 \rightarrow CO_2)$ was conducted (Kojima et al., 2017), which is an important reaction for removal of harmful CO gas produced from combustors, including automobile engines. Co-based Heusler alloys showed higher activity than other alloys, as shown in Fig. 5 (higher activity means higher conversion (reaction rate) at lower temperature). A hierarchy of activity of X in X_2 TiSn, X_2 TiAl, and X_2 MnSn seemed roughly similar to that of pure Fe, Co, Ni, and Cu powders. This indicates that a main active element in Heusler alloys is X for CO oxidation. During a cycle of heating and cooling, the hysteresis of the activity was observed in most alloys, as shown in Fig. 6(a,b). This was due to the irreversible oxidation of catalysts, which was indicated by the excess consumption of O₂; however, Co2TiSn showed very small hysteresis, as shown in Fig. 6(c) due to high resistivity to oxidation. These results indicate that not only activity but also durability can be controlled by choosing the appropriate *X*, *Y*, and *Z*.

4. Hydrogenation of alkynes

4.1 Catalytic properties

As a simple reduction reaction, the hydrogenation of alkynes $(C_nH_{2n-2} + aH_2 \rightarrow bC_nH_{2n} + (a-b)/2C_nH_{2n+2})$ was conducted (Kojima et al., 2017, 2018); such hydrogenation of hydrocarbons is important in various fields, including petrochemical industry. For propyne (C_3H_4) hydrogenation, most Heusler alloys showed very low activity (Kojima et al., 2017). This is likely due to the residual surface oxides of Al, Si, and Ti and due to the surface segregation of Sn. $Co_2(Mn \text{ or Fe})(Ga \text{ or Ge})$ alloys were active. Interestingly, Co_2MnGe and Co_2FeGe showed high alkene selectivity (fraction of alkene in products: $C_nH_{2n}/(C_nH_{2n} + C_nH_{2n+2}))$ (Kojima et al., 2018). **Fig. 7** shows alkyne conversion (percentage of reacted alkyne) and alkene selectivity during the hydrogenation of alkynes (C_3H_4 , C_2H_3) in the presence of



Fig. 5 CO conversion (percentage of reacted CO) in CO oxidation by (a) X_2 TiSn, (b) X_2 TiAl, (c) X_2 MnSn, and (d) pure X catalysts using a reactant of [1.2 %CO / 0.4 %O₂ / 98.4 %He]. 66.7 % is the ideal CO conversion because the reactant is CO-rich (CO:O₂ = 3:1). After Ref. (Kojima T. et al., 2017), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/acsomega.6b00299). Further permissions related to the material excerpted should be directed to the ACS.



Fig. 6 CO conversion in CO oxidation by (a) Fe₂TiSn, (b) Ni₂TiSn, and (c) Co_2 TiSn using a reactant of [1.2 %CO / 0.4 %O₂ / He balance] during heating and cooling cycles. After Ref. (Kojima T. et al., 2017), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/ acsomega.6b00299). Further permissions related to the material excerpted should be directed to the ACS.





Fig. 7 Alkyne conversion and alkene selectivity in the reaction using the reactant of (a1,b1,c1) [0.1 %C₃H₄ / 10 %C₃H₆ / 40 %H₂ / 49.9 %He] or (a2,b2,c2) [0.1 %C₂H₂ / 10 %C₂H₄ / 40 %H₂ / 49.9 %He] for (a1,a2) Co₂MnGe, (b1,b2) Co₂FeGe, and (c1,c2) Co₂FeGa. After Ref. (Kojima T. et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).

a large amount of alkenes (C_3H_6 , C_2H_4). In general, alkene selectivity decreases with an increase in alkyne conversion as Co_2FeGa (**Fig. 7c1,c2**), which is due to the promotion of alkene adsorption along with the consumption of strongly adsorbed alkyne molecules. In contrast, Co_2MnGe and Co_2FeGe kept high selectivity even when the conversion was high enough (**Fig. 7a1–b2**). **Fig. 8** shows the results of C_3H_4 hydrogenation without C_3H_6 and C_3H_6 hydrogenation without C_3H_4 . **Fig. 8 (a1–b2)** indicate that Co_2MnGe and Co_2FeGe essentially do not have ability to hydrogenate alkenes in contrast to $Co_2FeGa_{0.75}Ge_{0.25}$ (**Fig. 8c1,c2**) as an example of ordinary catalysts.

The selective hydrogenation of alkynes in alkene feedstocks is a crucial process to remove alkyne impurities that hinder the polymerization of alkenes in the process to produce polyalkenes, such as polyethylene (Borodziński A. and Bond G.C., 2006, 2008). In industry, the selective hydrogenation is achieved by the precise control of reac-



Fig. 8 (a1,b1,c1) C_3H_4 conversion and C_3H_6 selectivity in the reaction using the [0.1 % C_3H_4 / 40 % H_2 / 59.9 %He] reactant and (a2,b2,c2) C_3H_6 conversion in the reaction using the [0.1 % C_3H_6 / 40 % H_2 / 59.9 %He] reactant for (a1,a2) Co_2MnGe , (b1,b2) Co_2FeGe , and (c1,c2) $Co_2FeGa_{0.75}Ge_{0.25}$. After Ref. (Kojima T. et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).

tion conditions, including temperature, pressure, H_2 concentration, and the introduction of CO gas as an inhibitor because Pd-based practical catalysts do not have essential selectivity. Therefore, these Heusler alloy catalysts would be useful in terms of replacing noble metals.

4.2 Elemental substitution effects

The effects of elemental substitution were investigated for C_3H_4 hydrogenation using $Co_2Mn_xFe_{1-x}Ga_yGe_{1-y}$ catalysts (Kojima et al., 2018). **Fig. 9** shows the results of the Mn and Ga substitutions for Fe and Ge, respectively, of Co_2FeGe . The reaction rate and the selectivity systematically changed with the amount of the substitution (**Fig. 9a**). The Mn substitution increased the reaction rate while maintaining high selectivity. The Ga substitution significantly increased the reaction rate but decreased selectivity.

An experimental apparent activation energy (E_a)



changed with a d band center (ε_d) calculated for bulk states (Fig. 9b). ε_d means an average energy of d states, dominating a strength between adsorbates and metals; that is, higher (lower) ε_d makes higher (lower) energy levels of the adsorbates, resulting in lower (higher) occupation of anti-bonding states. Thus, ε_d affects relevant energy quantities in elementary steps, such as adsorption energy and activation energy (Nørskov J.K. et al, 2011). The good correlation between E_a and ε_d in Fig. 9(b) proves that the electronic modification by elemental substitution certainly affected the elementary steps. Actually, the fine modification of electronic structures was achieved in good accordance with the calculated results, which was indicated by photoelectron spectroscopy and first-principles calculation, as shown in Fig. 10. These results indicate that a precise control of catalytic properties through the fine-tuning of electronic structures is possible by elemental substitution of Heusler alloys.

As a result of further experiments and analyses, including the estimation of reaction orders and the deduction of reaction mechanisms, the Mn and Ga substitution effects were concluded to be mainly ligand and ensemble effects (Fig. 2), respectively (Kojima et al., 2018). In other words, Mn substitution changes catalysis through the modification of the whole electronic structure, while Ga substitution changes catalysis through the replacement of surface Ge atoms by Ga atoms that have a greater ability to adsorb molecules. In addition, Mn-Fe substitution and Ga-Ge substitution affect catalysis independently. For example, Mn substitution for Co2FeGa caused a similar change in catalysis to that for Co₂FeGe, while Ga substitution for Co₂MnGe caused a similar change in catalysis to that for Co₂FeGe (Kojima et al., 2018). Therefore, the fine-tuning of catalysis is possible depending on the target reaction by (1) choosing a main active element X and sub-elements Yand Z, (2) substituting Y to optimize electronic structures, (3) and substituting Z to optimize surface ensembles. Furthermore, this precise controllability would be useful to reveal a general relation between electronic structures and catalysis, which are only partially understood thus far.

5. Steam reforming of methanol

The steam reforming of methanol (SRM: $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$) is a candidate to produce hydrogen from a safe hydrogen carrier, which is often studied using intermetallic catalysts (Tsai A.P. et al., 2004, 2017; Armbrüster M. et al., 2014; Furukawa S. and Komatsu T., 2017). As another type of reaction different from those mentioned above, SRM was used to investigate Heusler alloy catalysts (Kojima et al., 2019b). Among the 14 Heusler alloys listed in **Table 1**, most alloys did not produce H_2 at a low temperature of ≤ 450 °C, as shown in **Fig. 11(a–d)**. Several alloys



Fig. 9 Elemental substitution effects on (**a**) C_3H_4 reaction rate at 50 °C and C_3H_6 selectivity at 200 °C and (**b**) E_a and ε_d in the reaction using the [0.1 % C_3H_4 / 40 % H_2 / 59.9 %He] reactant. Mn substitution for Fe and Ga substitution for Ge of Co₂FeGe are represented. The rate is relative to that of Co₂FeGe per surface area. The figure was excerpted from Ref. (Kojima T. et al., 2019a) licensed under CC-BY, which was remade using the data in Ref. (Kojima T. et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).

did not produce H₂ even at 600 °C, as shown in **Fig. 11(e)**. Surface microstructural changes, such as the formation of fine particles, were observed in most alloys that showed a certain activity, as shown in **Fig. 12(a–d)**. In many catalysts consisting of group 8–10 metals, the first step of SRM is the decomposition of methanol (CH₃OH \rightarrow 2H₂ + CO) (Sá S. et al., 2010). This reaction is structure sensitive; that is, larger particles show a lower reaction rate per surface area. Thus, the diameter of 20–63 µm was likely too large, while the precipitation of fine particles yielded activity.

In particular, Ni₂TiAl exhibited high activity due to the formation of Ni fine particles, as shown in **Fig. 13(a,b)**. A higher activity at 400 °C during cooling than heating implies fine particle precipitation at \geq 450 °C (**Fig. 13a**). A Ni₃Al catalyst is known to precipitate Ni fine particles during methanol decomposition through the selective oxidation of Al (Chun et al., 2006). On the other hand, Ni₂TiAl likely precipitates Ni fine particles through the selective oxidation of Ti, as shown in **Table 2**. Co₂TiAl showed a similar change in catalytic properties along with fine particle precipitation (Kojima et al., 2019b). In contrast, Cu₂TiAl did not form Cu fine particles as indicated by the decrease in the surface Cu composition after the reaction





Fig. 10 (a) DOS calculated for the bulk and (b) valence band spectra of hard X-ray photoelectron spectroscopy (HAXPES). The figure was excerpted from Ref. (Kojima T. et al., 2018) licensed under CC BY-NC (http://creativecommons.org/licenses/by-nc/4.0).



Fig. 11 Production rates of H_2 and byproducts (CO, CO₂, CH₄) in the reaction using a reactant mixture of CH₃OH and H₂O (molar ratio 2:3) fed at 0.07 g min⁻¹ corresponding to 20 µmol s⁻¹ of CH₃OH. After Ref. (Kojima T. et al., 2019b), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/acsomega.9b01837). Further permissions related to the material excerpted should be directed to the ACS.



Fig. 12 Surface microstructures after the SRM reaction observed by scanning electron microscopy for (a) Co_2MnSn , (b) Ni_2MnSn , (c) Co_2TiSn , and (d) Ni_2TiSn .



Table 2 Surface composition [%] of *X*, *Y*, and *Z* in X_2YZ before and after SRM reaction analyzed by X-ray photoelectron spectroscopy^a.

Catalyst	Reaction	X	Y	Ζ
Ni ₂ TiAl	Before	8	19	74
	After	13	36	51
Co ₂ TiAl	Before	13	19	68
	After	23	46	31
Cu ₂ TiAl	Before	13	11	76
	After	4	41	56

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Table 3 Standard Gibbs energy of oxide formation (ΔG°) [kJ (O₂ 1 mol)⁻¹] at 400 °C^a.

Element	Oxide	ΔG°
Fe	Fe ₃ O ₄	-444
Со	CoO	-373
Ni	NiO	-355
Cu	Cu ₂ O	-239
Ti	TiO ₂ (rutile)	-821
Mn	MnO	-665
Al	$Al_2O_3(\alpha)$	-976
Sn	SnO ₂	-442

^a After Ref. (Kojima T. et al., 2019b), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/acsomega.9b01837). Further permissions related to the material excerpted should be directed to the ACS.

(Table 2), thus not gaining activity. Standard Gibbs energies of oxide formation (ΔG°) are similar between Co and Ni but fairly different between them and Cu, as shown in Table 3. This is likely the reason for the difference in the structural change. Co2MnSn and Ni2MnSn showed similar structural changes (Fig. 11a,b) (Kojima et al., 2019b). Co₂TiSn and Ni₂TiSn also showed similar structural changes (Fig. 11c,d), but Fe₂TiSn showed a different change, likely due to the difference of ΔG° between Co, Ni, and Fe (Kojima et al., 2019b). These results indicate that the tendency of structural changes through oxidation is determined by a balance of the oxidizability of components. The activity of Ni₂TiAl was enhanced by preheating under [1 %O₂/99 %He] flow at 500 °C for 1 h before the reaction due to the enhancement of the Ni fine particle precipitation, as shown in Fig. 13(c,d). Co₂TiAl showed similar results by O₂ preheating (Kojima et al., 2019b).

Many alloys mainly produced CO as a byproduct, meaning that methanol decomposition predominantly occurred.



Fig. 13 Results of SRM for (**a**,**b**) Ni₂TiAl and (**c**,**d**) Ni₂TiAl with O₂ pretreatment. (**a**) and (**c**) show the production rates of H₂ and byproducts during heating and of H₂ during cooling. (**b**) and (**d**) are surface microstructures after the reaction. After Ref. (Kojima T. et al., 2019b), reproduced with permission by ACS (https://pubs.acs.org/doi/abs/10.1021/acsomega.9b01837). Further permissions related to the material excerpted should be directed to the ACS.



Fig. 14 Production rates of H₂ and CO in the decomposition of methanol fed at 0.04 g min⁻¹ (20 μ mol s⁻¹) for Co₂FeGe. After Ref. (Kojima T. et al., 2019b), reproduced with permission by ACS (https://pubs.acs. org/doi/abs/10.1021/acsomega.9b01837). Further permissions related to the material excerpted should be directed to the ACS.

In contrast, all the alloys containing Mn mainly produced CO_2 as a byproduct (**Fig. 11a,b**). During the reaction, all these alloys formed MnO (Kojima et al., 2019b), which catalyzes a water-gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$), eventually achieving SRM by converting CO that was produced by methanol decomposition. This study revealed a variety of structural changes through oxidation, which suggests a development of multi-functional catalysts consisting of several phases using Heusler alloys as a



precursor. Intermetallic compounds are atomically homogeneous in essence, even in ternary systems. This is an advantage of being used as a precursor of catalysts with less inhomogeneity.

 Co_2FeGe was active for methanol decomposition using a pure methanol reactant without steam, as shown in **Fig. 14**. Interestingly, the initial metallic state was likely active because a certain activity appeared even at ≤ 400 °C and because a significant structural change was not observed after the reaction at 600 °C (Kojima et al., 2019b). A specific electronic structure or a specific reaction field created by atomic ordered structures might be suited to this reaction. The origin of the activity is attractive to be studied.

6. Perspectives

For other reactions, we are currently investigating the dehydrogenation of 2-propanol and the methanation of carbon monoxide. Screening for the dehydrogenation of methylcyclohexane (MCH) and its reverse reaction, the hydrogenation of toluene, was also conducted; however, no activity was observed in the tested alloys. These molecules, which have a six-membered ring, are highly stable, and most studies on MCH dehydrogenation have used Pt-based nanoparticles (Nakano A. et al., 2017). Thus, the diameter of 20-63 µm (surface area: ca. 0.1 m²·g⁻¹) was considered too large to exhibit activity. Aside from an extreme case, such as MCH dehydrogenation, even ammonia synthesis, which must break a very stable triple bond of N₂, can be achieved by good intermetallic catalysts (LaCoSi, LaRuSi) with a surface area around $1 \text{ m}^2 \cdot \text{g}^{-1}$ (Gong Y. et al., 2018; Wu J. et al., 2019). Intermetallic compounds are usually brittle and thus easily crushed into powder with surface areas over 1 m²·g⁻¹ by ball-milling, which may reduce the particle size down to < 100 nm depending on milling conditions as well as other milling methods, including bead milling and jet milling (Yokoyama T. and Huang C.C., 2005). Thus, screening is possible using metallurgically synthesized powders for most reactions without extremely stable reactants.

Although we have adopted arc-melting for synthesis, powder metallurgical methods are applicable, such as sintering and mechanical alloying, from pure metal powders. Simply, sintering can be done by annealing tablets made by pressing, for example, at > 10 MPa. Mechanical alloying can be done by ball-milling for a long time, for which the equipment is much less expensive than that for arc-melting. Instead of sealing the quartz tubes for annealing, using a tubular furnace under N₂ flow is simple, which can be easily self-built, although air contamination should be excluded for easily oxidizable powders. For arc-melted ingots, annealing, for example, at 800 °C for 48 h is sufficient for many systems, though we have adopted longer conditions to surely obtain high-quality samples. The variation of quality among samples in different systems is smaller in metallurgical synthesized powders than chemically synthesized nanoparticles. This is an advantage for the correct discussion with reducing uncertainty. This is also suitable for an informatic approach to predicting new catalysts because a smaller variation of quality reduces the number of data sets required to ensure accuracy.

After identifying new catalysts by screening, a specific surface area must be enlarged for practical application. Supported nanoparticles are normally used but not easy to synthesize in ternary intermetallic compounds, as mentioned; however, the synthesis is possible for experts and/ or through considerable effort. Supported Co2FeGa and Cu₂NiSn nanoparticles were successfully synthesized with sufficient quality: the L2₁ structure, small second phases, a small size, and a small size distribution (Basit L. et al., 2009; Wang C. et al., 2010, 2012, 2014; Wang C.H. et al., 2010; Ernst S. et al., 2019). One reason for the lack of reports on ternary intermetallic nanoparticles is that there was no specific application until recently. Thus, research to develop ternary intermetallic nanoparticles would increase in relation to catalytic applications. Recently, a novel method to synthesize supported nanoparticles has been developed, which achieved the preparation of several nanometer-sized Au, Pt, Ag, Cu, and Ni particles from micrometer-sized powders by ball-milling under a gas flow of CO/O2/He (Schreyer H. et al., 2019). This dry metallurgical method can be attractive for intermetallic nanoparticles.

Aside from our studies, there are few early studies on Heusler alloy catalysts: the theoretical calculation for ammonia dissociation by Ni₂MnGa and Co₂CrGe (Senanayake N.M., 2016) and the screening of supported Heusler alloy catalysts (Mueller U. et al., 2018). BASF did not obtain a sufficient quality of samples in the latter study but then succeeded in the development of the aforementioned Cu₂NiSn nanoparticles (Ernst S. et al., 2019). Recently, experimental studies have been conducted on methanol synthesis using Ni₂FeGa (Smitshuysen T.E.L., et al., 2020) and on ammonia dissociation using Co2CrGe (Chao H. et al., 2019). For other ternary intermetallic catalysts, aforementioned RTX (R: rare earth, T: transition metal, X: *p*-block element) compounds (LaCoSi, LaRuSi) have been recently reported on ammonia synthesis, which were prepared by arc-melting (Gong Y. et al., 2018; Wu J. et al., 2019). In these catalysts, the property as an electride, the ability for hydrogen storage, and an electron transfer from La to active elements (Co, Ru) play key roles. Thus, ternary systems exhibit novel catalytic properties that are not realized in binary systems. The screening of ternary intermetallic catalysts would be accelerated for the potential discovery and development of novel catalysts.



Acknowledgements

We are grateful to Prof. Shinpei Fujii of Kagoshima University and to Dr. Shigenori Ueda of National Institute for Materials Science for collaborating with us for the electronic structure evaluation by first-principles calculation and HAXPES. The HAXPES was conducted at BL15XU at SPring-8 under the approval of NIMS Synchrotron X-ray Station (proposal no. 2017B4905). This work was partially supported by JSPS KAKENHI grant number JP19H02452, the Hattori Hokokai Foundation, the Iwatani Naoji Foundation, the Noguchi Institute, and NIMS microstructural characterization platform as a program of 'Nanotechnology Platform' (project no. 12024046) of MEXT, Japan. We also thank the supports from the Program for Creation of Interdisciplinary Research from FRIS, Tohoku University, and from Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials.

Sections 3–6 were partly written based on the review paper in Japanese (Kojima T., 2020).

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Authors' Short Biographies



Takayuki Kojima

Dr. Kojima majored in materials science during his student career (2001–2006: Kurume National College of Technology; 2006–2013: Tohoku University for bachelor, master, doctoral). He researched magnetic material thin-films when he was a graduate student. He then came up with the idea of using Heusler alloys as catalysts, which are popular as magnetic materials, inspired by Prof. A.P. Tsai's lecture on "like electronic structure, like catalysis", and began conducting catalytic studies in Tsai's group in 2014. He is currently researching catalysts and functional materials, including magnetic materials, through an interdisciplinary approach as an Assistant Professor of FRIS.



Authors' Short Biographies



Satoshi Kameoka

Dr. Kameoka is an Associate Professor at the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University. He received his PhD from University of Tsukuba in 1996. In 2004, he moved to IMRAM as a Research Associate. His research interests are catalysis by metals and alloys. He has performed collaborative research with Prof. Tsai and Dr. Kojima in studies on the metallurgy for advanced catalysis materials since 2002 and 2014, respectively.





Dr. Tsai was an outstanding researcher who is well-known for the first discoveries of a stable quasicrystal and a binary quasicrystal. Most quasicrystals were discovered by him. He received his PhD from Tohoku University and many honors, including the Medal of Honor with Purple Ribbon (Japan), and was elected as a member of Academia Sinica (Taiwan). He became a Professor of IMRAM in 2004 after working at the Institute for Materials Research of Tohoku University and the National Institute for Materials Science (NIMS). He began research on catalysis from a metallurgical viewpoint about 20 years ago. He passed away on May 25, 2019 (age 60).

Particle Preparation and Morphology Control with Mutual Diffusion Across Liquid-Liquid Interfaces[†]

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Abstract

Advanced functional materials require sophisticated control of particle characteristics. The bottom-up process has been extensively used to produce functional materials for controlling the particle properties of composite particles. We propose crystallization at liquid-liquid interfaces as an advanced particle formation method. This review introduces crystallization at a liquid-liquid interface based on several case studies used in various applications. Conventional crystallization has been generally used to produce crystals and particles with homogeneous particle properties. Liquid-liquid interfacial crystallization makes it possible to create composite particles with hetero-phase structures and interfaces. Liquid-liquid interfacial crystallization with an inkjet technique can control the droplet size accurately, and the shape and particle size distribution are successfully controlled in inorganic-organic composite particles. In addition, we succeed in creating organic-organic composite particles on the particles is enhanced using the ultrasonic spray nozzle. The coating efficiency of organic particles on the particles is enhanced using the ultrasonic spray nozzle in comparison with anti-solvent crystallization. In this study, the fabrication of inorganic-organic composite particles using a coaxial tube reactor on the liquid-liquid interfacial crystallization is proven successful. These findings suggest that liquid-liquid interfacial crystallization is a promising means of efficiently producing composite particles because of their applicability to infusion in various processes.

Keywords: composite particles, crystallization, liquid-liquid interface, morphology, supersaturation

1. Introduction

Fine particular material is employed in various industrial applications such as chemical, pharmaceutical, cosmetics, and food products. The physicochemical properties of particles originally affect the performance or features of products composed of powder. The ability to control particle properties such as shape, morphology, size, and size distribution is indispensable to developing industrial fields (Provis et al., 2010; Saallah and Lenggoro, 2018; Fuji et al., 2013). Particle-generation approaches that create fine particles can mainly be divided into two processes: break-down and bottom-up (Yokoyama and Huang, 2005; Tavares, 2017; Opalski et al., 2019). The bottom-up approach is commonly used to control the particle properties during fabrication processes. In particular, the bottom-up approach has recently gained attention due to its several advantages such as lower energy processes, lower cost, and simpler instrumentation (Sinha et al., 2013; Vece, 2019). Previously, numerous bottom-up approaches such as crystallization have been successful in controlling particle properties for the purpose of obtaining powder products with different features (Fuchs et al., 2008; Horn and Rieger, 2001; Kadota et al., 2006; Worlitschek and Mazzotti, 2004). The bottom-up approach has been extensively used in producing composite materials in terms of controlling the particle properties of composite particles (Leon et al., 2014). Hetero-phase structures and interfaces in composite materials can provide additional functions to products and approaches that creation of interfaces and structures have been regarded as a driving force of new innovative product development (Shirakawa et al., 2006; Shirakawa et al., 2010). Several composite materials such as inorganic-organic and organic-organic products have been developed. Inorganicorganic composite materials have gathered attention for use in catalysts and photoelectronic materials, whereas organic-organic composite materials are currently being developed as biomaterial and pharmaceutical products (Alam et al., 2018; Lazzara et al., 2018).



Received 26 October 2019; Accepted 3 March 2020
 J-STAGE Advance published online 29 April 2020

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Composite materials using inorganic-organic or organic-organic materials have been proceeded for delivering drugs and other bioactive molecules for over 30 years. Several products are ongoing or have been approved worldwide as nanocarriers of drug delivery systems (Natarajan et al., 2014). Most of these nanocarrier products have focused on target drug delivery such as cancer chemotherapy and effectively utilize the size advantage of nanocarriers to provide a favorable distribution of the drug carrier to the human body. Several researchers have previously succeeded in generating sustained-release products to nanocarrier applications (D'souza and DeLuca, 2006; Washington, 1990). The accomplishment in sustained release of bioactive molecules has broken ground as nanotherapeutics. As a representative product of composite materials, nanocarriers that provide spatiotemporal control of drug release contributed to the improvement in the therapeutic efficacy of drugs and the reduction in toxicity. Among composite materials, nanocarriers confront tough and original challenges in drug-release kinetics control because of the large surface area per volume ratio and small diffusion. For development of nanocarriers such as composite particles with favorable release kinetics for drug delivery applications, understanding the mechanisms by which a carrier retains and releases a drug (Lee and Yeo, 2015) is crucial.

The silica nanoparticles with porous and hollow structures for controlling release kinetics of drugs were previously prepared using bottom-up approaches (Li Z. et al., 2004). Porous hollow silica nanoparticles with drugs were prepared through a sol-gel method and using a CaCO₃ template method (Nakashima et al., 2018). The prepared porous hollow silica nanoparticles were utilized as a carrier to investigate the controlled release kinetics of model substances. A drug injected into the inner core and fused onto the surfaces of the silica nanoparticles was released more gradually into a solution as compared to the general silica nanoparticles, exhibiting a typical sustained release without any burst phenomena. The results showed that porous hollow silica nanoparticles have a prospective potential in controlled drug delivery systems. Aw et al. (2012) also applied porous hollow silica as a biocarrier of drug delivery systems of indomethacin (IMC) as a model of a slightly water-soluble drug. The effectiveness of porous hollow silica as an oral-drug delivery system showed a high load capacity of drugs and sustained drug release over a long period. These natural materials based on silica can be successfully utilized as a biocarrier for both oral and implant drug delivery systems.

Except for silica, metal-organic frameworks (MOFs), which are hybrid materials formed by bottom-up approaches such as the self-assembly of polydentate bridging ligands and metal-connecting points, have been gathering attention as new drug delivery systems (Rocca et al., 2011). The MOFs have been reduced in size to nanometer sizes, and the nanoscale MOFs were developed as biomedical applications because of several attractive advantages over conventional nanomedicines, including their chemical and structural diversity, intrinsic biodegradability, and high loading capacity. Nano MOFs have been employed to deliver anticancer drugs and other chemotherapeutics. Nano MOFs are attractive as potential materials for the accurately effective delivery to targeted cells or organs in vivo. Murugan and Krishnan (2018) focused renewed attention on mesoporous silica for the application of "on-demand" drug delivery because the conception of targeted and sustained delivery of therapeutic compounds has been oriented into a more effective and attractive approach of drug release. These drug delivery systems have been extensively examined for site-specific delivery of single and multiple therapeutic agents. Although various types of external stimuli have been widely examined to bring about triggered and sustained drug release from mesoporous silica, chemo-responsive systems provide more therapeutic effectiveness with minimal collateral damage commonly associated with external stimuli. Therefore, these systems have been interpreted as "on-demand" drug release in mesoporous silica carriers and could achieve different strategies in response to various types of chemical stimuli.

This review introduces several case studies for crystallization with mutual diffusion across liquid-liquid interfaces used in various applications. Crystallization at a liquid-liquid interface was developed to synthesize asymmetric particles and composite particles. This liquidliquid interfacial crystallization was applied to various advanced processes, which enabled finding a new possibility for creating advanced functional materials.

2. Crystallization at liquid-liquid interface

Crystallization at liquid-liquid interfaces was proposed as an advanced particle synthesis technique in our previous works (Kadota et al., 2007a; 2007b). This technique is a production method used to precipitate solute particles at the interface in partially miscible liquids. As a representative example, emulsions prepared as templates in liquidliquid dispersion systems have been expanded in the biomedical applications as tissue engineering materials and drug carriers (Wu and Ma, 2016). Several studies conducted by Ramsden (1903) and Pickering (1907) revealed another means of stabilizing droplets using solid particles without surfactants (Fujii and Murakami, 2008). Pickering emulsions can be widely employed in various fields such as food, biomedicine, fine chemical products, and cosmetics (Linke and Drusch, 2018). We developed a liquid-liquid interfacial crystallization using mutual and Trout B.L., 2010). The organic solvents of 1-butanol

diffusion phenomena between an aqueous solution and an organic solvent that occurs at a liquid-liquid interface. The techniques could be applied to various fields such as chemical engineering, food industries, and pharmaceuticals (Mori et al., 2019b). For example, different kinds of asymmetric particles were prepared through interfacial crystallization, and the preparation of glycine particles with porous structures was successful (Tanaka M. et al., 2011). Recently, Janus particles have been a unique class of multifunctional particles that combine two dissimilar chemical or physical functionalities at their opposite sides as asymmetric particles (Agrawal G. and Agrawal R, 2019).

An inkjet nozzle was installed to crystallization at liquid-liquid interfaces, because there is a possibility that an inkjet nozzle can control the shape and morphology of particles by preparing uniform spherical droplets (Tamura et al., 2014). The inkjet technique has garnered significant attention for universal particle production (Böhmer et al., 2006). Since the inkjet process can give narrow particle size distributions and control over particle morphology and precise dosage volume, this technique can be extended to manufacturing tablets for tailored medicine (Daly et al., 2015). Wijshoff (2010) fabricated polymer particles using an inkjet process. In another study, the size distribution and morphology of metal particles were successfully controlled (Böhmer et al., 2006). We applied the inkjet technique to liquid-liquid interfacial crystallization, and through an instillation, we present its effectiveness in controlling particle morphology and shape as compared with the batch process.

Glycine and alanine were selected as solutes, and 1butanol and 2-butanone as solvents for crystallization at liquid-liquid interfaces. Alanine has no crystal polymorph, but glycine has three crystal polymorphs (Chen J. or 2-butanone were set next to the liquid-liquid interface to contact with the aqueous solution. Fig. 1 depicts a schematic diagram of the experimental apparatus and an instillation of particle precipitation with an inkjet nozzle. In this apparatus, several droplets of the aqueous solution were discharged from the inkjet nozzle into the organic solvent with slight miscibility (Tanaka M. et al., 2011). Alanine or glycine immediately precipitated at the interface of droplets. For the batch process, particles of amino acids were obtained by mixing the aqueous solution with an organic solvent under fixed stirring. The emulsion including droplets of glycine or alanine solution in the organic solvent was stirred. The droplet size was estimated from SEM photographs. The crystal structure of both particles was measured through powder X-ray diffraction (XRD). The internal structure of both particles was also observed by SEM with cutting off particles using an ion milling apparatus.

Fig. 2 displays the relation between the mean particle size of alanine and the droplet size of instillation with the inkjet nozzle. The mean particle size of alanine was approximately 1.2-fold higher than aqueous droplet size in 1-butanol. Additionally, the mean particle size of glycine was larger than the corresponding droplet. The results suggest that the interface between the 1-butanol and aqueous solution expanded following their mutual diffusion during crystallization. The particle size of alanine was almost monodispersed as the coefficient of variation, and the control of the particle size was demonstrated to be feasible by controlling the droplet size using the inkjet nozzle.

Figs. 3 and 4 show SEM photographs of glycine and alanine particles produced by the batch process and by



Fig. 1 Overview of the schematic experimental apparatus for instillation using an inkjet nozzle for liquid-liquid interfacial crystallization. Reprinted with permission from Ref. (Tominaga et al., 2018). Copyright: (2018) Elsevier.



instillation with an inkjet nozzle, respectively. In the batch process, most alanine particles were needle-like and most glycine particles were rod-like. In comparison with the batch process, glycine and alanine particles precipitated by instillation with an inkjet nozzle had a spherical shape. During this crystallization process by instillation with an inkjet nozzle, the interface part immediately reaches a supersaturated state once an aqueous solution contacts an organic solvent. Consequently, instillation process with an inkjet nozzle made spherical particles since nucleation and crystal growth of the solute material made progress along the spherical interface. Both particles prepared by the instillation exhibited more spherical and uniform particle size distribution than those by the batch process. The supersaturation ratio near the interface required a tiny gradient in the droplets due to the limita-



Fig. 2 Change in mean particle size of alanine against droplet size during the instillation process with an inkjet nozzle. Reprinted with permission from Ref. (Tamura et al., 2014). Copyright: (2014) Elsevier.



Fig. 3 SEM photographs of alanine and glycine particles by the non-inkjet process: (a) glycine particles using 1-butanol, (b) alanine particles using 1-butanol. Reprinted with permission from Ref. (Tamura et al., 2014). Copyright: (2014) Elsevier.



Fig. 4 SEM photographs of alanine and glycine particles during the instillation process using an inkjet nozzle: (a) glycine particles using 1-butanol (b) alanine particles using 1-butanol. Reprinted with permission from Ref. (Tamura et al., 2014). Copyright: (2014) Elsevier.

tion to the crystallization area with the spherical interface of the droplets. Observation of the cross section of glycine and alanine particles by SEM emerged the presence of porous hollow structures. In the saturated aqueous solutions of alanine and glycine, the amount of glycine solute was greater than that of alanine solute in droplets. This difference in the amount of solute between alanine and glycine in saturated solutions may lead to hollow structures of alanine and porous structures of glycine.

The crystal structures of glycine particles prepared by instillation with the inkjet nozzle and by the batch process were evaluated by XRD. β-Glycine, which is an unstable polymorph, was identified in the instillation with inkjet nozzle, whereas the glycine particles prepared by the batch process were of the metastable α form (Matsumoto et al., 2019). In general, the α and β forms of glycine precipitate preferentially at lower and higher supersaturation ratios, respectively (Matsuoka 2005; Bouchard et al., 2008). Comparing the instillation to the batch process, the diffusion phenomenon within the strictly confined droplet generates regions of higher concentration at the interface. Consequently, several nuclei of glycine were homogenously formed within the well-defined droplet by the inkjet nozzle. It is likely that the concentration of aqueous solution affects the size distribution and morphology of particles during interfacial crystallization (Fujii et al., 2007). According to Takiyama (2004), uniform crystals can be easily prepared from an unsaturated solution in anti-solvent or cooling crystallization. Concentration dependence of the amino acid solution on particle size, size distribution, and morphology was examined for the inkjet process. The size distribution of glycine and alanine particles moved toward larger sizes with an increase in concentration. The morphology of glycine prepared by instillation with an inkjet nozzle changed from spherical to ellipsoidal with an increase in glycine concentration. It is considered that the growth of glycine crystals proceeded along the minor and major axes depending on the crystal form.

The alanine particles were prepared by instillation using two types of anti-solvents: 1-butanol and 2-butanone. Here, the mutual solubility of 1-butanol and 2-butanone to water is different (Kitayama et al., 2009a). The surface morphology of alanine particles prepared using 2butanone was coarser than that of particles prepared using 1-butanol. The difference in surface morphology derives from the mutual diffusion behavior following the organic solvent. Phase diagrams of water/1-butanol and /2butanone were previously reported (Kitayama et al., 2009b; Kadota et al., 2013; Deki et al., 2016). In the solubility of 1-butanol in water, the amount of water diffusing into 1-butanol was much greater than that of 1-butanol diffusing into water at 25 °C. The diffusion of the solution from droplets could go ahead and performed with



maintaining the spherical shape. The converse phenomenon occurred in the usage of 2-butanone and water. The size of particles became larger than that of droplets because the diffusion of the organic solvent predominated in the mutual diffusion at the interface. This different behavior in mutual diffusion affected the particle formation with different shape and morphology.

3. Crystallization in a tube reactor

Another case study involved particle preparation of zirconia using a tube reactor (Kadota et al., 2016). Microchannels in tube reactors have attracted attention for preparing many types of particles since production in a single step is possible (Hattori et al., 2015). As part of an inexpensive and simplified approach, zirconia particles, which are widely used as a ceramic material with functional properties such as high mechanical strength, were prepared by neutralization reaction at the interfacial within a tube reactor. Micro reactors are generally applied to gas-liquid or liquid-liquid reactions (Sotowa et al., 2007; Asano et al., 2016). Many kinds of micro-reactors are utilized in various applications. A micro channel reactor was used for the synthesis of monodispersed zirconium dioxide particles in a continuous flow process. Size distribution and morphology of zirconium dioxide particles were controlled by two types of coaxial tubular reactors.

Water and 1-butanol were prepared for applying interdiffusion in the liquid-liquid interface following their mutual solubility curves. Zirconium oxychloride was used as a starting ingredient. Ammonia solution and sorbitan monooleate were mixed into 1-butanol for neutralization with zirconium oxychloride. The flow rates of water and 1-butanol in the tube reactor with a single step were adjusted by syringe pumps connected to the microchannel. The crystal structure and morphology of zirconium dioxide particles were characterized by powder XRD and SEM, respectively. Most zirconium dioxide particles exhibited spherical shape with uniform size by the coaxial tubular reactor in the one-step process. In this synthesis, droplets in the tube reactor were stabilized by the addition of a surfactant. The cross section of the zirconium dioxide particle had a solid structure. Yamaguchi et al. (2004) revealed the flow dynamics and behavior of droplets in a micro-reactor through simulations. The simulation results demonstrated that the circulating flow occurred in the droplets. Suryo and Basaran (2006) also showed the circulating flow in droplets generated by the micro-reactor process. The particle size distribution of zirconium dioxide showed a monodispersed type. The mean particle diameter was nearly consistent with that of NaCl particles prepared by the coaxial tube reactor. This result indicated



Fig. 5 Schematic view of the experimental apparatus using in the twostep process.

that the particle size strongly related to the size of droplets in the reactor. In addition, the selected solvents affected the particle size regardless of the species of solute substances. The design of liquid surface tension is necessary for further control of the particle size in the microreactor. The neutralization reaction between ammonia and zirconium oxychloride occurred in the liquid-liquid interface after ammonia was diffused into aqueous solutions from the solvent phase in the tube reactor. Concerning the morphology, the convected flow occurred in the droplet, resulting in solid zirconia particles being formed without a hollow structure.

A coaxial tube reactor of a two-step process was applied to synthesize zirconium dioxide particles with porous structures. One part involved the formation of droplets, and the other part involved the neutralization reaction in the liquid-liquid interface of the droplets. Schematic diagram of the experimental apparatus with the coaxial tubular reactor is shown in Fig. 5. The two-step process connected to reactors X and Y. Zirconium oxychloride solution was provided from the A side, 1-butanol that included sorbitan monooleate was supplied from the B side, and 1-butanol including ammonia solution was supplied from the C side. Most zirconia particles synthesized by the micro tube reactor in both the one- and twostep processes displayed a uniform size and spherical shape. SEM images of the cross section of the zirconia particles in the two-step process revealed their porous and hollow structure, resulting in the formation of zirconium dioxide particles along the spherical interface.

4. Synthesis of organic-organic composite particles in a spray atomization process

We introduced the synthesis of organic-organic composite particles by using an ultrasonic spray nozzle in the

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interfacial crystallization. Glycine and starch were selected as model substances for the process (Gonda et al., 2015). Glycine and starch are commonly used as a model drug for pharmaceutical products and as an excipient, respectively. The composite particles prepared in the ultrasonic spray process were compared with those in a conventional anti-solvent crystallization process. The effect of using an ultrasonic spray nozzle on the polymorphism of glycine was also studied because the polymorphism had affected the particle properties, particularly its solubility.

The droplets from the aqueous glycine solution with starch particles were ejected from the ultrasonic spray nozzle into 1-butanol, which are slightly miscible with water. Ultrasonic atomization crystallization can be controlled by vibrating the spray nozzle with the ultrasonic oscillator. The contact or the operation time between 1-butanol and aqueous solution on the starch particles affects particle properties such as morphology and particle size distribution because the supersaturated ratio increases at the interface between aqueous solution and organic solvent (Kadota et al., 2007c).

In an analysis of SEM photographs, the composite particles produced with 1-butanol were spherical as shown in Fig. 6(a) and consisted of a starch core and glycine shell. Fig. 6(b) is a SEM photograph of a cross section of the composite particles. The cross section of the particles confirmed the appearance of coating particles or the coreshell structures of starch particles covered with fine glycine crystals. By contrast, composite particles of starch and glycine crystals produced by anti-solvent crystallization showed non-spherical particles with a wide particle size distribution. Moreover, many needle-like glycine crystals had already precipitated. From the comparison of results between ultrasonic atomizing crystallization and the anti-solvent method, we demonstrated that the production of the core-shell structure in the precipitation space was limited during liquid-liquid interfacial crystallization, as shown in Fig. 7. In addition, ultrasonic irradiation particularly affected the mean crystal size and size distribution of coating crystals. Consequently, the coating efficiency of fine crystals on starch would be affected.

Many studies on the effect of ultrasonic irradiation on crystal size have been studied (Kurotani et al., 2009; Kurotani and Hirasawa, 2010; Guo et al., 2005; Hatkar and Gogate, 2012; Stelzer et al., 2013). Kurotani et al. (2009) investigated the relation between the ultrasonic irradiation and the generation of the primary nucleation of amino acids in supersaturated solutions. They succeeded in obtaining the demanded crystal size of products by optimally adjusting the conditions of ultrasonic irradiation and supersaturation. Furthermore, Yoshizawa (2004) classified microparticles into three structures from morphological control.

We reported the effect of operation time on the particle morphology by liquid-liquid interfacial crystallization (Kadota et al., 2007b), and succeeded in controlling the crystal growth rate and crystal shape by changing the operation time. The effect of operation time on the particle morphology during ultrasonic irradiation was examined under a constant glycine solution. The coating thickness of starch particles was calculated from the size difference between coated and bare particles. The shell thickness was independent of the operation time after several minutes. This was because nucleation was promoted by the effect of ultrasonic irradiation for a short time (Miyasaka et al., 2006). Ultrasonic irradiation enabled the fine crystals to enhance crystal generation in the initial stage of nucleation.

XRD patterns of the composite particles by the change in the glycine solution concentration were measured. Both α - and β -glycine crystals were coexistent on starch particles at lower glycine solution concentrations. However, only β -glycine crystals were covered on the starch particles at higher glycine solution concentrations. This phenomenon can be explained by the Ostwald step rule (Kitamura 1989; 2004). Initially, we investigated the variation of glycine polymorphism without starch particles because of clarifying the polymorphic transformation of glycine crystals on starch particles. XRD patterns of



Fig. 6 SEM photographs of composite particles of starch with glycine prepared by ultrasonic spray nozzle: (a) composite particles; (b) cross section of composite particle framed by dot-line is the starch of the core particle. Reprinted with permission from Ref. (Gonda et al., 2015). Copyright: (2015) Elsevier.



Fig. 7 Schematic of the composite particle. Guest particles on the core particles precipitated through a liquid-liquid interfacial crystallization.

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glycine particles revealed that α - and β -glycine were precipitated and coexistent in all concentrations of glycine solution without starch core-particles. This indicates that the hydroxy groups on the surface of starch particles act as a template for β -glycine. The secondary nucleation of β-glycine crystals may preferentially occur by adhesion of glycine molecules, as β -glycine crystals are attracted by hydrogen bonds aligned on the starch particles. The effects of the template generated by additive addition on crystalline polymorphism were previously revealed by Kitamura (2004). The interaction between the core and guest molecules is a major factor in creating the composite particles. Both α - and β -glycine crystals were precipitated without core particles. β-Glycine crystals transform to α -glycine crystals for the solution-mediated phase without starch particles. With starch core particles, the hydroxy groups on the starch particle surfaces could function as a template for β -glycine and stabilize β glycine structures. Furthermore, forming the solutionmediated phase on the starch particles may be difficult because the β -glycine crystals on the core particles of starch are thick.

5. Synthesis of organic-inorganic composite particles by using a tube reactor

We demonstrated in synthesis of the inorganic-organic composite particles of NaCl and Indomethacin (IMC) by using a coaxial tube reactor based on liquid-liquid interfacial crystallization (Hattori et al., 2015).

In the process, inorganic-organic composite particles precipitated at the liquid-liquid interface by individually feeding two different solute materials from 2-butanone and the aqueous solutions. The ability of composites strongly depends on the difference in precipitation rate between two solutes and is directly related to controlling the composite particle structures. NaCl has a relatively higher precipitation rate. Therefore, we selected IMC with a low precipitation rate into 2-butanone. IMC exhibiting analgesic activity is a non-steroidal anti-inflammatory. Some research concerning IMC was previously investigated to improve its poor solubility in water (Zhang et al., 2011; Kigasawa et al., 1981).

The experimental apparatus for the coaxial tube reactor used in this process is shown in **Fig. 8**. The flow rate in the tube reactor was adjusted using a micro-syringe pump system. Water was run through the inner tube, and the organic phase flowed through the outer tube. As a preliminary experiment, the flow rate was varied to observe and comprehend flow patterns in the tube reactor. A previous study showed that when flow patterns form in a micro-reactor, the critical factors are the inertial force and the interfacial tension (Zhao et al., 2006). We used the Weber number for expressing flow patterns, and precipitated particles were observed by SEM. The quantitative amount of IMC was measured by Ultraviolet-visible (UV) spectroscopy.

Three types of flows (parallel, plug, and dispersed) were observed by flow visualization in the tube reactor. Dispersed flow consisted of water droplets suspended in 2-butanone that formed a spherical shape. The interfacial tension of water and the inertial force of 2-butanone were dominant in the dispersed flow with a high flow rate of 2-butanone. We produced NaCl crystals using the coaxial tube reactor by parallel, plug, and dispersed flow formed from the aqueous solution and 2-butanone. Precipitated NaCl crystals were cubic with a hollow dispersed flow. Channel blockages occurred in the parallel flow and were a major problem for continuous operations. The parallel flow was not appropriate for liquid-liquid interfacial crystalization using the tube rector. The other two flows did not show any blockages.

We calculated the nucleation and crystal growth rates of precipitated crystals by the mass balance and number of crystals to clarify the behavior of crystal nucleation and growth in the tube reactor. The calculation results show that the crystal nucleation rate dramatically decreased at a residence time in the tube reactor. The crystallization growth rate moderately increased with increasing residence time and gradually decreased thereafter. These results correspond to the change in the degree of supersaturation. When NaCl solution reached a high supersaturated ratio or an unstable state, several nuclei of NaCl were generated in a short period of time. After nuclei were generated, NaCl concentration rapidly decreased and the solution reached a meta-stable state for a limited number of NaCl solutes in the droplet. This suggests that this crystallizer helped to control the particle shape with a narrow distribution by the residence time.

Crystallization at the interface of the NaCl aqueous and



Fig. 8 Schematic of the experimental apparatus in the continuous operation. Reprinted with permission from Ref. (Hattori et al., 2015). Copyright: (2015) Elsevier.



IMC organic solutions was conducted in the tube reactor. Then, it had to facilitate nucleation for the crystals of IMC because the precipitation rate of IMC was very slow. Some researchers have reported that ultrasonic irradiation is effective at enhancing nucleation (Kudo and Takiyama, 2012; Guo et al., 2005; Kurotani et al., 2009; Miyasaka et al., 2006). The precipitation of IMC by ultrasonic irradiation to the liquid-liquid interface was examined. From the results of the crystallization of NaCl and IMC in separate operations, we expected that precipitation of composite particles consisting of NaCl and IMC would occur. The precipitation of NaCl/IMC composite particles in the dispersed flow was examined and composite particles were obtained. The obtained particles had a spherical shape and were aggregated particles consisting of many NaCl primary crystals. SEM photos revealed that IMC precipitated only on the surface of the aggregated NaCl particles. The aggregated composite particles of NaCl/IMC had a near mono-dispersion size distribution. We can propose that the precipitation mechanism of the composite particles in the dispersed flow can be expressed as shown in Fig. 9. The precipitation of IMC dominantly occurred on the surface of NaCl from the kinetic crystallization parameters (Mersmann, 1998; Kawashima et al., 2002).

NaCl crystals were first precipitated at the interface of 2-butanone and the aqueous solutions and agglomerated during the flow of the droplet. Second, the droplet transferred to the area with ultrasonic irradiation, and IMC crystals were precipitated on the aggregated NaCl particle surface under ultrasonic irradiation. Then, NaCl/IMC composite particles were formed. This process in a dispersed flow can realize the fabrication of composite particles in one path continuously.

6. Preparation of a Pd-supporting TiO₂ catalyst using the inside surface

Capsulation is a basic technique for adding functions to particles (Kameta, 2014; Mori et al., 2019a). We introduced the synthesis of hollow titanium dioxide particles by using the inkjet process and showed the functionalization by charging Pd particles on the inside surface (Tanaka T. et al., 2016). We prepared the titania particles



Fig. 9 Precipitation mechanism of composite particle with ultrasonic irradiation in a dispersed flow. Reprinted with permission from Ref. (Hattori et al., 2015). Copyright: (2015) Elsevier.

during the liquid-liquid interfacial sol-gel process with an inkjet nozzle and made an evaluation of the photocatalytic activity of the composite titania particles (Kadota et al., 2014).

Titanium tetraisopropoxide (TTIP) and hexane were used as a starting precursor of preparing titania particles in the sol-gel process and as an organic solvent to create the liquid-liquid interface with water, respectively. Acetonitrile was selected to vary the reaction rate of water because of being miscible with water but unfavorable for hexane. The aqueous solution was fed from the inkjet nozzle into the TTIP solution by controlling 1000 drops per second for 1 hour. The precipitated titania particles were a porous and hollow structure. For comparison of particle properties by inkjet nozzle, titania particles were also synthesized by using a pipette.

A photodeposition process of palladium on the porous hollow titania particles was performed (Ismail et al., 2013; Maicu et al., 2011; Camposeco et al., 2014). Porous hollow titania particles were added to an aqueous solution that included ethanol, and ultrasound was irradiated toward the suspension. Then, a palladium chloride solution was added to the suspension. The palladium chloride solution was charged into the particles under a low pressure to support palladium on the inner portion of the porous hollow titania particles. The palladium precipitated in the porous hollow titania particles. The suspension was irradiated with a black light in the dark, resulting in that palladium was supported on the titania hollow particles in a reduction of the number of palladium ions by the photocatalytic effect of titania. Prior to the examination of its photocatalytic effect, we examined the titania particle properties such as inner structure and pore characteristics. The element mapping state of Pd on the titania particles was evaluated by using an energy dispersive X-ray (EDX) analyzer. It was connected to a field emission type scanning electron microscope (FE-SEM). The photocatalytic performance between Pd supported on titania particles and non-supported titania particles was compared by evaluating the photocatalytic degradation of methylene blue solution (Nuno et al., 2015). Here, crystal structures of titania had three distinct polymorphisms (anatase, rutile, and brookite) and the photocatalytic activities were very sensitive to the crystal structures (Wen et al., 2015; Koelsch et al., 2004). The titania structure was controlled through the calcination of the particles.

The morphology and appearance of the titania particles prepared with and without the inkjet process were observed. Most titania particles prepared by the normal batch process without inkjet nozzle were irregular-shaped particles, whereas most of those prepared with the inkjet process displayed spherical particles with uniform size distribution. According to the observation of cross section, titania particles had porous hollow structures,

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indicating that the crystal growth of titania particles occurred along the spherical interface. As described in **section 4**, the crystal growth of particles progressed along the interfacial droplet. This growth behavior of particles indicates the specific phenomena in liquid-liquid interfacial crystallization. Additionally, the particle size distribution of the titania prepared by the inkjet process was strictly narrower than that of the titania prepared by the batch process. The typical pore size distribution of titania particles prepared by the inkjet process was exhibited, whereas there were no peaks of the pore size distribution of titania particles prepared by the batch process.

The use of Pd supported on the surface of the porous hollow titania particles inside was expected to enhance the photocatalytic performance of titania. We compared the photocatalytic performances between the titania particles prepared by the non-inkjet and inkjet processes. Irrespective of preparing methods, the concentration of methylene blue gently decreased with increasing the irradiation time of ultraviolet-C (UV-C). In comparison of degradation rate, the titania particles synthesized by the inkjet process showed a slightly effective photocatalytic degradation than those by the non-inkjet process. This is because the photocatalytic activity of the titania particles by the inkjet process was advanced by increasing the specific surface area during photocatalytic degradation. This result could be supported by the specific surface area evaluated by BET.

Palladium element examination using EDX indicated Pd particles adhered on the inner surface of the hollow titania particles. The insertion of palladium onto the inner surfaces required the transmission of UV light to make a photocatalytic reduction of palladium chloride salt inside the hollow particle. Although the transmittances of titania generally show low values at wavelengths in the region of ultraviolet light (Chen X. et al., 2011), UV light can be transmitted through the titania shells with reduction of the electronic excitations. A previous study found that transmittance through ultrathin films of anatase-type titania rapidly increased for ultraviolet light wavelengths of more than 350 nm (Rezazadeh et al., 2015). In this study, titania particles by the inkjet process hardly showed any excited electrons because of having amorphous structures (Piccinini et al., 2013). UV light with 365-nm wavelength was irradiated on the porous titania particles relatively for the long time, and UV light was consequently transmitted through the shell to the inner surface of the porous hollow titania particles with the reduction in electronic excitation. Then, the palladium could be supported on the inner surface of the titania particles.

Fig. 10 shows the degradation behavior of methylene blue with the Pd-supporting titania particles. The concentration of methylene blue in the Pd-supporting titania particles gently decreased with increasing of UVC irradiation time, whereas the concentration of methylene blue in the non-supported particles was an almost constant. The Pd-supporting titania particles showed a faster rate of photocatalytic degradation than the non-supported titania particles. The results indicated that the photocatalytic activity was improved by support of palladium to the titania particles, whereas the non-supported particles did not exhibit any photocatalytic activity. Camposeco et al. (2014) previously investigated that the photocatalytic activity of titania was enhanced by adding support palladium particles on titania with a photodeposition method. The palladium was supported onto the titania particles with an amorphous structure which electrons are hardly excited under solar irradiation. Fig. 11 shows that the porous hollow titania particles supported by palladium on the outer and inner surfaces exhibited a faster rate of photocatalytic degradation than that for the palladium-supported titania particles prepared by the non-inkjet process. The result was attributed to the increase of the specific surface area. Importantly, the synthesis of the titania particles with a high specific surface area was needed even when the palladium was supported onto the titania particles. We have succeeded in synthesizing the Pd-supported titania catalyst using the sol-gel process with the inkjet nozzle, resulting in the improvement of the photocatalytic activity of titania particles supported by palladium on the inner and outer surface of titania hollow particles.

7. Release properties of vitamins from TiO₂ porous hollow particles

Another example of functionalization by charging vitamins into the hollow particles was profiled (Tominaga et al., 2018; 2019).

Titania particles with a porous hollow structure were prepared using the interfacial sol-gel processing preparation (Kadota et al. 2014) as described in the previous section. L-ascorbic acid encapsulated inside the porous hollow particles of titania by using two methods. The first



Fig. 10 Degradation behavior of methylene blue with photocatalytic titania particles obtained by different processes. Reprinted with permission from Ref. (Tanaka et al., 2016). Copyright: (2016) Elsevier.





Fig. 11 Change in methylene blue concentration of three types of titania particles prepared under different conditions. Reprinted with permission from Ref. (Tanaka et al., 2016). Copyright: (2016) Elsevier.

method was immersion preparation. Titania particles were added to the L-ascorbic acid aqueous solution. The supernatant solution was taken and dried in a desiccator until completely dry. The second method was the preparation by feed of a discharged solution containing L-ascorbic acid from the inkjet nozzle.

In vitro release study of L-ascorbic acid from the titania particles was conducted by using a dialysis bag method (Wang et al., 2008; Hanson 1982; Toomari and Namazi, 2016; Lasoń et al., 2016; Huang et al., 2017; Stebbins et al., 2017; Wei et al., 2010; Tanabe et al., 1988) in phosphate buffer saline as release media. A photostability test was conducted on the sample to investigate whether the effect of inhibiting degradation of L-ascorbic acid could be obtained by encapsulating L-ascorbic acid into the titania hollow particles. After irradiating UV, we conducted the same release test using the same amount of L-ascorbic acid as the encapsulated amount.

XRD analysis was performed on the obtained samples to confirm the crystal structural change by calcination treatments. From the XRD patterns, the samples without calcination were in an amorphous state, and those with calcination at 900 °C for 6 h were transferred to a rutile structure. The shape of titania particles was maintained in a uniform spherical shape even after the calcination treatment and encapsulation operations.

The cross sections of the samples and element mapping of the inner surface were evaluated using SEM and EDX, respectively. According to EDX evaluation, the samples derived from the encapsulating operation of L-ascorbic acid were detected. The results of element mapping revealed that L-ascorbic acid adhered to the inner wall surface of titania particles when prepared by this process.

The release profile of L-ascorbic acid from the titania particles was evaluated by using the UV-vis spectrophotometry. A peak of UV detection was observed within the absorption wavelength region from 244 nm to 265 nm (Liao et al., 2001). From the UV data, we found that L-ascorbic acid can be encapsulated using the immersion method. However, no peaks were observed for some sam-



Fig. 12 Time evolution of L-ascorbic acid concentration released from a sample (L-Asc) and bare specimen after UV irradiation for 12 h. Reprinted with permission from Ref. (Tominaga et al., 2018). Copyright: (2018) Elsevier.

ples in the absorption wavelength region of L-ascorbic acid. This causes the oxidation of L-ascorbic acid and the production of dehydroascorbic acid during the preparation of titania particles. The comparison of photostability results between pure L-ascorbic acid and encapsulated samples are shown in **Fig. 12**. The release rate of L-ascorbic acid reached approximately 94 % within 4 h and maintained a release rate of 90 % or more for a long time. However, pure L-ascorbic acid was completely released in 2 h. Accordingly, the release rate at that time was approximately 77 %. Therefore, it is considered that the remaining ~23 % was degraded by UV spectroscopy. Based on these circumstances, the degradation of L-ascorbic acid could be inhibited by encapsulation in the titania porous hollow particles.

8. Conclusion

Particle modification for functionalization and improved powder handling is a critical technique in powder technology. It can be realized by the sophisticated construction of composite structures in a wide range from nano- to micron-scale. In this study, we introduced the fabrication of composite particles with liquid-liquid interfaces and heterogeneous nucleation. The control of material transfer at liquid-liquid, liquid-solid, and solid-solid was a major factor in the production of complicated composite structures.

Acknowledgments

The authors express their gratitude to Professors Jusuke Hidaka, Yoshinobu Fukumori, Hideki Ichikawa, and Yuichi Tozuka as well as to Drs. Atusuko Shimosaka and Mikio Yoshida. All works were produced from major contributions by members of the Powder Technology



Laboratory at Doshisha University. Some works were partially supported by a grant from the Japan Society for the Promotion of Science KAKENHI (No. 16K06837) (Tokyo, Japan).

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Consideration of Metal Organic Frameworks for Respiratory Delivery[†]

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Abstract

Metal organic frameworks (MOFs) have garnered increased attention over the past 20 years. Due to their porosity, high surface area, and nearly limitless customization and tunability MOFs have been designed for applications ranging from gas storage and separation to catalysis to sensing to biomedical engineering. Within the latter category, MOFs offer an appealing function for drug delivery as they can be loaded with multiple therapeutic moieties tailored to target specific disorders with triggered and controlled release characteristics. However, there is an unmet need to assess their viability for pulmonary treatment via inhalation. Targeting pulmonary disorders including infectious diseases by delivering medication directly to the lungs attacks the primary site of infection rather than relying on systemic distribution. The inherent advantage of this strategy is maximizing local lung concentrations of the drug. An introduction to inhaled therapies is provided here as a preamble to a brief summary of the current development state of MOF drug delivery systems. This review is intended to highlight the relative disparity between research toward MOFs as pulmonary drug delivery vehicles compared to other delivery platforms. Prospective biomedical applications for inhalable MOFs are also discussed.

Keywords: metal organic frameworks, aerosol, coordination polymer, pulmonary delivery, dry powders

1. Introduction

Inhalation therapies continue to be important treatments for several pulmonary diseases including asthma, cystic fibrosis (CF), and chronic obstructive pulmonary disorder (COPD). Aerosol delivery can achieve a high local drug concentration in the lungs while minimizing systemic exposure, thus potentially resulting toxicity and patient adherence, generating promise as a therapeutic strategy for other pulmonary diseases and infections such as tuberculosis (TB). Metal organic frameworks (MOFs) are emerging drug delivery tools. MOFs offer, in addition to drug delivery, the inclusion of metals, presenting multiple therapeutic moieties tailored to target specific disorders with triggered and controlled release characteristics.

Metals have a long history of being utilized to treat various ailments. Cu has been used for treating pulmonary disorders, sanitizing water, and treating wounds (Borkow G. and Gabbay J., 2005; Grass G. et al., 2011; Ladomersky E.

[†] Received 27 May 2020; Accepted 1 July 2020 J-STAGE Advance published online 21 August 2020

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Add: 3040 East Cornwallis Road, Research Triangle Park, NC, 27709, USA E-mail: istewart@rti.org TEL: +1-919-541-5933 and Petris M.J., 2015). Eye ailments were treated with Zn compounds (Giachi G. et al., 2013). The Chinese had used gold to manage many disorders (Huaizhi Z. and Yuantao N., 2001). However, it was not until the 20th century that metals began to be better understood and utilized by the medical community.

As medicine has progressed into modern times and the essential biological processes associated with metals are known, the applications taking advantage of unique traits of metal (particularly transition metal) complexes as diagnostic, treatment, and preventative medicinal components have opened up. Since the relatively recent discovery of the anticancer Pt-based complex cisplatin in the mid-20th century (Lippert B., 1999; Rosenberg B. et al., 1969), the use of metals in medicine is largely centered on anticancer activity (Franz K.J. and Metzler-Nolte N., 2019; Ndagi U. et al., 2017), though there are other promising applications. Ag, Co, and Cu have antibacterial and antiviral uses (Borkow G. and Gabbay J., 2005; Chang E.L. et al., 2010; Clement J.L. and Jarrett P.S., 1994; Zhao G. and Stevens S.E., Jr., 1998), Ti and Ti-alloys are used for prosthetics and implants (Zhao L. et al., 2009), and Cu, Rh, Ru, and Zn have been explored for anti-malarial efficacy (Navarro M. et al., 2005; 2010; Sánchez-Delgado R.A. et al., 1996). The nano-biotechnology research field has blossomed in recent decades: silver nanoparticles (Ag NPs) have




become popular as bactericidal (Baker C. et al., 2005; Martínez-Castañón G.-A. et al., 2008) and anticancer agents (Foldbjerg R. et al., 2011; Ong C. et al., 2013) while gold nanoparticles (Au NPs) have shown promise in a wide variety of applications from imaging to drug delivery (Giljohann D.A. et al., 2010; Murphy C.J. et al., 2008). There are many comprehensive reviews detailing the use of metals in medicine (Dabrowiak J.C., 2017; Guo Z. and Sadler P.J., 1999; Lemire J.A. et al., 2013; Medici S. et al., 2015) and the inclusion of metals in biomedical research is expanding from its arguable origins in the 1960s (Franz K.J. and Metzler-Nolte N., 2019).

An intriguing 21st century approach to implementing metals in medicine is the use of metal organic frameworks (MOFs). The extensive interest in MOFs over the past two decades has garnered interest from a variety of disciplines including the medical community. There is an immense amount of customization available to a researcher when considering MOFs as a drug delivery platform: elevated porosity for drug encapsulation, unique drug and metal combinations, and controlled release via tuning linkages within the frameworks (i.e. cleavage of coordination bond in acidic media), to name a few. Thus, it is surprising that, compared to oral and injectable routes of administration, there is a lack of consideration of MOFs for aerosol delivery of therapeutics. This may, however, correlate to a similar lack of research in the biological fate of inhaled metals.

While pulmonary administration of drugs is not suitable for every treatment approach, there are advantages in targeting the lungs. The intent of this focused review is to first provide a cursory introduction to inhalation technology for drug delivery followed by a brief MOF background and review of current MOF applications in the biomedical field. The sparse activity with respect to MOFs for aerosolized delivery to the lungs will be apparent and should motivate future research in this area.

2. Aerosols for pulmonary therapy

In ~1500 B.C., the first use of inhaled drugs was recorded by the Egyptians. Individuals struggling to breathe were instructed to inhale vapours from hot black henbane (*Hyoscyamus* niger) (Breasted J.H., 1930). The Greeks also used Cu to treat pulmonary diseases (400 B.C.) (Borkow G. and Gabbay J., 2005). While inhaled therapies continued to evolve over the centuries, a breakthrough came in the 1950s with the invention of a portable metered dose inhaler (MDI) that reliably delivered medication to the lungs and ushered in modern pulmonary delivery (Stein S.W. and Thiel C.G., 2017). Inhaled therapies have progressed over recent decades and are now predominantly used to deliver therapies to the lungs to treat chronic ailments such as asthma (Alangari A.A., 2014), CF (Agent P. and Parrott H., 2015), and COPD (Patton J.S. and Byron P.R., 2007; Sims M.W., 2011). Research into inhaled drugs for other applications including antivirals (Jefferson T. et al., 2006; Zhou Q. et al., 2015), anticancer (Lee W.-H. et al., 2015; Zarogoulidis P. et al., 2012), gene therapy (Laube B.L., 2015; Davies L.A. et al., 2014), peptide and protein delivery (Okamoto H. et al., 2002), and antibacterials (Banaschewski B. and Hofmann T., 2019; Muttil P. et al., 2009) is ongoing. This is especially apparent in the latter area as emergence of drug resistant bacterial strains necessitates novel treatment regimens (Van Duin D. and Paterson D.L., 2016; Ventola C.L., 2015). The general reasoning is straightforward: deliver the cure to the site of infection rather than ingesting or injecting the drug (**Fig. 1**).

Pulmonary administration of therapeutics allows for direct drug delivery to the target organ. First pass metabolism is avoided thus limiting possible systemic side effects at a presumably much lower dose compared to other routes of administration (Borghardt J.M. et al., 2018; Lipworth B.J., 1996; Stein S.W. and Thiel C.G., 2017). Conversely there has also been an interest in using inhalation to rapidly deliver drugs, such as insulin, systemically to other parts of the body (Henry R.R. et al., 2003; Hickey A.J. and Da Rocha S.R., 2019; Laube B.L., 2005; Mortensen N.P. and Hickey A.J., 2014). In either case, designing a molecule for inhalation is no trivial task. There are challenges associated with formulating an active pharmaceutical ingredient (API) into a respirable aerosol capable of producing the desired therapy. These include broad considerations such as excipient inclusion, pharmacokinetic/pharmacodynamics (PK/PD) of the inhaled formulation, drug product manufacturing, physicochemical properties, and stability which are recounted more thoroughly elsewhere (Hickey A.J. and Da Rocha S.R., 2019; Huaizhi Z. and Yuantao N., 2001; Maa Y.F. and Prestrelski S.J., 2000; Mortensen N.P. et al., 2014). Though arguably, the first hurdle to be overcome when considering pulmonary delivery is producing an aerodynamic diameter suitable for respiration and delivery



Fig. 1 Rationale for aerosol delivery to the lungs. This method presents higher lung concentrations of the drug compared to systemic delivery. Reprinted from Journal of Controlled Release, 240, A.J. Hickey, et al., Inhaled drug treatment for tuberculosis: Past progress and future prospects, Pages 127–134, Copyright (2016), with permission from Elsevier (Hickey A.J. et al., 2016a).



to the lower airways.

The lungs contain a vast network of internal branches that confer an enormous canvas for particle deposition. **Fig. 2** shows a diagram of adult lungs and corresponding cross-sectional areas of the 24 bifurcating airway generations, increasing from 2.54 cm² to 10^4 cm². However, it is generally accepted that only particles with an aerodynamic diameter of roughly 1–5 µm will be respirable. The aerodynamic diameter of a particle, which equates the particle to a sphere of unit density with the same settling velocity regardless of its actual shape and density, is defined, in simplified form from Stokes' law, as

$$d_{\rm ae} = d_{\rm v} \sqrt{\frac{\rho_{\rm p}}{\chi}} \tag{1}$$

where d_{ae} is the aerodynamic diameter, d_{v} is the equivalent volume diameter equal to the non-spherical volume diameter of the particles in question (can be determined experimentally (DeCarlo P.F. et al., 2004)), ρ_{p} is the density of the particles and χ is the dynamic shape factor. Full derivations and considerations can be found in the literature (Crowder T.M. et al., 2002; DeCarlo P.F. et al., 2004; Hickey A.J. and Edwards D.A., 2018). One generally cannot rely on the geometric mean size of particles (found via optical techniques) and their bulk/tapped density to predict aerodynamic diameter and size distributions without detailed knowledge of the particle's density and considerations for any internal cavities and shape factors. Indeed, particle diameter and density do not need to both be explicitly specified (Edwards D.A. et al., 1997; Hickey A.J. and Edwards D.A., 2018). Rather, an experimentally determined descriptor of an aerosol's aerodynamic particle size distributions (APSD) can be measured via inertial impaction. This mass based characterization will generate an APSD from which mass median aerodynamic diameter (MMAD or the median particle size at which 50 % of the aerosol mass lies below and above calculated from a lognormal cumulative distribution), geometric standard deviation (GSD), and fine particle fraction (FPF) can be determined. These are several basic standard quantifiable attributes for aerosol drug characterization prior to in vivo experiments that give the researcher a detailed idea of particle behaviour under the influence of an airstream. The theory and practice of inertial impaction can be found in the literature (Marple V.A. et al., 2003; Mitchell J.P. and Nagel M.W., 2003). The United States Pharmacopeia (USP), among other compendiums such as European Pharmacopoeia (Ph. Eur.), contain several useful chapters detailing proper characterization of pharmaceutical aerosols to better anticipate performance prior to in vivo studies (see for example chapters <601> and <1601> in the USP). Finally, research regarding predicting in vitro – in vivo correlations and airway modelling is also available (Byron P.R. et al., 2010; Hofmann W., 2011; Olsson B. et al., 2013).

Many factors contribute to inhaled aerosol deposition including airway geometry, temperature and humidity, particle solubility and crystallinity, and the breathing patterns of the individual. However, there are three primary outcomes dictated by aerodynamic particle size which are summarized in **Fig. 3** (Finlay W.H., 2019; Labiris N.R. and Dolovich M.B., 2003). Particles with MMAD larger than ~5 µm typically a) impact the back of the throat and



Fig. 2 a) Breakdown of lung branching generations and b) corresponding surface area. Compiled figure: a) adapted with permission from (Kleinstreuer C. et al., 2008), Copyright 2008 by Annual Reviews; b) reprinted from xPharm: The Comprehensive Pharmacology Reference, Robert M. Lust, The Pulmonary System, Pages 1-6, Copyright (2007), with permission from Elsevier (Lust R.M., 2007).





Fig. 3 Summary of particle size and regional pulmonary deposition percentage. The curve on the right gives an estimation of particle size vs. deposition percentage corresponding to the alveolar region (solid black line), airways (dashed line), and mouth and throat (solid gray line). This figure is from Loco-regional administration of nanomedicines for the treatment of lung cancer, Gabriela Garrastazu Pereira, Amanda Jane Lawson, et al., Drug Delivery (Garrastazu Pereira G. et al., 2016), 2016 Taylor and Francis, reprinted by permission of the publisher (Taylor & Francis Ltd, http://www. tandfonline.com). Originally adapted from Springer Nature, Nature Reviews Drug Discovery, Inhaling medicines: delivering drugs to the body through the lungs, Patton J.S. and Byron P.R., Copyright 2007 (permission granted for the present publication as well) (Patton J.S. and Byron P.R., 2007).

conducting airway above the 10th lung generation, b) are swallowed and never reach the lungs, or c) are removed in the upper airways via mucociliary clearing. Particles with MMAD \sim 1–5 µm deposit via impaction and gravitational sedimentation. Lastly, particles $< 1 \, \mu m$ generally arrive through diffusion or Brownian motion; there is a chance they are exhaled due to slow settling in the airways. There are other considerations involved in the inhalation of particles at lower primary size in the nano range (Muralidharan P. et al., 2015; Paranjpe M. and Müller-Goymann C.C., 2014; Yang W. et al., 2008; Zhang J. et al., 2011). Thus particles with mass median aerodynamic diameter between $1-5 \mu m$ have the best chance of reaching the lower airways. (Labiris N.R. and Dolovich M.B., 2003; Patton J.S. and Byron P.R., 2007). Additionally, alveolar macrophages have evolved to phagocytose particles in this size range (especially 2-3 µm). This spurs the design of aerosolized treatments for bacteria that reside in the macrophage, such as Mycobacterium tuberculosis (Mtb), the causative organism of TB (Biggs D.L. et al., 2003; Champion J.A. et al., 2008; Edwards D.A. et al., 1997; Gharse S. and Fiegel J., 2016; González-Juarrero M. and O'Sullivan M.P., 2011; Skoczen S.L. et al., 2011). Other factors to consider for particle size engineering are: controlled release strategies (Adi H. et al., 2010; Cook R.O. et al., 2005; Smyth H.D. and Hickey A.J., 2011), specific lung disease target and API (which could help determine necessary size and release kinetics of the aerosol particles) (Patton J.S. and Byron P.R., 2007), and inspiratory flow of the individual patient (Kleinstreuer C. et al., 2008; Labiris N.R. and Dolovich M.B., 2003).

It is worthwhile to note again that it is the aerodynamic diameter that is important for respirable particles. For example, it has been shown that engineered porous particles with seemingly irrespirable (> 5 μ m) mean geometric sizes were actually more suitable for respiration compared to solid particles at a similar size (Edwards D.A. et al., 1997). For more detailed pharmaceutical aerosol formulation troubleshooting, design considerations, and synthetic strategies, the reader is directed to the literature for reviews (Finlay W.H., 2019; Hickey A.J. and Da Rocha S.R., 2019; Pilcer G. and Amighi K., 2010; Vehring R., 2008).

Respirable therapeutic aerosols can be delivered from several devices (Hickey A.J. and Da Rocha S.R., 2019; Ibrahim M. et al., 2015; Sims M.W., 2011). Pressurized metered dose inhalers (pMDIs) and nebulizers deliver an API from solution or suspension. Both devices offer a classical view of an aerosol mist or cloud that delivers the drug directly from a liquid formulation that is atomized to form aerosol droplets. In both devices, careful consideration is needed when selecting surfactants, cosolvents, and, in the case of the pMDI, propellants that do not a) degrade the API or b) impact resulting APSD. Nebulizers offer a more predictable delivery simply depending on the tidal breathing pattern of the individual while the device is continuously generating and aerosol. On the other hand, pMDIs require more coordination between device and patient. Dry powder inhalers (DPI) contain a solid dosage form of the API and are gaining increasing attention for pulmonary delivery (De Boer A.H. et al., 2017; Frijlink H.W. and De Boer A.H., 2004; Timsina M.P. et al., 1994). While there is still some coordination necessary for delivering drug to the patient, the devices can be made cheaply, do not rely on a power supply or compressed air (as with nebulizers), and only depend on the inspiratory flow of the individual to disperse the powder. There are unique physical mechanisms to consider when dispersing dry powders in the micrometer size range including electrostatics, Van der Waals,



and capillary forces (Dunber C.A. et al., 1998; Hickey A.J., 2018). However, a solid dosage form offers better chemical stability compared to those in solution. And while pMDIs and nebulizers are more or less dependent on the device to dictate APSD, dry powders can be manufactured to well controlled particle sizes as via milling, physical mixing, supercritical fluid, or spray drying (Telko M.J. and Hickey A.J., 2005; Vehring R., 2008).

Given the rise in impactful research in the fields of medicinal metals and inhalational therapies from the mid-1900s, there is very little overlapping study. Fe-chelates delivered via nebulization have been suggested as an option for CF treatment (Musk Jr. D.J. and Hergenrother P.J., 2008). However, there are not many groups suggesting delivering metals therapeutically to the lungs. This may be due to a lack of specific research into metals as a pulmonary therapy as well as a concern over inflammation and toxicity (Bierkandt F.S. et al., 2018; Borm P.J.A. et al., 2006; Donaldson K. et al., 2002; Jamuna B.A. and Ravishankar R.V., 2014; Nel A. et al., 2006; 2013). However, there is evidence that a variety of transition metals can be advantageous in the treatment of pulmonary bacterial ailments. Ag, Cu, Fe, Pd, and Zn have been suggested for tuberculosis (TB) (Chao A. et al., 2019; Ellis T. et al., 2018; Palazzo F. et al., 2013; Pieters J., 2008; Poole K., 2017), Ag and Pt for lung cancer (with some evidence of dose-dependent toxicity) (Foldbjerg R. et al., 2011; Ndagi U. et al., 2017), and Ag, Cu, and Zn for viruses, including coronavirus (Bright K.R. et al., 2008; Raha S. et al., 2020; Ranford J.D. et al., 1993; Shittu M.O. and Afolami O.I., 2020; Skalny A.V. et al., 2020). Indeed, with the emergence of drug resistance, novel therapeutics and unique drug delivery strategies are needed to overcome said resistance to traditional regimens. Utilizing metals may be an intriguing option provided toxicity concerns are addressed (Allahverdiyev A.M. et al., 2011; Chen C.-W. et al., 2014; Ong Y.C. et al., 2019; Sloan D.J. et al., 2013; Turner R.J., 2017; Van Duin D. and Paterson D.L., 2016). MOFs and coordination polymers are an emerging class of materials that may be suitable as a drug delivery vehicle to the lungs.

3. Biomedical applications of MOFs

MOFs are highly crystalline and porous coordination polymers that are assembled by the formation of multiple coordination bonds between inorganic metal nodes (either metal ions or metal oxide clusters) and multidentate organic ligands. MOFs offer structural designability at the molecular level together with tunable porosity and chemical functionalization. Due to their tailored features, especially elevated surface area and hybrid organicinorganic compositions, MOFs have been studied for a myriad of applications such as gas storage and separations (Sumida K. et al., 2012), nonlinear optics (Yu J. et al., 2012), catalysis (Corma A. et al., 2010; He X. and Wang W.-N., 2019; Luz I. et al., 2010), sensing (Kreno L.E. et al., 2012), or molecular-based magnetisms (Coronado E. et al., 2013). During the last decade, MOFs have also been considered for medical applications ranging from precisely-controlled release of drugs to imaging (Chen W. and Wu C., 2018; Della Rocca J. et al., 2011; He C. et al., 2015a; McKinlay A.C. et al., 2010).

Nano and micro sized MOF particles are required to exploit certain biologically relevant mechanisms (Novio F. and Ruiz-Molina D., 2017). For instance, particle sizes ~500 nm influence the circulating time in the blood stream and facilitate their introduction into cells by endocytosis. Particles smaller than 250 nm are most suitable for crossing the vascular endothelium (Giménez-Marqués M. et al., 2016). Fortunately, MOFs of many size ranges can be easily prepared by conventional methods (i.e., solvothermal/ hydrothermal synthesis, microwave-assisted, sonochemical) (Stock N. and Biswas S., 2012) or alternative methodologies ranging from microemulsion and templating (Luz I. et al., 2017; 2019) to spray-drying (Carne-Sanchez A. et al., 2013) and continuous-flow techniques (Friščić T., 2011). MOFs also exhibit a high external surface-area-to-volume ratio which aids in colloidal stability, biocompatibility, recognition capabilities, and biodistribution (Oh M. and Mirkin C.A., 2005). Showcasing their potential for stability in biological pH, MOFs can be made to withstand pH as low as 1.2 (as in the gastrointestinal tract) (Ding M. et al., 2019; Rojas S. et al., 2018) and there have even been reports of manufacturing MOFs with local "buffer" environments that were appropriate for pH 1.5-12.5 (He H. et al., 2018).

The surface of MOF nano- and micro-metric crystals can be functionalized to address specific biological and medical needs via two attachment techniques: covalent (i.e. condensation, click chemistry, and conjugation reactions) or non-covalent (i.e. electrostatic interactions, dispersion forces, and hydrogen bonding) (Sapsford K.E. et al., 2013). On one hand, organic or inorganic nanomaterials have been considered to address the challenges related to the use of conventional treatments, diagnosis, monitoring, and control of biological systems (i.e., drug resistance, systemic toxicity, poor treatment efficacy, and safety) (Patra J.K. et al., 2018). But MOFs are hybrid organic-inorganic materials that offer potential advantages compared to these purely organic or inorganic carriers for biomedical applications. These advantages are: size control over nano and microscale and the ability to compose MOF superstructures of individual MOF sub-components; tailored structures (physicochemical properties including metal-ligand compositions, crystallinity, particle size, and morphology) allowing for the incorporation of multiple functionalities that can demonstrate multi-stimuli-responsive controlled



release (accounting for biological compatibility and stability in physiological environments); large surface areas and porosities to facilitate higher drug loading capacity; weak coordination bonds that ensure MOFs are biodegradable (Wu M.X. and Yang Y.W., 2017).

Biodegradability and stability of MOFs are arguably the most important concerns that need to be addressed prior to potential therapy. The decomposition of MOFs at a desired region is recommended to avoid endogenous accumulation. As illustrated by Fig. 4, three main approaches have been developed to incorporate drugs or biologically active components in MOFs and are classified by the type of interaction (bond strength) between them. They include 1) encapsulation of the drug within the MOF pore system (weak interaction) (Horcajada P. et al., 2008), 2) the drug is the organic linker in the MOF via coordination bond (medium interaction) (Rojas S. et al., 2017), and 3) the drug is bonded via post-synthetic modification to the MOF framework via covalent bond (strong interaction) (Taylor-Pashow K.M.L. et al., 2009). This variety of possibilities enables the pinpoint triggered release of therapy at the target by different biologically induced stimuli, such as pH, temperature, magnetic field, ionic species, pressure, or even light radiation. For bio-applications, the precise chemical stability of MOFs is also crucial to enable targeted drug release and avoid the excessive early decomposition and/or accumulation of the MOF individual chemical constituents. The most widely investigated approach is pH-responsive MOF carriers, especially for cancer therapy (Wu M.-X. and Yang Y.-W., 2017), because the acidic tumor microenvironment can disassemble the MOF scaffold via cleavage of the coordination bonds (which are sensitive to external acidic pH), thus releasing the hybrid components. Therapies targeting endo-lysosomal release of MOF cargo in macrophages may benefit from this strategy as well since the pH value in a macrophage lysosome is between 4-5 while the phagosome remains neutral (Chen T.-T. et al., 2018; Russell D.G. et al., 2009).

The first examples considering MOFs as potential drug delivery systems via drug encapsulation (Fig. 4a) within

the MOF pores were reported by Horcajada et al. (Horcajada P. et al., 2006; 2008). These MOFs (intended for general administration) were built from low-toxic iron and multi-carboxylate ligands (MIL-100, MIL-101, and MIL-53) and were suggested for the delivery of the drug ibuprofen, exhibiting high drug-storage capacity and a complete drug-controlled release under physiological conditions. The large "breathing" effect of the flexible framework of MIL-53 was demonstrated to be an interesting feature for potential applications in drug delivery. The same group also reported the first biodegradable therapeutic MOF with pellagra-curative, vasodilating, and antilipemic properties (BioMIL-1) (Horcajada P. et al., 2008). This MOF was built up from a non-toxic Fe species and a therapeutically active linker nicotinic acid (Fig. 4b). The release of the drug, a constituent of the framework, was achieved via degradation of the hybrid crystalline phase simulated physiological conditions (Miller S.R. et al., 2010).

The ability to combine metals and organic molecules in a single element in the MOF hybrid structure (Fig. 4b), opens up the possibility of pursuing synergetic effects between metal and drug upon delivery via framework degradation (Rojas S. et al., 2017). For example, in the work by Tamames-Tabor et al., azelaic acid was combined as a linker with an endogenous transition metal cation, in this case Zn²⁺ (Tamames-Tabar C. et al., 2015). The authors asserted that since both linker and metal exhibited interesting antibacterial and dermatological properties for the treatment of skin conditions, both components should be combined into a biocompatible and bioactive MOF (BioMIL-5), which they found to be stable in water and in bacterial culture medium. The progressive slow release of both active constituents allowed growth suppression of Staphylococcus epidermidis over 7 days, suggesting that this MOF can be a good candidate for future bio applications in skin care and cosmetics.

Taylor-Pashow and coworkers demonstrated that both an optical contrast agent (BODIPY dye) and an anticancer prodrug (ethoxysuccinato-cisplatin) could be covalently bonded to the free amine functionalization of (Fe)MIL-



Fig. 4 Strategies for drug inclusion within MOFs: **a**) encapsulation of the guest drug within the MOF host pore system (*weak interaction*); **b**) the guest drug acts as organic linker within the MOF host bonded by coordination bonds (*medium interaction*); **c**) the guest drug is bonded via post-synthetic modification to the MOF host framework via covalent bond (*strong interaction*).



 $101(\text{NH}_2)$ nanocrystals via post-synthetic modifications (see **Fig. 4C**). These constituents were then released upon disassembly of the MOF framework under acidic conditions present in a tumor environment. In addition, the rate of cargo release was further controlled by coating the MOF sub-constituents with an inert silica shell. The potential utility of this multicomponent MOF drug system for optical imaging and anticancer therapy was demonstrated in vitro using HT-29 human colon adenocarcinoma cells (Taylor-Pashow K.M.L. et al., 2009).

Research concerning the toxicity of MOFs and overall regimen implications (Sajid M., 2016) continues to be conducted. It is thought that MOF constituents will progressively break down in the body; however, since the field maturing, there is still work that needs to be done to elucidate MOF toxicity and pharmacokinetics further (regardless of administration route), both at the superstructure level and for the fate of each sub-constituent (He C. et al., 2015b; Horcajada P. et al., 2012; Novio F. and Ruiz-Molina D., 2017; Sun C.-Y. et al., 2013). On the other hand, the desirable triggered release and biocompatibility properties, along with their large surface areas and high porosities, have positioned MOFs as promising materials for drug delivery and other therapeutic applications (Beg S. et al., 2017; Giménez-Marqués M. et al., 2016; Horcajada P. et al., 2012; Liang Z. et al., 2018; Wu M.-X. and Yang Y.-W., 2017; Rojas S. et al., 2018). MOF lung delivery via a systemic route (Simon-Yarza T. et al., 2017) has been considered but the manufacture and delivery of MOFs as an aerosol has not until recently been explored.

4. Facile generation of MOF aerosols via spray drying

The wide applicability of MOFs has generated wide appeal across scientific research fields as summarized above. MOFs are especially gaining traction in the medical field for enhancing drug delivery via oral (Abuçafy M.P. et al., 2018; Chen Y. et al., 2018) and intravenous (Bian R. et al., 2015; Zhao H.-X. et al., 2016) routes. One area that has thus far remained largely unexplored is the use of MOFs as inhalation therapies for pulmonary disorders. This is despite the existence of a relatively facile manufacturing method commonly used to generate respirable microparticles: spray drying.

Spray drying is used as a controllable, continuous process to generate solid nano- and micro-particles from solution for various applications from food additives to fuel cells to ceramics to pharmaceuticals (Eldridge J.A. et al., 2014; Ramavath P. et al., 2014; Santana L.P. et al., 2008; Ziaee A. et al., 2017). Its main pharmaceutical application is manufacturing amorphous particles from an otherwise water insoluble API for use in solid dosage forms, i.e.

tablets. Among other things, this strategy increases drug product bioavailability (Baghel S. et al., 2016). As mentioned above, however, dry powders suitable for therapeutic inhalation delivery can also be produced with a spray dryer. Recently, spray drying has been demonstrated by Carne-Sanchez et al. (Carne-Sanchez A. et al., 2013; Garzón-Tovar L. et al., 2016) as a versatile continuous flow method to assemble nanoMOFs into micrometric hollow spherical superstructures (Fig. 5). This strategy conceptually mimics the standard emulsions used to confine the synthesis of MOF materials but does not require secondary immiscible solvents or surfactants, which can reduce production time and cost. In the work by Carne et al. in 2013, the generality of this continuous flow strategy was proven for a broad range of MOFs (i.e. ... HKUST-1, Cu-BDC, NOTT-100, MIL-88A, MIL-88B, MOF-74, UiO-66, and ZIF-8, among others). Members of this research group have also demonstrated the synthesis of UiO-66 in aqueous solution (Avci-Camur C. et al., 2018), addressing one of the challenges currently precluding the industrial exploitation of nanoMOFs: the lack of water-based, efficient methods for their synthesis. This unique MOF morphology obtained by spray drying (the arrangement of MOF nanocrystal sub-components into hollow spherical microparticulate superstructures) can seemingly address three attributes of aerosolized drugs: 1) generation of hollow, low density spherical particles suitable for respiration, 2) potential for MOF microparticle disassembly into MOF nanocrystals suitable for a wider range of endocytosis, and 3) controlled pH-triggered coordination bonds to be cleaved under acidic macrophage or tumor environment releasing the active drug(s). A review of MOF spray drying can be found in the literature (Troyano J. et al., 2020).

The synthesis of MOFs via spray drying starts with atomization of a precursor solution into microdroplets using a two- or three-fluid nozzle (Fig. 5). This step is accomplished by simultaneously injecting the solution at and compressed air or nitrogen. Each precursor droplet contacts (and is suspended by) a gas stream heated to a certain temperature. The solvent then begins to evaporate causing the precursors to diffuse radially to the droplet surface (Fig. 5b). It is important to note that spray drying can be utilized under completely aqueous conditions and the inclusion of organic solvents is not necessary, but can aid in the formulation process (dissolving solutes, impacting precipitation rate of the solid particles, etc.). As the evaporating droplet shrinks, precursor concentrations at the droplet surface increase until supersaturation is reached at which point MOF nanocrystals begin forming and arranging into a well-packed shell at the drop surface. Spray drying is a mature technology that can be transferred from bench to pilot to manufacturing scale in many industries, including pharmaceutical (Dobry D.E. et al., 2009; Kemp I. et al., 2016; Poozesh S. and Bilgili E., 2019). Theoretical





Fig. 5 Spray drying synthesis of spherical hollow HKUST-1 superstructures. **a**, **b**) Schematic showing the spray-drying process used to synthesize HKUST-1 superstructures. **c**) Photograph of the spray-dryer. **d–f**) Representative FESEM images showing a general view of the spherical HKUST-1 superstructures. Scale bars: 5 mm (**d**), 500 nm (**e**, **f**), 200 nm (**f**, inset). Reprinted by permission from Springer Nature: *Nature Chemistry*, A spray-drying strategy for synthesis of nanoscale metal–organic frameworks and their assembly into hollow superstructures, Arnau Carné-Sánchez et al., Copyright 2013(Carne-Sanchez A. et al., 2013).

and experimental considerations for particle engineering via spray drying can be found elsewhere (Vehring R., 2008; Vehring R. et al., 2007).

The discovery that this robust technique could be used to manufacture hollow hybrid microparticles incorporating metal species, i.e. MOFs, had the potential to initiate more research toward their aerosol characterization specifically for pharmaceuticals. But there have been very few accounts suggesting the use of MOFs for pulmonary delivery and even less using this widely available and scalable manufacturing technique.

5. Aerosolized MOFs for pulmonary therapy: Pioneer works and future prospects

The specific potential for aerosol delivery of MOFs for pulmonary therapies has recently begun to appear in the literature. Hu et al. showed that budesonide (an anti-asthma drug) can be loaded into γ -cyclodextrin (CD) MOFs that exhibit acceptable respirable particle sizes (MMAD just under 5 µm), good cell viability and biocompatibility in A549 human lung alveolar cells, similar budesonide distribution and PK as the commercial control, and were well tolerated in rats when administered via insufflation (DP-4R Penn-Century insufflator) (Hu X. et al., 2019). However, this version of MOF does not contain transition metals. Iron based MOFs (MIL-88A(Fe) and MIL-100A(Fe)) were shown to be endocytosed by alveolar macrophages in vitro subsequently accumulating in acidic regions where airway-based pathogens, such as Mtb, are known to reside (Guo A. et al., 2019). Wyszogrodzka et al. (Wyszogrodzka G. et al., 2018) reported that Fe-MIL-101-NH₂, a widely studied biocompatible Fe-MOF carrier for drug delivery, can be an effective carrier for isoniazid (INH), a first-line anti-TB drug. This group demonstrated that MOF particles accumulate in the cell cytoplasm. They reported sustained drug release inside cells in contrast to fast dissolution of crystalline INH powder. Additionally, these MOFs had low cytotoxicity and can serve as MRI contrast agents; i.e. a theranostic system combining diagnostics and delivery. Their work was extended to theophylline, an anti-asthma and COPD drug, loaded into Fe-MIL-100 microparticles (via traditional MOF synthetic routes). As in the previous case, the drug was found to have sustained release in vitro and was nontoxic against human epithelial cells and murine macrophages after uptake. There were minor increases in reactive oxygen species which subsequently returned to baseline after 72 h. (Strzempek W. et al., 2019). These studies showcased promise for biocompatibility of MOFs for lung delivery, but aerosol characterization was lacking.

Even with the discovery that MOFs could be spray dried into hollow spheres in size ranges suitable for respiration in 2013 (**Fig. 5**), there are very few accounts utilizing this



proven aerosol generation technique as a possible drug product manufacturing mechanism. Anti-TB MOF delivery to the lungs would be a reasonable therapy target considering that MOFs and MOF composites have been suggested for use as antimicrobial applications previously (Shen M. et al., 2020; Wyszogrodzka G. et al., 2016). To reach this end, designing MOFs to efficiently deposit in the lungs via dry powder aerosol to locally attack TB can be realized by spray drying. To the best of our knowledge, there are only three reports that characterize aerosolized spray dried MOFs for potential pulmonary delivery - all motivated by anti-TB potential. This strategy is understandable as DPIs have shown promise as an alternative treatment for TB with benefits over standard oral and intravenous regimens such as lower systemic toxicity, local access to the lung granulomas containing Mtb, and avoiding painful injections. Activity in this research area is well documented (Braunstein M. et al., 2019; Dharmadhikari A.S. et al., 2013; Hickey A. et al., 2016a, b; Mehta P. et al., 2018). In a more recent work using the same MOF-based delivery system as above, Wyszogrodzka et al. produced MOFs where INH was encapsulated in Fe-MIL-101-NH₂. Afterwards, it was combined with poly(lactide-co-glycolide) and leucine via spray-drying leading to a microparticle composite (Fig. 6a) (Wyszogrodzka-Gaweł G. et al., 2019). This MOF exhibited good aerodynamic properties, controlled release of INH, uptake by macrophages in vitro, low cytotoxicity, and extended their theranostic application. Importantly this was the first reported use of MOFs as a dry powder for inhalation. Similarly, Fernandez-Paz et al. recently produced nanoparticle aerosols from (Fe) MIL-100 MOFs and various biocompatible carbohydrates (i.e. mannitol) via spray drying (Fernández-Paz C. et al., 2020). Notably, these MOF composite particles did not result in an inflammatory response when delivered to rats intratracheally and the release of the intact MOF constitu-



Fig. 6 SEM images and schemes for two recent MOF-based aerosol drug delivery systems prepared via spray drying: **a**) active drug encapsulated in inactive MOF and combined with excipient (drug@MOF/ excipients), SEM extracted from reference (Wyszogrodzka-Gaweł G. et al., 2019); **b**) active metal and active drug are combined to form a metal-drug bioMOF, SEM extracted from reference (Luz I. et al., 2020).

ent nanoMOFs embedded within the superstructure carrier was determined to be uniform along the lungs, reaching the bronchioles and alveoli. Therefore, state-of-the-art MOFs can be spray dried, subsequently filled with drugs, and utilized as aerosolized microparticles using soluble gluelike excipient components. However, despite the existence of the initial work of Carne-Sanchez et al. (Carne-Sanchez A. et al., 2013) demonstrating the continuous-flow preparation of several MOF compounds via spray drying, the utilization of "pure" MOF hollow spheres, i.e. where all metal and organic MOF components are considered active (bioMOFs), as aerosolized drug caariers was not considered in these first publications (Horcajada P. et al., 2012; Rojas S. et al., 2017).

Our group has experience with the preparation of inhalable anti-TB drugs via spay drying and the characterization of dry powder aerosols (Durham P.G. et al., 2016; Durham P.G. et al., 2015; Hickey A.J. et al., 2020; Mortensen N.P. et al., 2014; Pitner R.A. et al., 2019; Stewart I.E. et al., 2019). Given the rise in multi drug resistant (MDR) and extensively drug resistant (XDR) TB (Sloan D.J. et al., 2013; Van Duin D. and Paterson D.L., 2016), novel treatments are necessary including via a) inhalation, b) new drugs, and/or c) inclusion of metals. Therefore, we recently developed a spray drying procedure for preparing Cu-POA (pyrazinoic acid) hollow spherical microparticles (Fig. 6b). Our choice of Cu was based on evidence of its anti-TB potential (Festa R.A. et al., 2014; Neyrolles O. et al., 2015; Speer A. et al., 2013; Wolschendorf F. et al., 2011) as well as demonstrated in vitro synergy with other known anti-TB drugs (Manning T. et al., 2015a; 2015b; 2017; Speer A. et al., 2013). POA has been explored as an anti-TB candidate since it is considered a prodrug of pyrazinamide (PZA), a current first line TB drug experiencing drug resistance from Mtb (Durham P.G. et al., 2015; Via L.E. et al., 2015). Our results show that this potential anti-TB MOF can be spray dried in one step from a mostly aqueous solution, excipient-free, to produce a dry powder with APSD suitable for respiration (Luz I. et al., 2020). The use of pure metal-drug compounds linked by coordination bonds can enable the controlled local release of the organic drug and the metal "codrug" simultaneously, in this case Cu²⁺ and POA (Fig. 6b). This approach avoids the use of unnecessary inactive components, i.e. organic ligands or metal ions typically found in MOF carriers. These do not contribute to the therapeutic treatment and only provide structural roles, thus removing them can reduce possible toxic contributions. As well, since the polar functional groups of POA are coordinated to the Cu, moisture uptake can be avoided. However, that is not to say excipients are unnecessary during spray drying the formulation process in general; indeed excipients are a common formulation strategy to prevent moisture ingress, encapsulate particles, control release, or aid in dispersion (Bosquillon C. et al., 2001; Gordon M.S. et al., 2000;



Sarrate R. et al., 2015; Telko M.J. and Hickey A.J., 2005). Rather this is an alternative approach that designs inhalable MOFs or coordination polymers composed of solely therapeutic metal and organic components. In addition to mitigating the risk of possible toxic responses higher doses can be achieved (no excipient).

To facilitate this design, non-essential MOF properties for drug release applications can be obviated depending on the requirements of the delivery system, i.e. porosity or crystallinity. This unleashes a myriad of possibilities for designing multifunctional drugs containing the suitable metal-drug components linked by stimuli-responsive coordination bonds widening the range of pulmonary disease targets. These materials may be considered as MOFs, if porous and crystalline, or simply as coordination polymer particles (CPP) if amorphous or non-porous (Novio F. et al., 2013).

Although TB has been the primary potential target for most of the early work on spray dried therapeutic aerosolized MOFs, it is certainly not the only potential pulmonary target. As mentioned above, lung cancer, other chronic conditions such as asthma, and viruses might benefit from a unique respirable therapy that includes coordination metal-organic components. As well, using the lungs as a strategy to deliver drugs via MOFs systemically can also be considered once more information on toxicity and pharmacology is discovered.

Considering MOFs can be fabricated to remain stable in neutral solution, it may be possible to formulate active species for inclusion in nebulizers and pMDIs as suspensions (Wang G.-Y. et al., 2014). Indeed, metal-phenolic (Fe) capsules have recently been explored as nebulized drug carriers for pulmonary delivery while not specifically defined as MOFs. Accumulation in alveolar macrophages with low inflammation was indicated in vivo which suggests that MOFs could be utilized in similar nebulizer applications (Ju Y. et al., 2020). MOFs can also be spray dried into aerosolized microparticles for use in DPIs. Since MOFs and traditional organic APIs are capable of being spray dried separately as well, this might enable combination therapy of several distinct inhaled (or otherwise administered) drugs; synergistic and additive effects might be possible with the inclusion MOFs. Additionally, several APIs and/or metals could be coordinated to the MOF scaffold. This may aid in controlled release and the well-triggered delivery of several medications at their appropriate time.

6. Conclusion

The goal of this review was to briefly present two promising individual areas of research (MOFs and aerosol drugs) whose potential intersection has not been, to our knowledge, thoroughly investigated. While there is risk associated with utilizing inhaled metals as a therapeutic agent given toxicity concerns, there exists dose-dependent toxicity associated with almost any drug. Moreover, MOF metal and organic synthetic components can be diluted or concentrated to adjust their final concentration levels to reflect a desired therapeutic window. Therefore, expanding the use of metals in medicine to include pulmonary administration should not be discounted as there are inherent tradeoffs with any regimen once a toxicity threshold is established. To facilitate this work we believe MOFs, as an emerging class of drug delivery vehicles, offer a unique approach toward inhaled therapy. They are capable of being formulated into highly porous, hollow microparticles or manufactured as low-density dry powders with appropriate aerodynamic diameters thus hurdling the first barrier for use as a pharmaceutical aerosol. However, there is a need for further contributions toward characterizing the aerodynamic performance of MOFs to ensure suitability for pulmonary delivery and assessing or connecting their activity and efficacy toward specific lung targets in vitro and in vivo. We believe considering this area of research offers great potential for collaboration and advancement over several disciplines including materials science, aerosol physics, biology, pharmacology, and medicine.

Nomenclature

API	active pharmaceutical ingredient
APSD	aerodynamic particle size distribution
BDC	benzene-1,4-dicarboxylate
BODIPY	boron-dipyrromethene
CF	cystic fibrosis
COPD	chronic obstructive pulmonary disorder
СР	coordination polymers
CPP	coordination polymer particle
CD	cyclodextrin
DPI	dry powder inhaler
EPR	enhanced permeability and retention effect
FPF	fine particle fraction
GSD	geometric standard deviation
HKUST	Hong Kong University of Science and Technology
INH	isoniazid
MMAD	mass median aerodynamic diameter
MDI	metered dose inhaler
MOF	metal organic framework
MIL	materials of Institute Lavoisier
MRI	magnetic resonance imaging
NP	nanoparticle



NOTT	University of Nottingham
PD	pharmacodynamic
РК	pharmacokinetic
PLGA	poly(lactide-co-glycolide) acid
pMDI	pressurized metered dose inhaler
POA	pyrazinoic acid
ТВ	tuberculosis
UiO	University of Oslo
USP	United States Pharmacopeia
ZIF	zeolitic imidazole framework
$d_{\rm ae}$	aerodynamic diameter
$d_{\rm v}$	volume diameter
$ ho_{ m p}$	particle density
γ	dynamic shape factor

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Authors' Short Biographies



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Mechanochemical Preparation of Mineral Based Adsorbent and Its Effective Purification Ability for Wastewater[†]

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Abstract

With the economic development, environmental pollution is getting worse in many developing countries including China. Traditional processing as CaO neutralization of acidic solutions is still a burden to many local governments of China and development of new process with lower cost is highly required. Mining exploitation produces large amounts of tailings in which industrial minerals such as carbonates, silicates and others have been left without proper utilization. Based on the intensive investigations in the field of mechanochemistry, we propose to use these mineral samples to deal with the purification of heavy metal polluted water by enhancing their reactivity through mechanochemical activation. The industrial minerals such as silicates (serpentine and kaolinite), carbonates (calcite) have been studied for the purposes on removal of contaminants from solution. In addition, the synergistic effects from mixtures of calcite with other material have been investigated to give their excellent adsorbent performance for purification of the wastewater. This review summarizes the recent progresses for mechanochemical preparation of mineral based adsorbent and its effective purification ability for toxic matter-containing wastewater.

Keywords: mechanochemical preparation, non-metallic mineral, industrial minerals, adsorbent, purification, waste water, milling

1. Introduction

Industrialization of the human society may begin with the exploitation of various kinds of minerals. Mineral processing has been an important technique to support the development of civilization. The applicable minerals can be categorized mainly into two groups: the first one is metallic mineral resource such as hematite, magnetite, chalcopyrite and galena, which are used to produce metals such as iron, copper and lead, and another one is non-metallic mineral resource, so called as industrial minerals, such as silica, gibbsite, clay, calcite, mica and talc, which are used particularly as additives and fillers in the productions of paper, plastic, paint, as well as raw materials in the productions of cement, ceramic, glass and so on. Metallurgical processing of metallic minerals is also a main source to emit heavy metals to pollute the environment, but strange though it may seem, the abandoned mines are actually the other source, seeping pollutant into the environment with underground water or raining.

A key technology enabling to develop new applications for processing these industrial minerals is mechanochem-

Received 22 May 2020; Accepted 22 June 2020
 J-STAGE Advance published online 17 July 2020

 Corresponding author: Qiwu Zhang; Add: 430070 Wuhan, China E-mail: zhangqw@whut.edu.cn ical activation, mainly triggered by a simple operation of ball milling, which is widely used in mineral processing for concentration and enrichment of target minerals. When powder particles are trapped between balls colliding inside a mill pot, then the particles deform elastically and/or plastically, and are finally fractured into fine fragments, which are easily agglomerated due to the mechanical activation. The force of the impact during the grinding acts on the powder particles, leading to crystallographic bonds broken and new surface is produced. The new surfaces created enable the particles to aggregate and agglomerate each other easily and this leads to an increase in the degree in the activation of solid material. Profound changes affecting the surface as well as the chemical, physicochemical and structural properties may also take place. This is manifested by the presence of a variety of crystal defects such as increased number of grain boundaries, dislocations, vacancies and interstitial atoms, stacking faults, and deformation with rupture of chemical bonds. The presence of such crystal defects enhances the diffusivity of chemical components in the solid.

We have been doing investigations from the viewpoint of mechanochemistry, involving a wide range from mineral processing, materials synthesis, metallurgical extraction to detoxification of hazardous materials. Accumulations of our obtained knowledge and understanding of the nature of mechanochemistry allow the development of





new mechanochemical route for preparing mineral based adsorbent and its effective purification ability for toxic matter-containing wastewater. This review gives brief points reflecting our recent issues in this field, with related publications listed.

2. Current status in heavy metal pollution and applications of industrial minerals activated and modified by mechanochemical treatment in order to purify wastewater

At the early stage of economic growth, developing countries may face serious environmental problems, and one of them is the heavy metal pollution. The large amounts of metal sulfate wastewater produced in the mining and other industries are the major cause of heavy metal pollution to the environment. The solution to such problem requires imminent action. In this regard, the action would be important to work out it by two approaches; one is a positive one improving the processing efficiency, reducing the amount of waste emissions, and the second is a passive one purifying and decontaminating wastewater. Lime precipitation is currently the main method for purification purpose, but it has brought us obvious disadvantages such as high pH of water, high water percentage to the sediment, difficult filtration and so on. The use of non-metallic minerals for the purification purpose does not cause normally significant negative problem, so that it would be recommended in practical application, if such disadvantages are improved. One of the methods for improving them would be chemical modification of adsorbents.

Heavy metal contamination is a growing concern in the world, inadequate polluted water and/or wastewater treatments, coupled with increased industrial activity, have brought about serious heavy metal contamination in rivers, lakes, water reservoirs and so on, spreading over the vast area. However, popular technological methods for removing heavy metals from water sources such as membrane filtration, activated carbon adsorption and electrocoagulation are not always feasible for developing countries due to the viewpoints of economy and infrastructure. As a result, many researches have been attempted for the applicability of low-cost adsorbents to remove heavy metals in the solution. Several scientific papers discussed on the use of alternative adsorbents such as agricultural waste, soil, mineral deposits, aquatic and terrestrial biomass and waste materials.

On the other hand, clay minerals, which are typical non-metallic minerals, exhibiting the adsorbent characteristic, and have been excavated as sedimentary or residual deposit from the earth. This implies that the minerals are normally cheap and abundant natural resources found easily in the world. The minerals have been examined as adsorbents of many contaminants in mainly aqueous solutions. Clay minerals are very reliable and an environmentally friendly remediation material for heavy metal contaminated media. Also, several methods are available for the modification of clay minerals in order to increase their adsorption capacity. However, in order to take first preference in the use of clay minerals as heavy metal remediation materials compared to other methods, further technological investigations are required, leading to determine the best modification type for clay minerals as well as their least dosage required for the adsorption of heavy metals.

Similar to the clay minerals, carbonate minerals such as calcite and dolomite are also widely studied as economical adsorbents to dispose in heavy metal polluted water by neutralizing typical acidic wastewater. Due to the relatively low capacity in these raw minerals as absorbents, chemical modification is, in general, required to enhance the adsorption ability as well as its regeneration and reduce the waste sludge amount after the disposal.

Grinding operation of the raw mineral samples has widely been used to reduce the particle size, to increase the specific surface area together with mechanical activation sites on the surfaces. This activation leads therefore to enhancement in the reactivity with heavy metals when it is suspended in the polluted water and its removal efficiency from the solutions. Besides the physical changes in particle size, structural deformation and so on, intense grinding a solid can induce its physicochemical changes, namely mechanochemical effects, by which high reactivity of the ground solid toward heavy metal removals in the solution may be expected. This result is, therefore, linked with considerable reduction in the amounts of the mineral samples with keeping efficient performance for environmental remediation. This special modifying method based on mechanochemical effects particularly resulting from intense ball milling is fully investigated and discussed in our group and serves as the main contents of this review paper.

3. Activation and modification of nonmetallic minerals by milling

3.1 Hydrated magnesium silicate: Serpentine

Serpentine, (Mg, Fe)₃Si₂O₅(OH)₄, is a generic term for a typical class of hydrous magnesium-rich phyllosilicate minerals. At present, serpentine is generally associated with some metal deposits in nature and often abandoned as a gangue mineral, which is not only a waste of serpentine resource, but also a serious impact on the environment. Serpentine has unique characteristics of phyllosilicate minerals on the adsorption of heavy metal ions, however the raw sample gives limited capacity on heavy metal removal





Fig. 1 Changes in dissolved Mg^{2+} concentration (a) and pH value (b) in the solution with the rotational speed of the stirred mill when the serpentine activated was dispersed in it (Huang et al., 2017).

from environmental pollution. When serpentine is modified and activated mechanically by milling, structural damage to this mineral would be a drawback, obstructing the use of its unique characteristics. However, if milling this mineral makes it possible to maintain its adsorption ability with keeping increment in the specific surface area, there would be possible to increase its reactivity to other species such as heavy metal ions and contaminants in solution.

One typical feature of serpentine milled is the gradual transformation of its crystalline structure to amorphous state, which is commonly observed with hydrated phyllosilicates by intense dry grinding. Investigations into further changes with the ground serpentine sample have revealed interesting phenomena. We have ground serpentine sample by a stirred mill, followed by a dissolution test on the sample into a distilled water. Typical results on this work are shown in Fig. 1 (Huang et al., 2017). The serpentine samples milled for 2 h at different speed were dispersed into distilled water for 4 h without any other chemicals, as seen in Fig. 1(a), Mg²⁺ ion content in the water increases rapidly with increase in mill speed and level off over 400 rpm milling operation. This means that the serpentine activated is dissolved into the water with releasing Mg²⁺, while the raw sample without activation has not shown such obvious dissolution behavior of Mg²⁺ in the water. This suggests that the serpentine milled has transformed into activated state even more than brucite of which an industrial mineral form is magnesium hydroxide, the chemical formula $Mg(OH)_2$. Furthermore, **Fig. 1(b)** show the pH of the water when the serpentine samples activated are dispersed in as a function of mill speed. As seen, the pH is changed from 6.25 in the initial stage to 10.8 at 500 rpm in mill speed, and it increases drastically in the rage from 200 to 400 rpm. According to the data on XRD analysis of the sample, the structural change in the sample is remarkable in the same mill speed range as described above. Both changes in specific surface area and crystalline structure may affect the Mg ions release and pH increase. It is understood that at mild milling with speed lower than 300 rpm, increase



Fig. 2 Changes in remaining copper concentration with the dosage of the activated serpentine at different milling speed (rpm) of the mill with 10 mg/L initial Cu²⁺ concentration (Huang et al., 2017).

in specific surface area may occur as the main factor and structural changes occur mainly at milling speed around 600 rpm, respectively.

We have extended the investigation on the reactivity of serpentine sample activated by the mill at different conditions to find out its adsorption ability in several polluted solution with Cu and Ni ions. The dosage, initial concentration of the solution and other factors were changed and tested in the experiments. A typical result on the adsorption of Cu²⁺ in solution by the serpentine sample activated under different mill speeds in the range from 200 to 400 rpm is shown in Fig. 2. At first, it is recognized from the figure that the activated serpentine sample exhibits the adsorption ability to Cu²⁺ in the solution. In addition, the residual Cu²⁺ ion content in the solution is decreased with an increase in the dosage of the sample, depending on the mill speed. The residual Cu²⁺ content becomes extremely low as the mill speed is increased, especially in the range from 300 rpm or more. In all cases for the sample activated, the content is much lower than that for the raw sample without activation. The residual Cu²⁺ content in the solution for the sample



activated at 400 rpm in mill speed and 0.1 g/L in dosage is about 0.5 mg/L or less, which reaches the Environmental Protection Agency (EPA) the copper discharge limit (1.00 mg/L). We also found that the sample activated by the milling under the condition of 400 rpm or higher brings about a remarkable effect on its adsorption capacity, while serpentine raw material itself has not obvious adsorption ability to Ni or Cu ions. To be concrete, we have confirmed that the capacity of the activated sample at the rotational speed of 600 rpm in the Ni and Cu solution reaches 226.04 mg/g and 538.84 mg/g, respectively.

We have examined adsorption behavior of the serpentine sample activated to alkali metals such as alkali cesium (Cs) ions in the solution. Normally fixing alkali Cs ions is a difficult task but of significant importance in radioactive wastewater treatment at nuclear power stations. Our approach started with the active Mg in the ground serpentine with an aid of phosphate anions, for example, $(PO_{4})^{3-}$, incorporating alkali Cs in solution base to form a complex phosphate as a struvite structure of $(CsMgPO_4)$. It is noted that the struvite, $NH_4MgPO_4 \cdot 6H_2O_1$, itself is sparingly soluble in neutral and alkaline conditions, but readily soluble in acid. A solution with three alkali ions of Na, K and Cs of phosphates to provide PO₄³⁻, was prepared in the experiment, and the serpentine samples activated for 2 h for different speeds were dispersed in it. Fig. 3 (Lei et al., 2019) is a result demonstrating changes in removal rate of three alkali ions in the solution with milling speed in the mill. The removal ions means their adsorption by the sample. As seen, the removal rate of only the Cs ion by the sample is increased marginally in the slow speed mill range, bit it increased rapidly in the speed range from 300 to 400 rpm, and reaches 95 % or more. This implies that Cs ion is transferred to precipitates which are adsorbed into the serpentine sample or settled down in the vial. According to the analysis by XRD, it was found that the serpentine



Fig. 3 Removal rates of Cs, Na and K ions in the solution with the serpentine sample activated by the stirred mill as a function of milling speed (Lei et al., 2019).

structure is broken at the speed over 400 rpm, suggesting release of active Mg in the solution. In fact, most of Cs ions in the solution is removed by the activated serpentine sample to form precipitation. The precipitation sample was checked by XRD analysis, then it was conformed to be $CsMgPO_4$ which is the struvite phase. Therefore, this activation technique to serpentine sample would be a promising and alternative one for adsorbing Cs in radioactive wastewater. Of course, the raw serpentine sample does not show such high adsorption behavior for Cs ions. It is interesting to note that both Na and K ions remain in the solution. The properties of alkali elements are very similar, and methods for Cs precipitation usually cause a similar effect to others like K and Na ions. This means that quite a large amount of serpentine sample has to consume for K or Na removal. It is known that alkali elements have different radius size and exhibit some slight difference in the stability when forming struvite phase. If such small difference is applied for selective precipitation of Cs ion on the ground serpentine, both disposing of radioactive Cs source and enrichment of it are achieved. The characteristics of K and Cs ions to the mechanical activated serpentine were not found in conventional chemical reactions. The key point is that mechanochemical processing may offer special solutions to those difficult cases and we are looking for the chances to solve particularly the environmental issues.

3.2 Hydrated aluminum silicate: Kaolinite

Coagulant has been widely used in the pretreatment of wastewater, and a simple and environment-friendly process to prepare high-efficiency coagulants is highly desired with increasing the amount of wastewater treatment. Kaolinite $Al_2Si_2O_5(OH)_4$, as one of the industrial minerals of kaolin group or clay minerals is a popular one, having 1:1 type layered silicate consisting of Si-O tetrahedron and Al-O octahedron. This mineral has been offered to industries of pottery products, additives in medicines and foods, daily necessities, agricultural soil, fertilizer reagent and so on. We have attempted to develop a novel process to prepare aluminum-based coagulant by the use of mechanochemical activation of kaolinite, followed by co-grinding with concentrated sulfuric acid (H_2SO_4) solution. Fig. 4 shows briefly the flowsheet for preparation process for such coagulant sample. The sample is composed of aluminum sulphate, $Al_2(SO_4)_3$, and it was then tested for removal of pollutant in solution.

The composition, structure and morphology of the coagulant samples were characterized using X-ray Diffraction (XRD), Fourier Transform Infrared (FT-IR), Spectrometer and Scanning Electron Microscopy (SEM) and so on. Capacity of the prepared product as coagulant, compared with pure aluminum sulfate, was evaluated by the removal efficiency of turbidity, phosphate (PO_4^{3-}), arsenate (AsO₄³⁻)





Fig. 4 Flowsheet for preparation process for kaolinite base coagulant sample (Zhao et al., 2019).

and humic acid (Zhao et al., 2019). The final values of these efficiencies are 99.9 % for turbidity clearing up, 91.2 % for phosphate, 89.6 % for arsenate and 92.3 % for humic acid, respectively. Moreover, during the preparation process, the formation of alum, was observed over a wide pH range from 4.3 to 9.0. XRD analysis has demonstrated that a reaction between kaolinite and sulfuric acid occurs during the milling operation and Al sulfate is formed to work as coagulant for the effectiveness confirmed as above.

Instead of the sulfuric acid addition, phosphoric acid (H_3PO_4) was added to the kaolinite sample activated in order to modify kaolinite. In this case, the final product sample was formed as aluminum phosphate, Al-PO₄, and was also tested for removal of pollution in the solution. Since Al phosphate is not water soluble, the sample keeps phosphate anions inside even in solution for adsorbing some target substances. In the case of modifying kaolinite by phosphoric acid, part of the free hydrogen ion of phosphoric acid is combined with the hydroxyl groups in the kaolinite structure, leading to the production of water molecules, so that phosphoric acid is fixed onto amorphous kaolinite to form Si-O-Al-P binding, which offers good adsorption sites for potassium ion (K⁺) (Lei et al., 2018).

The adsorbent through phosphoric acid modification of kaolinite provides a new option for recovering potassium from seawater and tailing wastewater. Further improvements may be obtained by together use with Mg-Al layered double hydroxide or the Mg silicate of serpentine activated as an example and the detailed information may be referred to other publications. The coagulant sample would be a promising one for pre-treatment process of sewage as well as a new route to rich tailings of coal mining gangue etc.

3.3 Calcium carbonate: Calcite

As described, the conventional precipitation method is not enough to solve the problems, due to large amount of chemical reagents needed in order to neutralize wastewater, besides difficulty in separation and recovery of precipitated metals and poor record for processing wastewater with low-concentration of heavy metals. One of the important issues would be to develop a sample exhibiting excellent capability of removal amount for pollutants such as heavy metal ions.

We have proposed a new method for preparation of such samples by using wet stirred ball milling a calcite sample (CaCO₃) with solutions containing Pb^{2+} , Cu^{2+} . Since precipitations of heavy metal ions are expected, a wetting grinding rather than dry grinding was used for such purpose. A systematic exploration was done to investigate effects of several factors such as calcite dosage, milling time and ball volume ratio in the milling on adsorbent capacity of calcite activated for Pb2+ and Cu2+ in the wastewater. It is not easy to analyze in situ the samples in the solutions directly, calcite activated by the milling as well as the precipitates of heavy metals from the water were characterized by XRD, TG-DSC, FTIR and other analytical methods. Fig. 5 shows the lead (Pb) removal rate (%) in the solution on the added ball volume to the solution (a) and the copper (Cu) removal rate (%) on the Ca/Cu molar ratio (b), respectively. The initial concentrations were 0.5 mM for Pb solution, and 1 mM for Cu solution, respectively, and the pH was fixed at 6.51. In the experimental work on Pb removal, shown in Fig. 5(a), the conditions were as follows; $CaCO_{2}/Pb^{2+} = 1$ in moral ratio, 120 min in milling time, 10 % in ball material ratio, and 200 rpm in rotation speed of the stirred mill. As shown in Fig. 5(a), the initial Pb²⁺ removal rate in the solution is 23.3 % at the agitation test (0 % in ball volume ratio), but it increased rapidly with an increase in the ball volume ratio, and reaches to almost 100 % is at 8 in the ball volume ratio, then levelled off. This suggests that the precipitation in the solution happens during the wet milling of calcite and Pb ions in its mill pot, even under low ball volume ratios in the range of 1 to 2 %. This precipitation happens more and more in the higher ball volume range from 5 to 13 %. The precipitates





Fig. 5 Pb removal rate (**a**) on the added ball volume ratio in the stirred milling and Cu removal rate (**b**) on Ca/Cu ratio using calcite activated by the stirred mill (Modified from Hu et al., 2017; 2019).

were confirmed as $PbCO_3$, according to the XRD analysis. Therefore, the remarkable increment range in Pb removal rate seems to be effective period to form such $PbCO_3$ precipitates and the milling with proper ball volume ratio facilitates this precipitation of Pb ion on the calcite sample surface in the solution. It may be noted that this milling period would activate the calcite sample adsorbing the Pb ion in the solution, and that no activation happens on the calcite sample, resulting in only the physical adsorption of Pb²⁺, which is insufficient to remove it, in the absence of balls in the milling (Wen et al., 2020; Xiong et al., 2020; Hu et al., 2019).

Similar trend in the Cu removal in the solution was also observed, as shown in **Fig. 5(b)**. Specific experimental conditions were as follows: 1 mM in initial concentration of Cu²⁺ solution, CaCO₃/Cu²⁺ = 1 in moral ratio, 90 min in milling time, 10 % in ball material ratio, and 200 rpm in rotation speed in the stirred milling. It is found that the Cu²⁺ in the solution can be precipitated from the solution, and the precipitates were confirmed as a solid of Cu₄(SO₄) (OH)₆·2H₂O. The removal rate is increased up to 99.62 %, at which the pH in the solution was 8.25. Then, the concentration of the solution with Cu²⁺ after the treatment is 0.35 mg/L, which is much lower than the National Emission Standards (Hu et al., 2017).

We have further extended the activated calcite sample to other metal ions such as iron (Fe), zinc (Zn) and cadmium (Cd). In the experiment, the calcite sample was milled and activated by a planetary ball mill, which can give the milling strength higher than that by the stirred mill. This may cause easily mechanochemical reactions between calcite and coexistent species. We have made a milling experiment using the calcite sample and heavy metal sulfates. It is very interesting to note that, depending on the type of element, the reaction behavior between metal sulfate and calcite were different: some were quite easy to form precipitation for efficient removals of the ions from the solution, but other metal ions remained in the solution, due to no reaction with calcite. The differences were mainly caused by two aspects: One is the characteristics of different metal ions, and another is the different conditions of reactions. Within the scope our research experiment, the reactivity of ions to calcite has been put in the order of Pb² $^{+} > Fe^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$, Ni²⁺. When the intensity of mechanical activation is very high, the coprecipitation of multiple metals would occur. One plausible reason for such differences in the reactivity may be attributed to the thermodynamic stability of hydrated ion, $M(H_2O)_n^{2+}$, where M denotes metal and n is the water coordination number. When the coordination number of around water is six for Fe²⁺, Ni²⁺, Cd²⁺, the spatial configuration of hydrated ion is octahedron. The spatial configuration corresponding to four for Pb²⁺, Cu²⁺, Zn²⁺ is a regular tetrahedron. The water molecules in the form of octahedron are more difficult to be removed away than those of the regular tetrahedron. It is understood that Pb2+, Cu2+ and Zn2+ are easier to react with CaCO₃ than Fe²⁺, Ni²⁺ and Cd²⁺ (Li et al., 2020). The reaction mechanism between Fe²⁺ and CaCO₃ seems to be a special case and will discuss in detail in the section 3.4, which will introduce synergistic effects of a composites to some anions of phosphate and arsenate.

Hydroxide precipitations of heavy metal ions take place with traditional alkaline neutralization, and calcium hydroxide, Ca(OH)₂, sample has been used as a chemical reagent, and its amount may be a lot, depending on the scale of pollution site. As described, it is possible to use calcite sample, CaCO₃, activated by wet stirred ball milling to treat heavy metals. Due to the high reactivity with heavy metal ions in the solution, it may be replaced with Ca(OH)₂ used in traditional alkali precipitation, and also realizing the chemical reaction of CaCO₃ and heavy metal ions even in equivalent molar and its solid concentration range lower than the current process. When the milling speed is high enough to allow calcite enabling to react with almost all the metal ions in solution to form precipitates (solid phase), the purpose of purification is environmental-friendly achieved. When the milling speed is controlled at mild condition, some metal ions may precipitate on the calcite surface, but



others may remain in the solution. In this case, a mutual separation for metal ions would be possible. More interestingly, it is possible to change the activation strength on the industrial minerals like calcite $(CaCO_3)$ by a mill operated under different conditions, the $CaCO_3$ sample activated shows different reactivity against the heavy metals in the solution. By applying the difference in the reactivity, we designed a new process to conduct a mutual separation of these metals by the use of calcite sample activated by a mill with solution containing the ions.

Fig. 6 shows the experimental data on mutual separation of different ions in the solutions with Cu-Ni (a), Cu-Co (b), Cu-Cd (c), Pb-Zn (d), Fe-Cu (e) and Fe-Mn (f) systems, respectively. In the case of (a) Cu-Ni separation, a mixture of CaCO₃, CuSO₄, NiSO₄ and few amount of distilled water (3 mL) was put into a pot of a planetary mill, and milled for 30 min. The milling speed, Ca/Metal molar ratio and so on were changed, and the products after milling was taken out for evaluation. CuSO₄ and NiSO₄ are the component of the solution, therefore no use of other chemicals is an advantage of our method, and the same procedure was done for other systems such as Cu-Co (b), Cu-Cd (c), Pb-Zn (d), Fe-Cu (e) and Fe-Mn (f). As seen in Fig. 6(a), with wide range of Ca/Cu molar ratio, the residual ratio in Cu²⁺ is almost zero, implying that they are completely precipitated, while Ni²⁺ remains at 90 % or more in the solution over the wide range of Ca/Cu ratio. Therefore, our sample prepared by wet milling of calcite and phosphates is possible to separate mutually Cu²⁺ and Ni²⁺ in the solution. If one would try this mutual separation by the traditional alkaline neutralization process using a chemical reagent, Ca(OH)₂, it would not be achieved the purpose, and more than this, enormous amount of reagent would need to precipitate these ions (Li et al., 2017a).

Similar results are seen in **Fig. 6(b)** and **(c)**. As for the case of selective precipitation of Cu from the solutions containing Co and Cu, the separation efficiency is not high in comparison with that in Cu-Ni system shown in **Fig. 6(a)**, but the residual ratio in Cu is very low over the whole range of Ca/Cu ratio. This means most of Cu²⁺ is precipitated, while most of Co²⁺ ion is still remained in the solution (Li et al., 2016). In the case of Cd-Cu-Fe ions in the solution, Cu and Fe ions are precipitated, while large amount of Cd ion is remained in the solution, as seen in **Fig. 6(c)** (Li et al., 2017b). It is, therefore, recognized that the proposed method could achieve mutual separation among Cd, Cu and Fe ions at fairly high possibility, although the separation efficiency is not so high as the case of Cu-Ni system, as shown in **Fig. 6(a)**.

Selective lead (Pb) removal from metal-containing wastewater such as acid mine drainage (AMD) is an important issue in environmental purification and secondary resources recovery. Similar test on copper (Cu) or iron (Fe) removal was done using CaCO₃ activated by wet ball milling with the solution containing Pb²⁺. The Pb²⁺ in the solution is precipitated to form PbCO₃, and this is achieved based on the reaction between Pb²⁺ and CO₃²⁻ in the solution, as shown in **Fig. 6(d)** (Zeng et al., 2020). The removal efficiency of Pb²⁺ from the solution is increased with an increase in the molar ratio of CaCO₃/Pb²⁺, and it reaches over 99 % at 1.0 in the molar ratio of CaCO₃/Pb²⁺, while more than 99 % Zn²⁺ is remaining in the solutions. During



Fig. 6 Summarized six groups of mutual separations between heavy metals by the use of $CaCO_3$ sample activated (Modified form Hu et al., 2020; Li et al., 2016, 2017a, 2017b; Wang et al., 2019; Zeng et al., 2020).



this removal change, the pH in the solution is changed from about 5.0 to 6.3. This result implies that the high selective precipitation in Pb²⁺ is attained in the range over 1.0 in the molar ratio of CaCO₃/Pb²⁺, without Zn as a contaminant. Looking at the solution after separation of Pb, it is possible to recover Zn as zinc carbonate, as an alternative precipitant to CaCO₃ in the separation process.

Iron (Fe) impurity in manganese sulfate (MnSO₄) solution will seriously affect the quality of manganese products if it is not purified. Ferric ions (Fe³⁺) will precipitate even in weak acidic solution, so that it is possible to remove Fe³⁺ from the manganese sulfate solution by controlling and regulating the pH value in the solution. However, it is not easy to remove Fe³⁺, and oxidization of ferrous ions (Fe²⁺) into Fe³⁺ is normally conducted for iron impurity removal. Our study was focused on removal of ferrous iron from manganese sulfate solution by the use of calcite $(CaCO_3)$ activated mechanically with manganese sulfate solution. This sample preparation was also wet milling used by a stirred ball mill. One of the results at 350 rpm in mill speed are shown in **Fig.** 6(f), and the removal rate of ferrous ions depends on the milling time as well as milling time, and it reaches approximately 100 % under the condition at 180 min in the milling time, 15 % in the ball/liquid volume ratio and 3/1 in CaCO₃/Fe²⁺ (Wang et al., 2019). Thus, selective ferrous iron (Fe²⁺) removal from manganese sulfate solution can be achieved by the sample proposed. Thus our sample preparation is to use calcite and the polluted solution(s), and no use any chemicals. This method would be useful for removing iron ion from manganese sulfate solution. The iron impurity removal can be applied also for purifying other solutions containing copper, nickel, cobalt or zinc.

Thus, the phenomena on the reactivity of $CaCO_3$ with heavy metals in the solution can be controlled by altering milling operation, and it may not be easy to manage this removal results by the traditional process using alkaline neutralization.

3.4 Composite of calcite with ferrous salt

The excessive use of pesticides, the discharge of municipal and industrial wastewater have led to a significant increase of phosphorus levels in water bodies and serious eutrophication pollution. For such high concentration eutrophic water and industrial/agricultural phosphorus wastewater, chemical precipitation treatment can immobilize the phosphate as solid compounds without the need for additional oxygenation or excessive post-treatment. This treatment involves the addition of soluble salts of aluminum and iron or even rare earth to wastewater. Ferric (Fe³⁺) salt is a kind of widely used reagent which is an economical and environmental-friendly reagent rather than aluminum and rare earth salts, and has an excellent precipitation ability, similar to the ferric orthophosphate (FePO₄) with free of toxicity. Applications of Fe³⁺ generated via the oxidation of ferrous (Fe²⁺) salt have received much attention due to its cost performance rather than direct usage of Fe³⁺. The main reason is that the precipitation reaction between Fe²⁺ and PO_4^{3-} occurs in the process of transformation from Fe²⁺ to Fe³⁺ hydroxyl oxides under aerobic condition, which avoids the formation of FeOOH by hydrolysis of Fe^{3+} . At the same time, the oxidation process of Fe^{2+} is greatly affected by OH-. We have noticed recently that the surface of CaCO₃ could provide a boundary for metal ions participation through the reaction with OH-, resulting from the hydrolysis of CO₃²⁻, a successful alternative to Ca(OH)₂ with a clear advantage of final pH in neutral range of the wastewater for direct discharge after the treatment. When Fe^{2+} was used with CaCO₃, the Fe(OH)₂ formed on its surface could be easily oxidized into Fe³⁺ hydroxide even in air, without addition of specific oxidant. It is interesting to note that the slowly generated fresh ferric compositions exhibit tremendous removal capacity for phosphate, without evident formation of FeO(OH). Fig. 7(a), (b) shows the experimental results for the removals of both arsenite anions (for example, AsO_3^{3-}) (a) and phosphate anions (for example, PO_4^{3-}) (b) from the solutions. The sample of calcite was mixed with the Fe²⁺ salt and milled



Fig. 7 Removal efficiencies of arsenite anions (a) and phosphate anions (b) with calcite and ferrous combination (Modified from Zhang et al., 2019a; Li et al., 2018).



by a planetary mill for some time. The results show the dramatic change in each anion, AsO_3^{3-} and PO_4^{3-} , from the solution by the use of CaCO₃ with Fe²⁺, which is oxidized into ferric (Fe³⁺) species (Zhang et al., 2019a; Zhang et al., 2019b; Li et al., 2018).

The mechanism is as follow: At first, CaCO₃ is added to Fe^{2+} salt and it is agitated with phosphate (PO₄³⁻) solution. Then, these components transform into an amorphous Fe³⁺-P or Ca-Fe³⁺-P precipitates. During this change, phosphate removal proceeds in the solution and finally reaches almost 100 % in removal rate. The concentration of phosphorus (P) in the solution is changed from 100 mg/L in the initial stage down to 0.03 mg/L, which is definitely lower than the discharge permissible limit (the National Emission Standards) (USEPA Office of Wastewater Management, 2010). This can be achieved under the conditions as low as 9 in a stoichiometric ratio of CaCO₃/PO₄³⁻ and 1.5 in ratio of Fe^{2+/} PO₄³⁻. It is amazing that the final pH of the solution does not change so much and remains around a neutral range from 5 to 8. Therefore, it is possible to discharge the water after treatment without any further additional treatment like acid neutralization used in the alkaline precipitation process. Mechanochemical ball milling could significantly reduce the size of calcite (CaCO₃) and enhance its reactivity to the anions and solubility in the solution, hence it could promote the efficiency of simultaneous oxidation of Fe²⁺ during the process of phosphorus (P) removal from the solution. When the ball milling speed was 600 rpm, the phosphorus removal process could be completed within 4 hours. The increase of temperature in the precipitation process could also promote phosphorus removal efficiency due to simultaneous oxidation of Fe²⁺ with $CaCO_3$. The percentage of P_2O_5 in the precipitate by agitation of Fe²⁺ and CaCO₃ in the phosphate solution is as high as 19.4 %, which is enough grade as phosphate source in fertilizer production. Difference from the conventional alkaline neutralization process with high concentration of OH⁻ group is the slow hydrolysis of CaCO₃, resulting in low concentration of OH- group for the formation of Ferrous (Fe²⁺) in the solution or its compound (Fe(OH)₂). The ferrous (Fe²⁺) is oxidized easily by air into trivalent Fe (Fe³⁺), achieving continuous formation of fresh ferric composition for phosphate precipitation and could avoid its rapid formation and subsequent transformation into stable FeO(OH) of large particle size to lose the activity. Our method introduced has significant advantage in the use of industrial mineral, CaCO₃ and common material, ferrous (Fe²⁺) salt, so that it may be possible to apply easily to phosphate precipitation.

In the meantime, arsenic pollution in water is also considerable and serious environmental problems in the world, and the damage of its toxicity to human health has brought a menace to our society. We have challenged to develop an efficient method for removal of arsenic ion, As(V), from polluted solution by using active iron species from ferrous-calcium carbonate system (FeSO₄-CaCO₃). Fig. 8 shows a schematic diagram of the formation of ferric compound from ferrous sulfate (FeSO₄) with CaCO₃ for arsenic removal. The basic idea of the ferric compound is similar to the case of phosphate anion removal, but the small difference is that the relatively slow hydrolysis of CaCO₃ would release gradually OH- which played a role to regulate the generation of active iron species and ensured the sufficient reaction time for adequately As⁵⁺ removal (Zhang et al., 2019c). At the same time, the reaction avoids the conversion of new ecological iron to low-reactive FeO(OH).



Fig. 8 Schematic diagram of the formation of ferric compound from ferrous (FeSO₄) with CaCO₃ for arsenic removal (Zhang et al., 2019c).



Moreover, as the content of the arsenic-removing sediment can be significantly reduced by using CaCO₃, the filtration speed is increased by nearly 6 times, and the volume of sediment is also reduced by about 2/3. The treating system in this work shows superior properties such as large sediment size, small sediment volume and high filtration rate, resulting in remarkable record in the processing of arsenic removal. Non-oxidative direct removal of As³⁺ in solution is possible by calcium carbonate with Fe³⁺, as shown in **Fig.** 7(a), and the Fe³⁺ hydrated oxide $(Fe(OH)_2)$ would be formed on the surface of CaCO₃ under the action of OHreleased by the slow hydrolysis, which is able to maintain high reactivity to As^{3+} . When the Fe/As molar ratio is 4.5, it can achieve directly precipitation of As^{3+} of about 100 % removal efficiency without pre-oxidizing from As³⁺ to As⁵⁺ by forming basic ferric arsenite of low solubility instead of high-soluble ferric arsenite. This would open a new approach for removal of arsenite anions in the solution without preoxidation.

3.5 Composite of calcite with zero-valent iron (ZVI)

As an efficient functional material to deal with environmental issues, zero-valent iron (ZVI) (Fe⁰) is widely used from the viewpoint of high reduction potential and environmental-friendly property. In order to prepare ZVI with high reactivity, many studies have been conducted with the focuses on sample preparation, modification or protection processes. To prevent the rapid oxidation of ZVI by oxygen dissolved in the process of the aqueous phase reaction, it is often necessary to pass through the inert gas such as helium, or to use organic solvent such as ethanol and acetone, to clean and preserve the ZVI product during the purification. Furthermore, bare ZVI tends to agglomerate due to its fine particles and magnetic property, which will hinder the adsorption and reduction capabilities. There has been investigation on coating the surface of ZVI with stable materials such as clay, graphene, carbon nanotubes (CNT), activated carbon (AC) and so on. The methods proposed are centered on protecting the fresh surface of the resultant ZVI and have achieved the desired results. However, most of them are the stage of lab research, and it would be better to enhance more, looking at the large-scale application of ZVI to the environmental use, for example.

We have attempted to prepare adsorbent of ZVI coated with CaCO₃ activated mechanochemically. Our expectation is to apply this ZVI-CaCO₃ composite to the removal of As³⁺ in solution, and its idea is shown in **Fig. 9**. The sample preparation starts from milling a mixture of CaCO₃ and ZVI in air, which remains as mixture after milling operation. As shown in the figure, the change in adsorption capacity of the product for As³⁺ is found to vary with the CaCO₃ content in the composite of (ZVI-CaCO₃) prepared



Fig. 9 The adsorption capacity of the ZVI-CaCO₃ samples to As^{3+} anions in the solution as a function of the content of CaCO₃ in ZVI-CaCO₃ system.

by the milling operation. Of course, neither ZVI nor $CaCO_3$ show the adsorption capacity for the arsenic anions, but the composite activated by the milling indicates clearly increment in the adsorption capacity with the content of $CaCO_3$ in it and reaches the maximum value at about 50 % in $CaCO_3$ content of the composite. The value, 50 %, in $CaCO_3$ content means the mass ratio of $CaCO_3$ to ZVI as 1:1, enabling us to produce this composite in large scale production.

As to the reaction mechanism of ZVI toward arsenic, both oxidization and reduction may happen depending on the atmosphere. With an oxidative atmosphere of air, oxidization mechanism proceeds to generate more high active oxidative intermediates. When the oxidation from As³⁺ and Fe²⁺ to As⁵⁺ and Fe³⁺, respectively, is accelerated by some reason, it results in the removal of As³⁺ from the solution. However, in general, ZVI itself is very active substance and the passivation layer formed on the surface of ZVI will prevent from its reaction with other substance. Milling operation to ZVI may cause some mechanical change like breakage in the passivation layer, and this may trigger the reaction, causing the oxidization of the fresh surface. In addition, the milling ZVI with CaCO₃ makes it possible to form coated layer like the passivation one over the fresh surface of ZVI without any agglomerates. This may be the reason why the surface of ZVI in the composite is kept detaching during the removal process of As³⁺ by the composite, ZVI-CaCO₃. Thus, the milling the mixture of ZVI and CaCO₃ plays a big role to continuous exposure of fresh ZVI surface promoting the excellent adsorption ability for arsenic anions.

Besides the oxidative effect of ZVI on arsenite with an aid of oxygen in air, another example for the composite of ZVI and $CaCO_3$ can be seen as follow: This phenomenon is attributed to reductive ability of this composite, indicating the reduction precipitation of hexavalent chromium





Fig. 10 SEM images of different samples, (a) the raw Fe^0 sample, (b) ground Fe^0 sample at 500 rpm for 8 h, (c) mixture of Fe^0 and $CaCO_3$ milled at 500 rpm for 8 h and (d) removal (%) as a function of the dosage for four kinds of samples under the same conditions (Gu et al., 2019).

 (CrO_4^{2-}) in solution. A tremendous improvement in the removal reaction by using the composite of ZVI and CaCO₃ was obtained, in comparison with the adsorption results for the samples of raw ZVI, ground ZVI without CaCO₃ addition. Fig. 10 shows SEM image of a mixture of the raw Fe⁰ sample, (a) ground Fe⁰ sample at 500 rpm for 8 h (b), ZVI and CaCO3 milled at 500 rpm for 8 h (c), and CrO42- removal from the solution as a function of the dosage for the four kinds of samples (d) ground by the stirred mill at the same condition (500 rpm for 8 h). Fine CaCO₃ particles in nanometer size coated on the ZVI particles in micron-meter size are clearly observed from the SEM image, demonstrating the protective effect of CaCO₃ fine particles to the ZVI ones. Three kinds of samples, raw ZVI, ZVI ground and CaCO₃ ground, did not exhibit observable performance for removing CrO_4^{2-} . This may be due to the passivation layer on the ZVI. However, the rate is increased drastically with an increase in the dosage of the sample for the ZVI-CaCO₃ composite, and the value reaches 99.68 % at 1.0 in the dosage. The milling time required to this highest value is 30 min, and the solution containing CrO_4^{2-} (10 mg/L) is obtained, and the ZVI mass ratio in the ZVI-CaCO₃ composite is 30 wt.%. Addition of CaCO₃ to the ZVI and its milling for some time plays significant role in both removal ability of CrO₄²⁻ in the solution and protection of the fresh surface of active ZVI, enabling us to give such superior performance as ZVI. Besides the environment-friendliness of the preparation process, waste solid materials containing iron particles may be one of the candidates as the starting sample in order to prepare such adsorbent of ZVI-CaCO₃ composite for practical use (Gu et al., 2019).

4. Conclusion

A simple milling operation can be used as a typical modifying tool for preparing and modifying non-metallic (industrial) minerals to increase the capacity as absorbents for environmental remediation. Depending on the purposes, either wet or dry milling operations is selected to achieve excellent performance of the adsorbents for pollutant removals in the solution. Intenseness in milling operation is depending on the milling conditions such as milling speed and time, mill vial size, ball charge, sample charge and so on, but it is also important to find out the most effective factor to trigger chemical changes of the target sample. Milling a material causes mechanochemical activation and/ or reaction to form the product which has unique properties and they are not the same one prepared by different milling conditions. In the precipitation of certain ions in solution, it is important to analyze its mechanism chemically in the solution, finding out the crucial aspects to remove a target ion, for example effectively and selectively. This means the both science and engineering knowledge and experience are the key to develop new futuristic methods and materials.

In this review, we have introduced current situation in wastewater treatment, and need adsorbents which would be environmental-friendly ones as much as possible. Under such circumstance, we have challenged and developed several new mechanochemical routes for preparing mineral based adsorbent with effective purification ability for toxic matter-containing wastewater. The minerals chosen in the experiments are non-metallic minerals such as hydrated magnesium silicate (serpentine), hydrated aluminum silicate (kaolinite), carbonate (calcite), calcite with ferrous compound and calcite with zero-valent iron. The mills used are mainly stirred mill and planetary mill in laboratory scale. The direction to prepare the adsorbent sample activated by the mill was shown in each section, and the main results are also introduced.

We have applied some adsorbents prepared by our methods to real and actual spots where solutions are contaminated with toxic substances and heavy metal ions in China. We have also obtained good data as a practical use so far, and in the near future, other spots will be selected for the removal of contaminants in solution by the use of the adsorbents. In the meanwhile, based on the requirement, it would be possible to prepare the adsorbent samples in large scale.

Acknowledgement

The authors are grateful to Emeritus Prof. Fumio Saito, Tohoku University, for his invaluable comments and suggestion on this paper.

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Coal Particle Devolatilization and Soot Formation in Pulverized Coal Combustion Fields[†]

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Abstract

In this paper, recent developments of the devolatilization model and soot-formation model for the numerical simulations of pulverized-coal combustion fields, and the technology used to measure soot particles in pulverized-coal combustion fields are reviewed. For the development of new models, the validation of the developed models using measurement is necessary to check the accuracy of the models because new models without validation have a possibility to make large errors in simulations. We have developed the tabulated devolatilization process model (TDP model) that can take into account the effect of particle heating rate on the volatile matter amount and the devolatilization-rate parameters. The accuracy of the developed TDP model was validated by using the laser Doppler velocimetry data for the bench-scale coal combustion test furnace. The soot-formation model combined with TDP model for the large eddy simulation (LES) has been also developed. The spatial distributions of both the soot-volume fraction and the polycyclic aromatic hydrocarbons were measured by virtue of laser-induced incandescence (LII) and laser-induced chemiluminescence (PAHs-LIF). The accuracy of the developed soot-formation model was validated by using the measured data.

Keywords: coal combustion, soot, devolatilization, numerical simulation, optical diagnostics, laser induced incandescence

1. Introduction

Pulverized coal combustion has been introduced to many coal-fired thermal power plants across the world. However, since the CO₂ emissions from coal-fired thermal power plants is larger than that from other power plants, efficient operation of these power plants and introducing new types of fuel that can be produced from renewable energy is expected. To realize that, modifications of coal-fired thermal power plants are needed. Because the cost of modifying large-scale power plants would be large, pre-evaluation of the modifications is necessary. Numerical simulation of pulverized coal combustion field can be a powerful tool for such pre-evaluation of the modifications or improvement of the operation for the coal-fired thermal power plants. The research group of the authors have conducted studies relating to the development of numerical simulation technology for coal combustion fields (Hashimoto N. et al., 2007, 2012a, 2012b, 2014, 2016b, 2017; Kurose R. et al., 2003, 2004, 2007, 2009; Watanabe H. et al., 2009; Muto M. et al., 2015; Ahn S. et al., 2017).

Fig. 1 illustrates an example of the prediction results of a coal particle's temperature in an actual large-scale coalfired boiler by the developed numerical simulation technology for coal combustion fields. Fig. 2 illustrates the calculated O₂ concentration distribution on the furnace wall surface and the comparison of measured and calculated O₂ concentrations at the inspection windows on the furnace wall for the same boiler as in Fig. 1. The circled numbers in Fig. 2(a) indicate the locations of the inspection windows. Indeed, the simulation suggests that the O₂ concentration at the inspection window at the rear side all above the burner zone (2) in Fig. 2(b)) is low compared to the front side wall. However, discrepancies exist between the simulation results and the measured data. Accordingly, room for improvement with respect to the accuracy of the numerical simulation exists, which can be achieved by understanding the processes involved in pulverized coal combustion fields.

Fig. 3 shows the basic concept of the pulverized coal combustion process. When the pulverized coal particle is heated up, moisture evaporates from the particle at the



[†] Received 21 October 2019; Accepted 15 January 2020 J-STAGE Advance published online 31 March 2020

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Fig. 1 Prediction of coal particle's temperature in actual 915 $\mathrm{MW}_{\mathrm{th}}$ class boiler.

temperature range of boiling point of water. The volatile matter, which includes various gas species and tar, evolves from the particle by the devolatilization process: the gaseous fuels are rapidly oxidized by oxygen in a combustion field. Indeed, it is well known that the majority of the tar is converted into soot particles in the secondary pyrolysis-reaction process. The soot particle emits strong radiation same as the char particle. In addition, the oxidation process of soot particles is relatively slow compared to that of gaseous fuel species. The char combustion process after coal-particle devolatilization has been studied by many researchers across the world. This is because unburned carbon in fly ash that is captured from the exhaust gas is the major concern in the coal combustion research field. Therefore, the researches on the devolatilization and soot formation processes in coal combustion field have been limited. However, the devolatilization process and the soot formation process is very important for the numerical simulation of coal combustion field, because the treatment of these processes strongly affects the prediction accuracy of the entire oxidation speed of the volatile matter and temperature field of the burner zone.

The research group of the authors have conducted studies concerning two major elements: (i) developing the devolatilization and soot-formation models for numerical simulations of the coal combustion fields and (ii) measuring the soot particles present in the coal combustion fields by using optical-diagnostic systems equipped with high power lasers. In this paper, recent attempts to develop accurate numerical simulation technology for coal combustion field are reviewed.

2. Coal-particle devolatilization

Coal-particle devolatilization is a crucial phenomenon in the entire coal combustion process. Volatile matter evolves from coal particles during the devolatilization process. Indeed, both the devolatilization rate and the volatile-matter amount affect the coal-combustion process significantly. In this chapter, the models for the prediction of the devolatilization process are reviewed, as well as methods that aim to unite the devolatilization process model and the numerical simulation of coal combustion fields.

2.1 Models for devolatilization of coal particles

Several devolatilization models have been developed by many researchers, such as the CPD model by Fletcher T.H. et al. (1990), FG-DVC model by Solomon P.R. et al. (1988), and FLASHCHAIN model by Niksa S. and Kerstein A.R. (1991). In the CPD model, percolationlattice statistics are employed in order to describe the generation of tar precursors of finite size based on the number of cleaved labile bonds in the infinite coal lattice. The FG-DVC model combines a functional-group model for gas evolution and a statistical model for tar formation, including depolymerization, cross-linking, external transport and internal transport. Finally, in the FLASHCHAIN model, the chemical constitution of coal in terms of typical refractory aromatic nucleus, two linkage types (labile bridges and char links), and a typical peripheral group are rendered, the labile bridges are regarded as the key reaction centers.

The following formula, which was proposed by Badzioch and Hawksley (1970), is commonly used in modeling the devolatilization process with respect to numerically simulating coal-combustion fields:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = K_{\mathrm{v}}(V^* - V) \tag{1}$$

$$K_{\rm v} = A_{\rm v} \exp\left(-\frac{E_{\rm v}}{RT_{\rm p}}\right) \tag{2}$$

where, *V* represents the mass of volatile matter that evolved from a coal particle (kg), *V** represents the mass of volatile matter in particle (kg), A_v represents the pre-exponential factor for the volatile-matter evolutionrate equation (1/s), E_v represents the activation energy for the volatile-matter evolution-rate equation (J/kmol), *R* represents the gas constant (J/(mol K)), and T_p represents the particle temperature (K).

$$V^* = QV^{*}$$

where V^* and Q are, respectively, the amount of volatile





(a) Calculated O_2 concentration on furnace wall surface and positions of inspection windows



Fig. 2 Comparison of measured and calculated O_2 concentrations at inspection windows on furnace wall surface for the 915 MW_{th} boiler. Reprinted with permission from Ref. (Hashimoto N. and Watanabe H., 2016b). Copyright: (2016) Elsevier B.V.



Fig. 3 Basic concept of pulverized combustion process.





Fig. 4 *V*/V*'* (Appropriate value for Q-factor) as a function of the coal particle heating rate calculated by FLASHCHAIN model. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

matter obtained by proximate analysis and the Q-factor, the latter of which is employed in order to identify the rate at which the amount of volatile matter increases according to the high particle-heating rate in pulverizedcoal combustion fields. In the conventional model for numerical simulations of coal combustion, A_v , E_v and Q are treated as constant values for all coal particles regardless of the particle-heating rate. However, the value of V^* is dependent on the coal particle-heating rate. Therefore, appropriate values for A_v , E_v , and Q are significantly affected by the diameter of each particle, as well as how each particle is injected to the coal-combustion field. Indeed, such effects are not considered in the conventional model.

To investigate the effects of the coal-particle heating rate on A_v , E_v and V^*/V^* , the FLASHCHAIN model was used to conduct devolatilization simulations. Fig. 4 shows V^*/V^* , which represents appropriate values for the Q-factor as a function of the particle-heating rate for different coal brands. Fig. 5 shows the effect of the particleheating rate on the devolatilization-rate coefficient, K_v , for Newlands' bituminous coal, which was predicted using the FLASHCHAIN model. From these figures, it is evident that both the volatile-matter amount and the devolatilization rate are significantly affected by the particleheating rate. We developed a new model to consider this significant effect of the particle-heating rate on the volatilematter amount and the devolatilization-rate parameters, the details of which are reviewed in the next section.

2.2 Tabulated devolatilization process model

To consider the variation of the devolatilization rate and the volatile matter amount for each coal particle in the numerical simulation, the tabulated-devolatilizationprocess (TDP) model was developed. In the TDP model, suitable values for the devolatilization parameters are automatically set for each coal particle according to the pro-



Fig. 5 Effect of the coal particle heating rate on K_v (in Eq. (1)) for Newlands bituminous coal calculated by the FLASHCHAIN model. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

cedure outlined below for a steady-state calculation.

- 1. The devolatilization parameters are set at initial values (① in **Fig. 6**).
- 2. An iteration of the CFD calculation is carried out using the devolatilization parameters (2) in **Fig. 6**).
- 3. After the iteration, the particle temperature history of each coal particle calculated in the most recent CFD iteration is compared with the temperature histories in the devolatilization database. The temperature history from the data base that is closest to the particle temperature history calculated from the most recent CFD iteration is selected (③ in **Fig. 6**).
- 4. The devolatilization parameters accompanied with the extracted temperature history are used in the next CFD iteration (④ in **Fig. 6**).

Steps 2–4 are repeated until the CFD calculation converges. The procedure mentioned above is for the steady state simulation. The procedure for unsteady simulations such as the large eddy simulation (LES), will be reviewed in **Section 4**.

In the TDP model, the mass fraction of volatile matter in the particle $m_{\rm vola}$ (kg/kg-coal) changes depending on the particle-heating rate. Indeed, variations in $m_{\rm vola}$ imply variations in the volatile matter calorific value and the chemical-element composition balance. Therefore, the mole fractions of the postulated chemical species as volatile matter vary depending on the value of $m_{\rm vola}$. This result means that the calorific value and the elementalcomponent balance of the volatile matter varies depending of the particle-heating rate. The detailed procedure used to conform both the calorific value and elemental component balance of a coal particle in the numerical simulation to the calorific value obtained by both proximate analysis and ultimate analysis is available in the relevant literatures: Hashimoto N. et al. (2012a, 2012b), and Hashimoto N. and Shirai H. (2014).





Fig. 6 Calculation flow chart of the TDP model for steady state numerical simulation. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

The validation of the model was conducted using the optical measurement data of the 760 kW_{th} coal-combustion test furnace (**Fig. 7**). A laser Doppler velocimetry (LDV) was employed to obtain the particle-velocity distributions in the test furnace. **Fig. 8** shows a schematic of the measurement system.

Fig. 9 shows the comparison of radial distributions of mean axial-particle velocities. Case 1 indicates the particle velocity predicted by the TDP model. Cases 2-4 indicate the particle velocities predicted by the conventional model. The devolatilization rate parameters used for the conventional model are listed in Table 1. Cases 5-7 indicate the particle velocities predicted by the two competing reaction-rate model (Kobayashi et al., 1977). The devolatilization-rate parameters for the two competing reaction rate model are listed in Table 2. In Fig. 9, the mean axial velocity, U_z , for the Case 1 (TDP model) is more agreeable with the LDV results compared to other cases, which tend to underestimate the values of U_z around the central axis. From the above results, it is clear that the TDP model (Case 1) is better at reproducing the coal-combustion experiment than the other models.

Fig. 10 shows the selection probability of temperature histories in the devolatilization database, when the particle-temperature histories calculated in the CFD iteration are compared with the temperature histories in the database (**Fig. 6**). Indeed, for the majority of particles, the heating rate is in the range of 10^4-10^6 K/s. Moreover, large variations in the particle-heating rate exist according to the initial diameter as shown in **Fig. 10**: the smaller the initial diameter is, the higher the particle heating rate

is. This result indicates that the particle-heating rate should be considered for all coal particles in the field, because it is affected by particle diameter and the position at which said particle is injected into the combustion field. Therefore, devolatilization models that consider the effect of the particle-heating rate on the devolatilization characteristics, such as the TDP model, are strongly recommended for the numerical simulations of pulverized-coal combustion fields.

3. Soot formation in pulverized coal combustion field

As discussed in Chapter 1, the majority of tar that evolves from a coal particle is converted into soot particles as a consequence of secondary pyrolysis. These soot particles emit the strong radiation same as the char particles. Therefore, accurate models with respect to the formation of soot particles can improve predictions about temperature distribution in pulverized-coal combustion fields. Unfortunately, soot formation in pulverized coal flames is yet to be fully understood. In this chapter, experimental research concerned with employing the optical diagnostics of soot particles for coal combustion fields are reviewed as well as research concerning the development of soot-formation models for the LES of coal-combustion fields. For the purposes of validation, the spatial distribution of the soot-volume fraction, which can be obtained by employing a strong pulse laser is one of the most valuable data.




Fig. 7 Computational domain for the validation of the TDP model for steady state simulation. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.



Fig. 8 Schematic illustration of laser Doppler velocimetry for the 760 kW_{th} coal combustion test furnace. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

Table 1Parameters for the conventional model. Reprinted with
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Case	Ref.	$A_{\rm v}$ [1/s]	$E_{\rm v}$ [J/kmol]	Q [-]
2	Tominaga et al., 1997	2.02×10^3	3.11×10^7	1.2
3	Solomon et al., 1983	4.5×10^{13}	$2.20 imes 10^8$	1.5
4	Johnson et al., 1988	$1.0 imes 10^{13}$	$1.8 imes 10^8$	1.8

3.1 Pulverized-coal jet flame burner and the conditions for non-intrusive soot diagnostics

To obtain precise soot formation data with respect to pulverized-coal flames, a simple co-axial pulverized-coal jet burner in CRIEPI (Hwang S.M. et al., 2005) was selected. The coal jet burner and the supplying system are illustrated in **Fig. 11**. Pulverized coal particles and air were supplied to a combustion field from the main burner port (diameter: 6 mm) as the "premixed coal/air flow". Methane was issued from a slit with a width of 0.5 mm





Fig. 9 Radial distributions of average axial particle velocities. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.



Fig. 10 Probability of selection for heating rate in the devolatilization database during the extraction process. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

Table 2 Parameters used for the two competing reaction rate models. Reprinted with permission from Ref. (Hashimoto N. et al., 2012a). Copyright: (2012) Elsevier B.V.

Case	Ref.	α_1	α2	<i>A</i> ₁ [1/s]	A ₂ [1/s]	E_1 [J/kmol]	E_2 [J/kmol]
5	Kobayashi et al., 1977	0.3	1	$2.0 imes 10^5$	$1.3 imes 10^7$	1.05×10^8	$1.67 imes 10^8$
6	Cho et al., 2007	0.38	0.8	$3.7 imes 10^5$	1.46×10^{13}	$7.4 imes 10^7$	$2.5 imes 10^8$
7	Ubhayakar et al., 1976	0.292	0.438	$3.7 imes 10^5$	1.46×10^{13}	7.4×10^7	$2.5 imes 10^8$

that was placed outside the main burner port, in order to stabilize the pulverized-coal flame.

Tables 3 and 4 show the properties of coal and the conditions for pulverized coal flame, respectively. Newlands bituminous coal was selected as the fuel. The mass-based median diameter measured by a laser diffraction particle size analyzer was 33 µm, and the number-based average diameter was 25 µm. The air/coal mass ratio was set to 1.58.

3.2 Preparation of the laser-induced incandescence (LII) in the pulverized-coal flame

Although the laser induced incandescence (LII) is a non-intrusive diagnostic that obtains the volume fraction of primary soot particles in the flame (Michelsen H.A., 2017), both the laser-sheet profile and the laser-pulse fluence should be carefully adjusted when applying LII to the pulverized-coal flame.

Fig. 12 shows the cross section of the laser-intensity profile at the center of the measurement plane (the center of the main burner port). A thin laser sheet was shaped by four cylindrical lenses with focus lengths of f = -300 mm, 25 mm, 700 mm, and 2,000 mm. (Note that this optical setup was same in all experiments in this chapter). The laser sheet has the Gaussian profile in the horizontal axis, as shown in Fig. 12. The laser sheet thickness was defined by taking $1/e^2$ of the maximum intensity. The LII signals obtained by the Gaussian profile (full sheet) and the ho-

mogeneous profile (partial sheet) were examined by Hayashi J. et al. (2013), in order to understand the effects of the laser profiles on the LII applied to the pulverizedcoal flame.

The relation between the signal intensity of the LII and the laser-pulse fluences are shown in Fig. 13. The values in Fig. 13 were normalized using the signal intensity of the LII at a laser fluence of 0.1 J/cm². Results obtained in the non-combustion case were normalized by the signal intensity of the LII in the Gaussian profile at the same laser fluence as other combustion cases. Indeed, from Fig. 13, it is evident that three regions in the combustion case exist: the heating region (a), the plateau region (b), and the superimposed region (c). In region (a), the signal intensity of the LII increases with an increase in the laser fluence. In this region, the laser fluence is insufficient with respect to heating all the soot particles in the measurement area up to the sublimation temperature. In region (b), the signal intensity of the LII decreases slightly with an increase in the laser fluence, ultimately plateauing. Indeed, these two regions—(a) and (b)—can also be found in the LII measurements of gaseous flames (Schulz C. et al., 2006). For gaseous and spray (Hayashi J. et al., 2011) flames, LII was conducted with the laser fluence in this plateau region. This is because the signal intensity of the LII does not change with an attenuation of the measurement field. However, to apply LII to the context of a pulverized-coal flame, the laser fluence should be care-





Fig. 11 Schematic of the coal jet burner and supplying system. Reprinted with permission from Ref. (Hayashi J. et al., 2019). Copyright: (2019) Elsevier B.V.

Table 3Properties of coal. Reprinted with permission from Ref.(Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

Item	Value
Higher heating value ^a	29.1 MJ/kg
Lower heating value ^a	28.1 MJ/kg
Proximate analysis	
Moisture ^b	2.60 wt%
Ash ^a	15.20 wt%
Volatile matter ^a	26.90 wt%
Fixed carbon ^a	57.90 wt%
Ultimate analysis	
Carbon ^a	71.90 wt%
Hydrogen ^a	4.40 wt%
Nitrogen ^a	1.50 wt%
Oxygen ^a	6.53 wt%
Total sulfur ^a	0.44 wt%
Combustible sulfur ^a	0.39 wt%

^a Dry basis, ^b As received

fully controlled according to region (c). While region (c) is evident in pulverized-coal flames, it does not appear in the LII measurements for the flames of both gaseous and liquid fuels. As shown in region (c) of **Fig. 13**, the signal intensity of the LII re-increases with an increase in the laser fluence. This result is because the signals of the LII from the pulverized-coal particles are superimposed onto the signals of the LII from the soot particles. Indeed, the LII signal in the non-combustion case, in which there are no soot formation, increases in the range of laser fluence with higher than 0.2 J/cm² (shown as the solid square in **Fig. 13**).

These results suggest that sufficient fluence of the laser is required to heat all the soot particles up to the sublima-

Table 4Experimental conditions. Reprinted with permission fromRef. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

Item	Value
Pulverized coal feed rate	$1.49\times10^{-4}~kg/s$
Thermal input of coal ^a	4.19 kW
Thermal input of CH ₄ ^a	0.83 kW
Air flow rate	$1.80\times10^{-4}\ m^{3}\!/\!s$
CH ₄ flow rate	$2.33 \times 10^{-5} \ m^{3}\!/\!s$
Bulk equivalence ratio	$\phi = 6.09$
Reynolds number, Re	2,544

^a Based on the lower heating value

tion temperature so that all the soot particles emit enough LII signals for the evaluation of the soot particle volume fraction in pulverized coal flames. At the same time, it should be mentioned that too high fluence of laser may cause the overestimation of the volume fraction of soot particles in pulverized coal flame due to the signals of LII from the pulverized coal particles.

3.3 Simultaneous measurements of LII and Mie scattering, and comparisons with OH-PLIF

In this section, the simultaneous measurements of Mie scattering and the LII in the pulverized coal flame are discussed in order to understand how the coal particles and soot formation are related. Two-dimensional images of Mie scattering and the LII with OH-PLIF (Hwang S.M. et al., 2005) are shown in **Fig. 14**, from which it is evident that the signals of Mie scattering are strong near the burner port and it decreases with an increase in height above the burner port (HAB). Contrastingly, the LII and the OH-PLIF signals increase with an increase in HAB. It is noteworthy that the full sheet (Gaussian) is adopted in **Fig. 14** for visualizing all signals. Moreover, from





Fig. 12 The laser sheet profile (a) width of the laser sheet $(1/e^2 \text{ value}) = 0.1 \text{ mm}$, (b) height of the Gaussian laser sheet = 29.6 mm, (c) height of the homogeneous laser sheet = 10 mm). Reprinted with permission from Ref. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

Fig. 14(b), it is evident that some discrete areas of soot are present near the burner port, the sizes of which increase with an increase in HAB. When the HAB reaches roughly 135 mm from the burner port, the shape of the soot-formation area changes from being discrete to being streaky.

To understand the interaction of coal particles with respect to combustion reaction and soot formation, the averaged radial distributions of the signals of the Mie scattering, the LII and the OH-PLIF at different HABs (60 mm and 120 mm) are shown in **Fig. 15**. The signal intensities of the OH-PLIF and the LII increase with an increase in HAB, as observed in **Fig. 14**. The overlapping region of signals expands with an increase in HAB; this result is due to the turbulent mixing and the expansion of burned gas. Note that the peak value of the OH-PLIF signal, which is formed by the methane pilot flame, appears at the furthest position from the burner center.

Fig. 16 illustrates the radial distributions of gaseous temperatures and oxygen concentrations obtained by using the results of the numerical simulation with TDP model applied to the coal jet burner (Hashimoto N. et al., 2012b), at the same HAB in the experiment. Indeed, the low oxygen concentration region expands in the radial direction with an increase in HAB, which corresponds to the tendency of the LII signal shown in **Fig. 15**. Moreover, from **Fig. 16**, it is evident that the oxygen concentration at the center line of the burner decreases with an increase in HAB. This result suggests that the combustion reaction of volatile matter from pulverized-coal particles consumes the oxygen even in the center of the flame. On the other hand, the LII-signal intensity near the center is low and does not change with an increase in HAB. This is because



Fig. 13 The LII signal intensity as a function of the laser pulse energy; (a) heating up region, (b) decreasing region, (c) superimposed region. Reprinted with permission from Ref. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.



Fig. 14 The instantaneous distributions of **(a)** Mie scattering signals, **(b)** LII signals and **(c)** OH-PLIF signals. Reprinted with permission from Ref. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

the temperature at the center of the burner was below 1,500 K, which is not sufficient for soot formation. In fact, the signal intensity of the LII in the high-temperature region (from r = 5 to 10 mm) increases with an increase in HAB. In addition, since the signals of the Mie scattering can be found in the same region as the high signal intensity of the LII, a sufficient amount of volatile matter for soot formation is supplied from the pulverized-coal particles in this region. From **Fig. 15**, moreover, it is evident that the signals of the Mie scattering are low in the region around the outer peak of the OH-PLIF signal,





Fig. 15 The ensemble-averaged radial distributions of the Mie scattering signal, LII signal and OH radical chemiluminescence signal normalized by the maximum value at 120 mm; (a) h = 60 mm, (b) h = 120 mm. Reprinted with permission from Ref. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

where the gas temperature is high, and the oxygen concentration is minimal. This result means that the required amount of volatile matter for soot formation cannot be formed, because the number density of coal particles is small in this region. Therefore, the signal of LII does not appear in this region in spite of the low oxygen concentration and the high gas temperature.

These results indicate that soot formation is enhanced at locations if the following conditions are satisfied: high gas temperature, low oxygen concentration, and the existence of pulverized-coal particles.

3.4 Primary soot particle distribution measurements in pulverized-coal jet flame

Primary soot-particle size is another important element, with respect to verifying the numerical-simulation models of soot formation for pulverized-coal flames. The spatial distribution of the primary soot particle size was measured employing a combination of a time-resolved LII (TiRe-LII) and the SEM images collected by thermophoretic sampling (TS). **Fig. 17** shows the schematic illustra-



Fig. 16 The radial distribution of temperature and the O_2 concentration (Obtained from Hashimoto et al. 2012b); (a) h = 60 mm, (b) h = 120 mm. Reprinted with permission from Ref. (Hayashi J. et al., 2013). Copyright: (2013) Elsevier B.V.

tion of TiRe-LII measurement. Fig. 18 shows the typical SEM images of soot particles collected by TS, the probability-density and the cumulative frequency functions of primary soot-particle size based on sphere equivalent volume of the soot particles (Hashimoto N. et al., 2016a). From Fig. 18(a-1), (a-2), and (a-3), it is clear that the number density of the soot particles on the SEM grid increases with an increase in HAB. This is consistent with the tendency of soot volume fraction measured by the LII as shown in Fig. 15.

The red solid circles in **Fig. 18(a-2)**, (**b-2**), and (**c-2**) represent the cumulative plots of the primary soot-particle sizes, which were calculated by randomly sampling the particles obtained in the SEM images. The approximated cumulative curves of the primary soot-particle sizes are shown as blue solid curves in **Fig. 18(a-2)**, (**b-2**), and (**c-2**) employing the log-normal function expressed by the following equation:

$$F(D_{\rm p}) = \frac{1}{2} \operatorname{erfc}\left[-\left(\frac{\ln(D_{\rm p}) - \ln(D_{\rm p,m})}{\sigma\sqrt{2}}\right)\right]$$
(4)

where $D_{\rm p}$ is the primary soot-particle diameter, and $D_{\rm p,m}$





Fig. 17 Schematic of measurement set up for time-resolved laser incandescence (TiRe-LII). Reprinted with permission from Ref. (Hashimoto N. et al., 2016a). Copyright: (2016) Japan Society of Mechanical Engineers.

is the median diameter based on the particle volume. The parameters σ and $D_{p,m}$ are determined by the least-squares method in order to fit the curves to the measured diameter distributions. The green dashed curves indicate the probability density function converted from the blue cumulative frequency curves, which are expressed by the following equation:

$$P(D_{\rm p}) = \frac{1}{\sqrt{2\pi\sigma}D_{\rm p}} \exp\left[-\frac{1}{2}\left(\frac{\ln(D_{\rm p}) - \ln(D_{\rm p,m})}{\sigma}\right)^2\right] \quad (5)$$

Indeed, the primary soot-particle size distribution shifts to the larger side with an increase in HAB. This result indicates that primary soot-particle size increases as said particles move downstream. Moreover, it is also evident that the distribution of the primary soot-particle size widens with an increase in HAB. This result means that the maximum value of the probability density function of primary soot-particle size decreases with an increase in HAB.

Fig. 19 shows the distributions of the primary sootparticle size and the soot-volume fraction. As shown in **Fig. 19**, while the primary soot-particle size increases and the region of soot expands in the radial direction, the radial position of the peak value of the soot-volume fraction does not significantly change with an increase in HAB.

3.5 Simultaneous imaging of Mie scattering, polycyclic aromatic hydrocarbons laser-induced fluorescence, and soot LII with respect to a lab-scale turbulent jet pulverized-coal flame

Since polycyclic aromatic hydrocarbons (PAHs) are known as a soot precursor, information relating to their formation is crucial with respect to the soot-formation processes (Michelsen H.A., 2017 and Desgroux P. et al., 2013). In order to understand the transitional soot formation processes in the pulverized-coal flame, Hayashi et al. (2019) conducted two different simultaneous measurements ("Mie scattering for coal particles with LIF for PAHs" and "LIF for PAHs with LII for soot") in the coal jet burner.

In the following reviewed work, LIF measurement for PAHs using a laser with a wavelength of 355 nm, which is referred to the results reported by Bejaoui S. et al., 2014 and Aizawa T. and Kosaka H., 2008, were conducted. Mie scattering and LII were conducted using the same wavelength as LIF, in order to achieve simultaneous measurements. Laser fluence was set to 0.25 J/cm², in order to ensure sufficient signal intensity. Two-dimensional distributions of the signals of Mie scattering, LIF, and LII are shown in Fig. 20. The signal intensities of the pulverizedcoal particles (Mie scattering), PAHs (LIF signal), and soot particles (LII signal) are represented in green, blue, and red, respectively. Indeed, PAHs exist at the center axis due to the turbulent mixing as shown in Fig. 20(b). This occurs because the PAHs measured according to the LIF are gaseous, and therefore, they follow the gaseous flow. This trend is similar to that of the OH-LIF signal (Hwang S.M. et al., 2005). Conversely, the discrete regions of LII are observed apart from the center line as shown in Fig. 20(c).

The overlaid images of both the Mie scattering and the LIF are shown in **Fig. 21**, from which it is evident that the existing regions of pulverized-coal particles and PAHs slightly overlap. Due to the configuration of this work, the devolatilization tends to begin from the outer side of the main coal/air premixed flow. As a result, a continuous and high-intensity LIF signal can be found in the surrounding area of the Mie-scattering signals. Subsequently, the LIF-signal region expands toward the central region due



(c-1) Typical image of soot particles sampled at h = 95 mm



(b-1) Typical image of soot particles sampled at h = 65 mm



(a-1) Typical image of soot particles sampled at h = 35 mm



(c-2) Cumulative frequency and probability density functions for primary soot particle diameter (h = 95 mm)



(b-2) Cumulative frequency and probability density functions for primary soot particle diameter (h = 65 mm)



Fig. 18 Typical SEM images of soot particles, probability density and cumulative frequency functions for primary soot particle diameter. Reprinted with permission from Ref. (Hashimoto N. et al., 2016a). Copyright: (2016) Japan Society of Mechanical Engineers.

to the mixing of the surrounding gases. This result is consistent with the numerical results obtained by Hara et al. (2015). Here, it is known that the volatile matter of PAHs with two to three aromatic rings can be formed directly from coal particles (e.g., Zhang L. et al., 2017). This result means that PAHs can exist wherever coal particles exist, so long as the temperature is sufficiently high for devolatilization.

In essence, the existing regions of LIF and LII do not correspond with each other—see **Fig. 21(bottom**). It is noteworthy that the interference of the LII signal and PAHs-LIF signal cannot be excluded during the scheme of excitation and detection in this work. On the other hand, the LII signal collected at 400 nm with the gate delayed by around 70 ns from the laser incident is unambiguously issued from soot incandescence. The signals of the LII shown in **Fig. 21(bottom)** are well separated from the prompt signal of the LIF. While only a few overlapping locations of LIF and LII are observed, which require careful interpretation, no ambiguity in assigning the prompt signal to the LIF from PAHs exists in any other location. The existing soot region (the regions of LII signal) is limited and discrete at the bottom of the jet flame; moreover, the relative soot-volume fraction increases with an increase in HAB. However, the soot formation was inhibited in the center axis. This occurs because the temperature in this region was relatively low and, moreover, because oxygen was still present at the relevant HAB. Lee S.M. et al. (2004) measured the LIF of PAHs using different wavelengths, showing that the displace-





Fig. 19 Ensemble-averaged distributions of primary soot particle diameter and soot volume fraction. The color indicates the primary soot particle diameter and the height indicates the soot volume fraction. Reprinted with permission from Ref. (Hashimoto N. et al., 2016a). Copyright: (2016) Japan Society of Mechanical Engineers.



Fig. 20 Two-dimensional distribution of Coal-Mie (in Green), PAHs-LIF (in Blue) and soot-LII (in Red) at different HAB. Reprinted with permission from Ref. (Hayashi J. et al., 2019). Copyright: (2019) Elsevier B.V.

ment of both small PAHs and soot is much larger than that of large PAHs. This result suggests that a necessary period of time is required for the development of PAHs to soot, during which time discrete regions form, as shown in **Fig. 21**.

The averaged radial-signal distributions of the Mie scattering, LIF, and LII are shown in **Fig. 22**, from which it is evident that the pulverized-coal particles are spatially distributed and, moreover, that the existing region of them expands with an increase in HAB. The distribution of the LIF signals expands from the fringe to the central axis of coal flame with an increase in HAB; this occurs because the PAHs contained in the volatile matter is evolved from the pulverized-coal particles at high temperatures. Indeed, the signal distribution of LII does not expand from the fringe to the central axis of the coal flame with an increase in HAB.

The volatile-matter mass-fraction distribution for the radial direction at each HAB predicted by the numerical



Fig. 21 Overlaid images of Coal-Mie (green) and PAHs-LIF (blue) (top), PAHs-LIF (blue) and soot-LII (red) (bottom) at different HAB. Reprinted with permission from Ref. (Hayashi J. et al., 2019). Copyright: (2019) Elsevier B.V.

simulation conducted by Hashimoto et al. (2012b) is shown in **Fig. 23**. Indeed, a good correlation between the measured LIF signals (**Fig. 22**) and the predicted volatile-matter mass fraction (**Fig. 23**) exists, even though there are some discrepancies.

3.6 Numerical simulation for soot formation in pulverized-coal combustion fields

Pioneers for the development of soot-formation models for the numerical simulation of coal-combustion fields are Brown A.L. and Fletcher T.H. (1998), who developed a model for RANS-based CFD software. The accuracy of this model was validated using data obtained by TS in a laminar-flow reactor (Ma J. et al., 1996). However, said data were insufficient with respect to validating the accuracy of the model for a turbulent coal combustion field. As mentioned in previous sections, the detailed data including two-dimensional soot-particle volume-fraction distributions in the coal combustion field are now available. Xu K. et al. (2017) developed a soot formation model for RANS-based numerical simulations same as the





Fig. 22 Radial distributions of Mie Scattering, PAHs-LIF and Soot-LII Reprinted with permission from Ref. (Hayashi J. et al., 2019). Copyright: (2019) Elsevier B.V.

model proposed by Brown A.L. and Fletcher T.H. (1998); they validated the simulation using our measured data (Hayashi J. et al., 2013). Muto M. et al. (2018) developed a soot-formation model for the DNS of coal-combustion fields. They used the detailed chemistry for soot formation; their simulation results are yet to be validated. Our research group developed a soot formation model for the LES of coal-combustion fields (Takahashi H. et al., 2019). We combined the soot-formation model proposed by



Fig. 23 Radial distributions of volatile matter obtained by Hashimoto N. et al. (2012b). Reprinted with permission from Ref. (Hayashi J. et al., 2019). Copyright: (2019) Elsevier B.V.

Brown A.L. and Fletcher T.H. (1998) and the TDP model proposed by Hashimoto et al. (2014), because the prediction accuracy of devolatilization strongly affects the soot formation, which is evident in **Fig. 3**.

In the developed model, the parameters V^* , A_v , and E_v are stored in the devolatilization database. The database produced by Hashimoto et al. (2012b) using the FLASHCHAIN model was employed in the study. Since LES is unsteady simulation, the extraction procedure introduced in Section 2.2, which was developed for steadystate numerical simulation, was modified so that the TDP model can be applied for LES (Takahashi H. et al., 2019). In the model, four temperatures, which are 500, 800, 1100, and 1400 K, were set to calculate the average particle heating rate for each group of particles with the same initial diameter. The averaged heating rate of 100 particles is compared with particle heating rates in the devolatilization database. Then, the devolatilization parameters associated with a heating rate in the database that is the closest to the averaged particle heating rate calculated from LES is selected are selected as new parameters for the next time step.

In the developed model, soot was treated as a gas phase substance. The conservation equation for soot particles is expressed as follows:

$$\frac{\partial \rho_{g}\varphi}{\partial t} + \frac{\partial}{\partial x_{j}} \left(\rho_{g} u_{j} \varphi - \rho_{g} D_{s} \frac{\partial \varphi}{\partial x_{j}} - \gamma \frac{\mu}{T} \varphi \frac{\partial T}{\partial x_{j}} \right) = S_{\varphi}, \quad (6)$$

where φ is either $N_{\rm C}$ (soot particle number density) or $Y_{\rm C}$ (mass fraction of soot). $D_{\rm s}$ and γ represent the diffusion coefficient for soot particles and the coefficient for the thermophoretic force acting on the soot, respectively. $D_{\rm s}$ is calculated by the following equation:

$$D_{\rm s} = \mu / \sigma \rho_{\rm g} \tag{7}$$

where μ , σ , and ρ_g represent the gas phase viscosity, the Schmidt number (= 700 (Brown A.L. and Fletcher T.H.,

1998)), and the density of the gas phase, respectively. $S_{Y_{\rm C}}$ (source term of $Y_{\rm C}$) is calculated by the following equation:

$$S_{Y_{\rm C}} = \rho_{\rm g} \left(\dot{r}_{\rm FC} - \dot{r}_{\rm OC} \right) \tag{8}$$

where $\dot{r}_{\rm FC}$ and $\dot{r}_{\rm OC}$ are the rates of soot formation and oxidation, respectively. $S_{N_{\rm C}}$ (source term of $N_{\rm C}$) is calculated using the following equation:

$$S_{N_{\rm C}} = \frac{\rho_{\rm g}}{N_{\rm A}} \left(\frac{N_{\rm A}}{M_{\rm C} \cdot C_{\rm min}} \cdot \dot{r}_{\rm FC} - \dot{r}_{\rm AN} \right) \tag{9}$$

where \dot{r}_{AN} , M_C , and C_{min} represent the soot agglomeration rate, the molecular weight of carbon, and the number of carbon atoms per incipient soot-particle, respectively. The term γ in Eq. (6) is the thermophoretic-transport coefficient, which is calculated by the following equation:

$$\gamma = \frac{3}{4\left(1 + \pi \cdot \frac{A}{8}\right)} \tag{10}$$

where A is the accommodation coefficient. The soot formation rate in Eq. (8) is calculated by the following equation:

$$\dot{r}_{\rm FC} = \rho_{\rm g} \cdot \left(\sum_{i=1}^{4} \frac{Y_{\rm s, Tar_i}}{MW_{\rm Tar_i}} \right) \cdot A_{\rm FC} \cdot e^{-\frac{E_{\rm FC}}{RT}}$$
(11)

where MW_{Tar_i} , A_{FC} , E_{FC} , and R represent the molecular weight of the tar species, the pre-exponential factor, the activation energy, and the gas constant, respectively. $Y_{\text{s, Tar}_i}$ represent the tar-mass fraction, and is obtained from the TDP model. The soot-oxidation rate in Eq. (8) is calculated by the following equation:

$$\dot{r}_{\rm OC} = SA_{\rm v,c} \cdot p_{\rm O_2} \cdot T^{-\frac{1}{2}} \cdot A_{\rm OC} \cdot e^{-\frac{E_{\rm OC}}{RT}}$$
(12)

where $SA_{v,C}$ and p_{O_2} represent the soot-particle surface area per unit volume and the partial pressure of oxygen, respectively. The shape of the soot particles is assumed to be a perfect sphere, and $SA_{v,C}$ is calculated by the following equation:

$$SA_{\rm v,C} = (\pi \cdot N_{\rm C})^{\frac{1}{3}} \cdot (6 \cdot Y_{\rm C})^{\frac{2}{3}} \cdot \rho_{\rm g} \cdot \rho_{\rm C}^{-\frac{2}{3}}$$
(13)

where $\rho_{\rm C}$ is the soot particle density (= 1,950 kg/m³ (Brown A.L. and Fletcher T.H., 1998)). The soot-agglomeration rate in Eq. (9) is calculated by the following equation:

$$\dot{r}_{\rm AN} = 2C_{\rm a} \left(\frac{6M_{\rm C}}{\pi \cdot \rho_{\rm C}}\right)^{\frac{1}{6}} \left(\frac{6\kappa T}{\rho_{\rm C}}\right)^{\frac{1}{2}} \cdot \left(\frac{\rho_{\rm g} \cdot Y_{\rm C}}{M_{\rm C}}\right)^{\frac{1}{6}} \left(\rho_{\rm g} \cdot N_{\rm C}\right)^{\frac{11}{6}} (14)$$

where C_a represents the collision frequency constant, which was set as 3 (Brown A.L. and Fletcher T.H., 1998). The values for the pre-exponential factors and the activation energies for \dot{r}_{FC} and \dot{r}_{OC} are listed in **Table 5**.

Radiative heat transfer was calculated using the discrete-ordinate method (Fiveland W.A., 1984) with the

Table 5Pre-exponential factor and activation energy for transportequation source terms. Reprinted with permission from Ref. (TakahashiH. et al., 2019). Copyright: (2019) Elsevier B.V.

Term	Ref.	Α	$E_{\rm v}$ [J/mol]
$\dot{r}_{\rm FC}$	Ma et al., 1996	$5.02 \times 10^8 \mathrm{m^3 \cdot mol \cdot s}$	198.9×10^3
<i>r</i> _{OC}	Lee et al., 1962	$1.09 \times 10^4 m^{-1} \!\cdot\! s \!\cdot\! kg^{-1} \!\cdot\! K^{-1/2}$	164.5×10^3

S4 approximation. The coal-particle emissivity, ϵ_p , was assumed to be 0.85, according to Kurose et al., 2004. The continuous phase absorption coefficient, k_a , was calculated by the following equation:

$$k_{\rm a} = k_{\rm g} + k_{\rm s} \tag{15}$$

where k_g and k_s represent the gas-absorption coefficient and the soot-absorption coefficient, respectively. The value for k_g was set to 0.075, and k_s was estimated by the following equation (Wen Z. et al., 2003):

$$k_{\rm s} = 1.8644 \times 10^3 f_{\nu_{\rm soot}} T \tag{16}$$

where $f_{v_{\text{soot}}}$ and *T* represent the soot-volume fraction, and the gas temperature, respectively.

Fig. 24 shows the overview of the computational domain for LES. The entire shape of the domain is a cylinder with a diameter of 200 mm and a length of 560 mm (-60 < HAB < 500 mm). The exit of the burner was set to HAB = 0 mm. The number of nodes was about 1.8 million, and the number of fluid cells was about 2.0 million. The time step of the calculation was set to 2×10^{-5} s.

Fig. 25 shows the comparisons of soot-volume fractions made between the measured and calculated data. In the left-hand side of the figure, the direct photo of the flame and the measured soot volume fraction distribution obtained by LII are shown. The soot-volume fraction was obtained by the ensemble average of 500 shots of the LII signal. Indeed, large soot-volume fractions can be observed at the outer region of the luminous flame. Moreover, from Fig. 25, it is evident that the soot-volume fraction increases with an increase in HAB. These tendencies can be reproduced by numerically simulating soot formation, as can be seen in the right-hand side of the figure.

Fig. 26 shows the various comparisons of the radial distributions. The tendency of the signal distributions of Mie scattering to expand radially with an increasing HAB can be reproduced by the calculated distributions of coal-particle surface area in numerical simulation, as shown in Fig. 26(a) and (b). In addition, the position of the calculated peak of the soot-volume fraction is almost consistent with the peak of the LII signal. Furthermore, the expansion trends of the soot-volume fraction distributions are evident in both experimental and theoretical results. In Fig. 26(e) and (f), it is evident that the conditions of low oxygen concentration, high gas temperature, and





Fig. 24 Computational domain for LES. Reprinted with permission from Ref. (Takahashi H. et al., 2019). Copyright: (2019) Elsevier B.V.

the existence of sufficient pulverized-coal particles are satisfied at the peak position of the soot-volume fraction. This trend can be explained by the following: the peak positions of the net soot-formation rate in Fig. 26(g) and (h) match the peak positions of the soot-volume fraction in Fig. 26(e) and (f). Negative net soot-formation rates are evident at both sides of the base of the soot-volume fraction peak, even though the soot-volume fraction steadily increases at these positions with an increasing HAB. This is because, due to the turbulence mixing effect, the soot particles diffuse from the soot-volume fraction peak toward both sides. Oxygen concentrations where a negative net soot-formation rate is observed are higher than those at the soot-volume fraction peak. This higher oxygen concentration causes a higher rate of soot oxidation. This position results in a significant effect on the formation of a high soot-volume fraction area, even though the absolute value of the net negative formation rate is not significantly high. Basically, the soot particles diffuse from the peak position of the soot-volume fraction; accordingly, in these positions, net soot does not form. This result is the reason why the high soot-volume fraction area is limited to a narrow range of radial distance.

Fig. 27 shows the average gas temperature distributions obtained by LES: (a) without soot radiation and (b) with soot radiation. From the figure, it is evident that there is the maximum gas-temperature difference of over 100 K between two cases. This temperature difference is caused by the difference in radiation heat flux to surroundings from the coal flame. Average heat flux at the position 100 mm far away from the burner central axis, with soot radiation was 2.95×10^2 W/m² while the average heat flux without soot radiation was 2.69×10^{-3} W/m². This large difference in heat flux causes significant differences in the predictions of the gas-phase temperatures. Indeed, this



Fig. 25 Comparison between measured (Hashimoto et al., 2016) and calculated soot volume fraction. Reprinted with permission from Ref. (Takahashi H. et al., 2019). Copyright: (2019) Elsevier B.V.

finding indicates the significance of a soot-formation model for numerical simulations of pulverized-coal combustion fields. After all, if a soot formation model is not considered, the gas temperature can be significantly overestimated. Moreover, the accuracy of the gas-temperature predictions significantly influences the majority of processes in coal combustion fields, such as the devolatilization of coal particles, the combustion reaction of volatile matter, char-particle surface reaction, and the formation of pollutants such as NO*x*. Therefore, the soot formation model such as the model in the reviewed study in this paper should be employed for simulations of coalcombustion fields.

4. Prospects for research and development for coal combustion

Although the great efforts for the development of accurate numerical simulation technologies for coal





Fig. 26 Comparison of the radial distributions for (a), (b) the soot LII signal (Hayashi J. et al., 2013) and the calculated soot volume fraction, (c), (d) the Mie scattering signal (Hayashi J. et al., 2019) and the calculated surface area of coal particles, (e), (f) the calculated gas temperature and the O_2 concentration, and (g), (h) the net soot formation rate at a HAB = 60 and 120 mm, respectively. Reprinted with permission from Ref. (Takahashi H. et al., 2019). Copyright: (2019) Elsevier B.V.

combustion fields have been made by various researchers, there are still a large room for improving the accuracy of the simulation technologies for coal combustion fields. Recently, the flamelet approach, which can treat detailed chemistries with relatively low computational cost by employing the tabulation method, has also been applied for





Fig. 27 Effect of soot radiation on the ensemble-averaged gas temperature distribution. Reprinted with permission from Ref. (Takahashi H. et al., 2019). Copyright: (2019) Elsevier B.V.

numerical simulations of coal combustion fields (e.g., Watanabe J. et al., 2017, Wen X. et al., 2019). However, the detailed chemistry for volatile matter combustion has not been developed yet, because detailed molecular for heavy species such as tar cannot be identified due to its complexity. Therefore, the postulated substances such as C₆H₆ are employed as volatile matter, although actual tar species are much heavier species than C₆H₆. Although the methods for flamelet approach have been already developed, the accuracy of numerical simulations cannot be improved until the detailed chemistries for volatile matter and soot particles will be developed. Thus, the clarification of detailed chemistries for volatile matter and soot particles is expected in the future. The accurate prediction technologies for NOx emission from coal combustion fields is another important issue. Although the NOx emission can be qualitatively predicted by the existing NOx models (e.g., Hashimoto N. et al., 2017), developments of more accurate NOx formation/reduction models are expected to improve the accuracy of the prediction. The prediction of ash behavior in boilers is also important issue (e.g., Matsui Y. et al. 2019).

In addition to those issues mentioned above, the plants themselves require efficient use; moreover, new types of fuel, such those produced from using renewable energy is expected, because the CO_2 emissions per unit of obtained energy from coal-fired plants are larger than those from other energy plants. One of possible new type fuels for coal-fired boiler is ammonia, which is promising energy carrier in the future. Since ammonia does not have carbon in its molecule, the direct combustion of ammonia can be an option. Many researches have been conducted on the fundamental combustion characteristics of ammonia (Kobayashi et al., 2019, Okafor E.C. et al., 2019, Ichimura R. et al., 2019, Hayakawa A. et al., 2015). Although verification tests and bench-scale tests using large-scale burners have been conducted for the mixed combustion of ammonia and pulverized-coal particles (Kobayashi et al., 2019), research is currently lacking with respect to the fundamental characteristics of mixed combustion of ammonia with pulverized coal particles.

Accordingly, our research group recently started to conduct the fundamental research on the mixed combustion characteristics of ammonia with pulverized coal particle cloud (Hashimoto N. et al, 2019a, 2019b). The flame propagation characteristics of an ammonia-coal particle cloud in turbulent fields has been investigated by using a fan-stirred constant volume vessel (Hadi K. et al., 2019). The developments of the mixing combustion models using the experimental results from these researches for the ammonia-coal particle cloud mixture for numerical simulations is expected in the near future.

5. Conclusions

In this review paper, recent progress of research concerning coal-particle devolatilization model and the soot formation in pulverized coal combustion fields is reviewed. Employing the developed models for coal particle devolatilization and the soot formation can greatly improve the accuracy of numerical simulations for coal combustion fields. The accuracy of the models has been validated by the experimental data measured by various optical diagnostics, such as LDV, LII, TiRe-LII, and LIF. Since non-validated models can cause significant errors in numerical simulations, the use of our measured data by various researchers will be welcomed.

Acknowledgements

Reviewed work in this paper were partly supported by JSPS KAKENHI Grant Number 15637712, MEXT as "Priority issue on Post-K computer" (Accelerated Development of Innovative Clean Energy Systems), JST research promotion program Sakigake (PRESTO) Grant Number JPMJPR1542 and JSPS KAKENHI Grant Number JP19180646.

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Review Paper

Scaling-up the Calcium-Looping Process for CO₂ Capture and Energy Storage[†]

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Abstract

The Calcium-Looping (CaL) process has emerged in the last years as a promising technology to face two key challenges within the future energy scenario: energy storage in renewable energy-based plants and CO_2 capture from fossil fuel combustion. Based on the multicycle calcination-carbonation reaction of $CaCO_3$ for both thermochemical energy storage and post-combustion CO_2 capture applications, the operating conditions for each application may involve remarkably different characteristics regarding kinetics, heat transfer and material multicycle activity performance. The novelty and urgency of developing these applications demand an important effort to overcome serious issues, most of them related to gas-solids reactions and material handling. This work reviews the latest results from international research projects including a critical assessment of the technology needed to scale up the process. A set of equipment and methods already proved as well as those requiring further demonstration are discussed. An emphasis is put on critical equipment such as gas-solids reactors for both calcination and carbonation, power block integration, gas and solids conveying systems and auxiliary equipment for both energy storage and CO_2 capture CaL applications.

Keywords: calcium looping, CO₂ capture, energy storage, CSP, solar energy

1. Introduction

Achieving a sustainable energy transition towards a low carbon society model is one of the main challenges facing humanity in the coming years. The immediate effects of climate change on the environment require urgent actions (IRENA, 2017). Despite important advances on the implementation of renewable energies (IEA, 2015), CO_2 emissions continue to grow, mainly due to the increase in energy demand worldwide (IEA, 2019). Technology pathways to reduce emissions are focused on the large-scale implementation of renewable energy and Carbon Capture and Storage (CCS) technologies.

In the last years, the Calcium-Looping (CaL) process has gained attention due to its huge potential to be integrated in future energy facilities as well as to retrofit ex-

[†] Received 13 June 2019; Accepted 4 September 2019

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TEL: +34 655783930 isting ones. Due to the potential applications of CaL, the process is fully aligned with some of the most important challenges to be solved within the future energy scenario (IRENA, 2018). Thus, the CaL process can be applied in both renewable and fossil-fuel-based power plants as energy storage and CO_2 capture systems, respectively. In addition to these main applications, the CaL process is being investigated for other applications such as Enhanced Oil Recovery (EOR) or hydrogen production (Hanak et al., 2018b). Despite the CaL process in these applications being based on the same basic calcination/ carbonation reaction which has been used in a myriad of other applications by humankind, the specific operating conditions in each case can be very different as imposed by the application (Benitez-Guerrero et al., 2017b).

$$\operatorname{CaCO}_{3(s)} \rightleftharpoons \operatorname{CaO}_{(s)} + \operatorname{CO}_{2(g)} \quad \Delta H^0_r = 178 \frac{\mathrm{kJ}}{\mathrm{mol}}$$
(1)

The CaL process relies on the multicyclic calcinationcarbonation of $CaCO_3$ (Eqn. 1), which can be obtained from limestone as the second most abundant material on earth after water. Regarding CO₂ capture, the CaL process is especially advantageous for its high efficiency and low CO₂-avoided costs (Zhao et al., 2013). The standard



J-STAGE Advance published online 31 March 2020

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cycle for CO_2 capture from flue gas streams uses CaO (previously derived from limestone calcination), to produce CaCO₃ by carbonation at high temperature (~650 °C) (Eqn. 1).

As a thermochemical energy storage system (TCES), the CaL process can be integrated in renewable power plants, e.g. Concentrating Solar Power (CSP) plants, to increase the dispatchability of the system. The process would work as follows: solar thermal power is used to decompose $CaCO_3$ in a solar calciner according to Eqn. 1. The resulting CaO and CO₂ products are stored independently and when energy is demanded, CaO and CO₂ react at high temperature (> 650 $^{\circ}$ C) in the carbonator to release the stored energy while CaCO₃ is regenerated (Chacartegui et al., 2016). The key advantages of TCES systems in comparison with traditional and sensible heatbased energy storage are the higher energy density and its capacity for long-term energy storage (Pardo et al., 2014). On the other hand, depending on the TCES system and the operation conditions, the energy consumption by auxiliary equipment could be higher than in commercial energy storage systems (Bayon et al., 2018; Ortiz et al., 2018a).

In recent years the study of the CaL process has attracted the attention of many researchers. A large number of works have been focused on the CaL process, mainly based on lab-scale analysis and process simulations (Blamey et al., 2010; Ortiz et al., 2019b; Perejón et al., 2016b). Pilot-scale demonstration plants up to 2 MWth have demonstrated the efficiency of the process (Arias et al., 2013; Hanak et al., 2015).

Because of the huge potential scope for the application of the CaL process within the present energy technology pathway in both renewable and non-renewable power plants and in new or retrofitted facilities, a rapid technology advancement as well as a reduction of costs are expected. This manuscript reviews the latest advances and results on an international level with a critical assessment on the technology requirements to scale the process up. Equipment and methods already proved as well as those requiring further demonstration are discussed.

This work is structured as follows: firstly, an overall summary of the CaL process and its applications are carried out. Later, a summary of the latest international R&D projects is present. Through the analysis of the main technology involved, a critical assessment of the current state of the art of the technology is carried out.

Next, steps to facilitate the commercial employment of the CaL process are finally drawn.

2. Current status and challenges on the road to the CaL process employment on a large scale

Based on a very abundant, non-toxic, non-reactive and

widely available natural material such as limestone, the CaL process is considered a cost-effective technology for post-combustion CO_2 capture. As such it could be integrated in the short-term for its relatively easy integration in currently existing fossil fuel power plants (Wang et al., 2011). **Fig. 1** shows the typical CaL process schematic for retrofitting power plants. Since flue gas from coal-fired power plants typically contains a CO_2 mole fraction in the range of 10–15 %, the optimum carbonation temperature would be around 650 °C to achieve a high capture efficiency (~90 %) in the necessarily short residence times of a few minutes (Romano et al., 2013).

Currently, there are several pilot-scale plants testing the CaL process for post-combustion CO_2 capture, with a total installed capacity around 5 MWth (Hanak et al., 2015). The largest facilities are located in Hualien (1.9 MWth) (Chang et al., 2014), La Pereda (1.7 MWth) (Arias et al., 2013) and Darmstadt (1 MWth) (Ströhle et al., 2014). However, several issues must be still addressed for a successful employment of the technology on a larger scale: to enhance the CaO multicyclic activity, achieving an efficient CO_2 capture energy integration and ensuring adequate handling of the solids.

The CaO reactivity towards carbonation decays progressively with the number of cycles before reaching a low residual value (Abanades, 2002; Perejón et al., 2016b; Valverde, 2013a). Under CO₂ capture conditions, the loss of multicycle activity is mainly due to the sintering of CaO grains at high temperature, which reduces the surface area available for fast carbonation (Borgwardt, 1989). As shown in Fig. 2, the evolution of CaO conversion with the number of cycles is, however, highly dependent on the carbonation-calcination conditions (temperature, reactor pressure and atmosphere) (Benitez-Guerrero et al., 2017a) and the type of CaO precursor used (Ortiz et al., 2016b). Conditions that would optimize the integration of the CaL process in CSP plants would involve calcination at lower temperatures, whereas carbonation would be carried out at higher temperatures under pure CO₂. CaO deactivation would be mitigated under these conditions if particles are small enough to avoid pore plugging (Benitez-Guerrero et al., 2017a). On the other hand, the particle size is not a determining factor under CaL conditions to capture CO₂, for which the main limiting mechanism is CaO sintering (Manovic et al., 2009). Pore plugging at CaL conditions can also be avoided if dolomite is used as CaO precursor instead of limestone (Benitez-Guerrero et al., 2017a).

CaO deactivation, which can be partially counterbalanced by introducing a certain amount of fresh CaCO₃ as a make-up flow (Romeo et al., 2009), leads to a large mass of recirculating inactive solids, which in turn leads to several issues: i) equipment oversizing; ii) higher energy consumption for cooling/heating; iii) lower energy storage density, and iv) higher energy consumption for solids





Fig. 1 Conceptual integration of the CaL process as a post-combustion CO_2 capture system. The process was originally conceived as two interconnected fluidized bed reactors (calciner and carbonator) (Shimizu et al., 1999).

conveying.

A proper energy integration is crucial for the feasibility of the CaL integration on a commercial scale. Due to the high enthalpy of the reaction and the high turning temperature (~896 °C at atmospheric pressure under CO₂), a huge amount of thermal power is required and released during the calcination and carbonation reactions, respectively. An adequate integration between both reactors is essential to reduce both the energy penalty in the power plant and the equipment size, which critically determines capital expenditures (Brown et al., 2016). Recent works have been focused on this issue (Hanak et al., 2018a; Lara et al., 2013; Ortiz et al., 2016a; Spinelli et al., 2017). Solids-solids heat exchangers would be useful for improving the integration, albeit they are not available yet at the commercial scale (see Section 4.6). The efficiency of integration greatly conditions the energy consumption per kilogram of CO₂ avoided (SPECCA), whose value for the already mature technology based on amines is around 4 MJ/kg CO₂ (CAESAR project, 2011). The CaL process has the potential to reduce further this value to around 2-3 MJ/kg CO₂ (Astolfi et al., 2019; Ortiz et al., 2016b; Romano, 2013). Energy penalty values in the range of 3-9 % are reported in the literature (Perejón et al., 2016b).

Other challenges for the CaL employment on a large scale are related to achieving an efficient solids handling through the different components of the plant. This involves high-temperature particle conveying, reactors and storage tank feeders to counteract the negative effect of cohesiveness on the powder flowability if fine particles are used (Espin et al., 2019; Valverde, 2013b) or attrition (Alonso et al., 2018; Ströhle et al., 2009).



Fig. 2 Effective CaO conversion (Xef) with the number of cycles (N) for limestone and marble (natural CaO precursors) for different CaL conditions corresponding to (a) CSP energy storage (calcination under He atmosphere at 725 °C, carbonation under pure CO₂ at 850 °C) and (b) CO₂ capture (calcination under 70 %v/v CO₂ at 950 °C, carbonation under 15 %v/v CO₂ at 650 °C). Effective CaO conversion is defined as the ratio of CaO converted to the total mass of sorbent including inert solids if existing. Reprinted with permission from Ref. (Benitez-Guerrero et al., 2017a). Copyright: (2017) Elsevier.

The CaL process is also considered a promising technology for improving dispatchability in CSP plants by means of thermochemical energy storage. The process was already proposed in the 1970-80s (Flamant et al., 1980; Wentworth and Chen, 1976). The CSP-CaL integration has been the subject of recent works (Chacartegui et al., 2016; Sakellariou et al., 2015). A comprehensive review on the CSP-CaL system was published by Ortiz et al., 2019b. Fig. 3 shows the conceptual process schematic for the CSP-CaL integration (TCES system). Due to the high temperature and the large enthalpy of the reaction, high thermal-to-power efficiencies could theoretically be reached from the CSP-CaL integration (> 45 % (Alovisio et al., 2017)). Remarkably, the system uses widely available, non-toxic and cheap (\$10/tonne (Hanak and Manovic, 2017a)) limestone as a raw material and allows a notable increase in the dispatchability of CSP plants because of the high energy density of the system (Pardo et





Fig. 3 Conceptual process for a thermochemical energy storage system (TCES) based on CaL.

al., 2014). A large number of lab-scale tests are being carried out to analyze the CaL process as a TCES system, mainly related to the reaction kinetics (Kyaw et al., 1996; Ortiz et al., 2018b; Salaudeen et al., 2018) multicyclic CaO conversion (Benitez-Guerrero et al., 2017a, 2017b; Sarrión et al., 2018) and process integration (Alovisio et al., 2017; Chacartegui et al., 2016; Ortiz et al., 2019a).

The integration of the CaL process as a thermochemical storage system in CSP plants shares the same three aforementioned drawbacks to be overcome for the integration as CO_2 capture system. Indeed, the TCES system is still far from commercial maturity. Currently only experimental solar calciners are available on a small scale of a few kWs (Abanades and André, 2018; Flamant et al., 1980; Meier et al., 2004). This is a major challenge that requires a significant effort to bring the CaL technology up to a commercial scale as a TCES system in CSP plants.

3. Current CaL research projects

During the last years, several research projects have been carried out worldwide with the aim of demonstrating the feasibility of the CaL process on a pilot scale, from a few kWth up to 2 MWth. Promising results from these projects are paving the way to scale up the process towards a demonstration stage under a relevant environment.

3.1 CO₂ capture projects

i) <u>SCARLET: Scale-up of calcium carbonate looping</u> technology for efficient CO₂ capture from power and industrial plants (2014–2017) (SCARLET EU project, 2014) The SCARLET project, funded by the European Union's Horizon 2020 research and innovation programme and recently finished, had the goal of validating the feasibility of the CaL technology in an upgraded 1-MWth pilot plant. Successful operation of the pilot plant and optimization of the process parameters was demonstrated, which has been used to provide essential information for scaling up the process to a future 20-MWth pilot plant.

ii) <u>CEMCAP: CO₂ capture from cement production</u> (2015–2018) (CEMPCAP EU project, 2015)

CEMCAP was a project funded by the European Union's Horizon 2020 research and innovation programme. It addressed the capture of CO_2 from cement production by integrating the CaL process. CEMCAP aimed to leverage to Technology Reediness Level (TRL) 6 cement plants with a targeted capture rate of 90 %. Technoeconomic results based on process simulations showed the cost of CO_2 avoided lies between 42–84 \notin t CO_2 depending on the CO_2 capture system.

iii) <u>CLEANKER: Clean clinker production by Calcium</u> <u>Looping process (2017–2021)</u> (CLEANKER EU project, 2017)

This project is also funded by the European Union's Horizon 2020 research and innovation programme. In the same vein as the CEMCAP project, CLEANKER aims at demonstrating at TRL7 the CaL concept in a configuration integrated with the cement industry. Entrained flow technology is considered for the reactors.

iv) FLEXICAL: Development of flexible coal power plants with CO₂ capture by Calcium Looping (2016–2019)



(FlexiCaL EU project, 2016)

FLEXICAL project, funded by the European Research Fund for the Coal and Steel Commission, aims to develop novel flexible calcium looping systems that can work under several flue gas loads. To this end, two process options are tested on a pilot-scale: a highly load-flexible plant concept and an energy storage system using CaO/ CaCO₃ silos.

v) LEILAC: Low emissions intensity lime & cement (2016–2020) (LEILAC EU project, 2016)

This project is funded by the European Union's Horizon 2020 research and innovation programme. The LEILAC project is based on the use of an entrained flow reactor to enable an efficient capture of CO_2 from lime and cement production.

3.2 Energy storage projects

Below, several interesting projects about integrating the CaL process as TCES are summarized:

i) <u>SOCRATCES: Solar calcium-looping integration for</u> <u>thermochemical energy storage (2018–2020)</u> (Socratces <u>Project, 2018)</u>

The SOCRATCES project, funded by the European Union's Horizon 2020 research and innovation programme, aims at exploring the feasibility of the CSP-CaL integration by erecting a pilot-scale plant that will serve to reduce the core risks of scaling up the technology as well as allow further understanding of the process integration.

ii) <u>Carbon Dioxide Shuttling Thermochemical Storage</u> Using Strontium (2014–2015) (Mei, 2015)

This project was awarded under the ELEMENTS program supported by the USA SunShot Initiative (DOE). The project was based on the calcination/carbonation of strontium-based carbonates, which would allow discharging the stored solar energy at very high temperatures (over 1000 °C), however, this can hardly be achieved with current CSP with tower technology. The much higher cost of the sorbent precursor (SrCO₃) –\$580/tonne (Jin et al., 2018) – as compared to a price of around \$10/ton for natural limestone (Hanak and Manovic, 2017a) is a serious drawback for commercial expansion on a large scale.

iii) Regenerative Carbonate-Based Thermochemical

Energy Storage System for Concentrating Solar Power (2015–2016) (Gangwal and Muto, 2017)

Within the ELEMENTS program, the Regenerative Carbonate-Based Thermochemical Energy Storage System for Concentrating Solar Power project was aimed at developing a TCES for CSP based on reversible gas-solids reactions of carbonate and silicate sorbent-based materials on a bench scale. Overcoming the multicyclic CaO deactivation was a key point of the project. A synthetic, highly refined and tailored reinforced CaO sorbent exhibited a very stable multicycle behavior with a residual sorbent capacity of around 0.3, although its use in practice would be conditioned by a considerable increase of material costs and technical issues in the Ca-based synthetic material fabrication.

iv) Demonstration of High-Temperature Calcium-Based Thermochemical Storage System for use with Concentrating Solar Power Facilities (2014–2018) (Muto and Hansen, 2019)

This project, funded by the APOLLO program (DOE), aimed to demonstrate a novel high-temperature calciumbased thermochemical storage system for use in CSP facilities, which is directly related to the CSP-CaL system. The results obtained are described in Muto and Hansen, 2019.

v) SOLPART: High-temperature Solar-Heated Reactors for Industrial Production of Reactive Particulates (2016–2019) (Flamant et al., 2018)

This project is funded by the European Union's Horizon 2020 research and innovation programme. The main objective of the SOLPART project is to develop, at high temperature (800–1000 °C), a pilot-scale (30–50 kW) 24 h/day solar process suitable for supplying the thermal energy requirement for CaCO₃ calcination by high-temperature solar heat (Flamant et al., 2018). Although this project does not consider thermochemical energy storage, its results are of utmost interest for the CaL process as they would expand the knowledge on solar calcination, high-temperature solar reactors, the transport of high-temperature solid materials and high-temperature thermal storage, all of which are fundamental for further development of the CaL process as a TCES.

4. Technology scale-up

The CaL process has been widely tested on a pilot scale (~2 MWth) as a post-combustion CO_2 capture system (Hanak et al., 2015), while the first facilities are being developed to test it as a TCES system (Muto and Hansen, 2019; Socratces Project, 2018). Despite the promising preliminary results achieved on the pilot scale, several technological challenges must be overcome to permit scaling up the technology. The main technologies needed that are already available at commercial level as well as those under development are reviewed next.



4.1 Calciner

Achieving a proper calcination of particles is crucial for a highly efficient CaL process. When applied to capture CO₂, calcination under a high CO₂ partial pressure requires a temperature of around 930-950 °C to occur over short residence times (few minutes) (Perejón et al., 2016b). The high enthalpy of the reaction and the high reaction temperature involves supplying a high amount of energy to the calciner, which can be satisfied by means of oxy-combustion to ensure an almost pure CO₂ stream at the calciner exit ready to be compressed and stored or reused. An important issue to be considered under these harsh calcination conditions is the enhanced CaO sintering, which negatively affects CaO conversion at the carbonator (Maya et al., 2018). To decrease the calcination temperature down to around 725 °C (Valverde and Medina, 2016), the CO_2 partial pressure should be reduced by introducing a certain amount of inert gas in the reactor such as steam or helium (Berger, 1927) that should be separable from CO_2 . In the case of steam, CO_2/H_2O separation could be carried out by condensation, whereas if He is used, CO₂/He selective membranes or Pressure Swing Adsorption (PSA) could be employed. In these cases, however, the energy penalty is increased as compared to calcination by oxy-combustion. Alternatively, calcination could be carried out under partial vacuum (Beruto et al., 2004), which, however, raises the level of complexity to avoid air leakages. Another option is to provide the heat for calcination in an indirect way through a heat transfer wall or heat pipes (Hanak and Manovic, 2017b). This option would avoid the need of oxy-fuel combustion, which contributes to most of the energy consumption in the CaL process (Ortiz et al., 2017b). On the other hand, heat transfer limitations are main challenges yet to be solved. The LEILAC project is currently assessing the possibility of providing heat through a heat transfer wall from natural gas combustion (Hills et al., 2017).

In general, a large-scale calciner should provide: i) enough residence time for particles to reach the target temperature and reaction completion; ii) fast calcination under the required conditions for each application; iii) good heat transfer coefficients; iv) minimization of thermal gradients and non-homogeneous conversion; v) prevention of particle attrition and agglomeration vi) proper management of elevated gas and particle flow rates.

Calcination is a well-known process on a large industrial scale since it constitutes the basis of cement production. The commercial reactor in this case is a rotary kiln, which consists of a steel tube with a length-to-diameter ratio in the range of 10–38:1 (Schorcht et al., 2013) with maximum working temperatures of ~2000 °C and scalable to large sizes (> 200 m long) in order to produce around 3600 tons/day (Schorcht et al., 2013). Usually, rotary kilns are coupled with particle preheaters where the gas effluent from the calciner at 1000 °C preheats the solids entering the kiln up to 700–800 °C. The existing knowledge on calcination on a large scale from the cement industry may play a key role for the development of the CaL process. In fact, the synergy between the cement industry and the CaL process has led researchers to investigate the integration of the CaL process in cement plants to capture the CO₂ released during calcination in rotary kilns (De Lena et al., 2019). CO₂ emissions from cement plants represent about 7 % of the total CO₂ emission from large stationary sources (Romano et al., 2014).

The CaL process for post-combustion CO₂ capture was originally conceptualized as a system of two interconnected fluidized bed (FB) reactors (calciner and carbonator) operating at ambient pressure (Shimizu et al., 1999). To date, most of the process schemes and pilot test facilities are based on FB reactors including moving bed (MB), circulating fluidized bed (CFB) or bubbling fluidized bed (BFB) reactors (Hanak et al., 2015). FB reactors, which are widely used in industrial processes, provide a large gas-solids contact surface, thus enhancing heat/mass transfer (Yates and Lettieri, 2016). Fluidizability is critically conditioned by particle size (Valverde, 2013b). In the case of fine cohesive powders ($d_p < 30 \mu m$), interparticle attraction forces prevail over hydrodynamic and gravitational forces (Castellanos et al., 1999), which leads to agglomeration, gas channeling and plugging phenomena that hinder uniform fluidization (Raganati et al., 2018). Fine particles, with a large surface-to-volume ratio, would, however, provide a high gas-solids contact if fluidizable. This represents an important advantage for the CaL process, as fast calcination is required. In its application for energy storage, the negative effect of pore-plugging during carbonation is minimized if fine particles are used, thus enhancing multicycle CaO conversion (Benitez-Guerrero et al., 2017a). A number of fluidization-assisting techniques have been proposed in the literature that could be employed to enhance the flowability of fine particles in the CaL process (Valverde, 2013b). Nevertheless, current commercial cyclones would not be able to trap particles elutriated in the fluidizing gas of a size below ~10 µm (Zhao et al., 2006).

Entrained-flow reactors, widely employed in the cracking industry (Chuachuensuk et al., 2013), can be an alternative technology to FB reactors for the calcination of fine particles and as such, reactors are being investigated for both CO_2 capture and energy storage CaL applications in (LEILAC EU project, 2016) and (Socratces Project, 2018) projects, respectively.

Rotary kilns have been also proposed for CO_2 capture as pilot-scale prototypes (Chang et al., 2013; Wang et al., 2010) (**Fig. 4**). In addition to the maturity and scalability of this technology, efficient heat-mass transfer and





Fig. 4 Calciner based on a rotary kiln for post-combustion CO_2 capture. This configuration takes advantage of synergies with the cement industry. Reprinted with permission from Ref. (Wang et al., 2010). Copyright: (2010) American Chemical Society.

gas-solids contact are key advantages of rotary kilns. Moreover, the solids residence time can be accurately controlled by adjusting the kiln rotation speed (Abanades and André, 2018), which is critical to achieve efficient calcination in the face of unforeseen changes in reactor conditions, mainly temperature variations. Thus, an increase of reactor temperature (with unwanted effects such as promoting sintering) could be counterbalanced by increasing the amount of solids and/or reducing the solids residence time. As in the case of entrained-flow reactors, rotary kilns could be properly operated even for fine particles (Moumin et al., 2019).

4.1.1 Solar calcination

Solar calcination has attracted the attention of esearchers since the early 1980s (Badie et al., 1980; Flamant et al., 1980). Using concentrated solar power to carry out the calcination reaction would allow: i) to store solar energy by means of the CSP-CaL scheme (Chacartegui et al., 2016); ii) to reduce non-renewable fuel consumption in CO_2 capture applications with added technical, economic and environmental advantages (Tregambi et al., 2015) and iii) to reduce the high energy consumption associated with the endothermic reaction in industrial processes (i.e. cement industry) (Flamant et al., 2018). Despite the huge potential of solar calcination, solar particle receivers still remain on the small demonstration scale (Moumin et al., 2019).

The main candidates such as solar calciners proposed are based on diverse technologies such as falling particle receivers (Ho, 2016), centrifugal reactors (Abanades and André, 2018) and fluidized bed receivers (Flamant et al., 1980). In general, solar particle receivers can be classified by the way particles are irradiated, either directly or indirectly. In the latter case, heated tubes or other receptors are used. A proper selection of the solar particle receiver to be used for carrying out the calcination of CaCO₃ particles is dependent on a multitude of factors, mainly related to the reaction conditions (temperature, atmosphere composition, particle size) that determine the residence time required to achieve full decomposition. Solar receiver characteristics (thermal emittance, solar absorptance, etc.) and thermal properties of the CaCO₃ and CaO particles entering the solar calciner also play a relevant role. CaCO₃ has a poor solar absorptance (Flamant et al., 1980). Thus, indirect heating would be preferred for calcination (Ho, 2016). Since carbonation of CaO in the carbonator reactor would not occur completely, a mixture of CaCO₃ and CaO solids would enter the solar calciner. CSP with tower technology is the most suitable system for integrating a solar-calciner because of the high temperature needed in the reactor close to the turning temperature of the calcination/carbonation reaction.

Falling particle receivers

Falling particle receivers are based on the direct heating of particles that fall while being irradiated by a beam of concentrated solar energy flux. According to Ho, 2016, the most interesting features of falling particle receivers are: i) unlimited maximum solar irradiance (> 2000 kW/ m^2); ii) maximum temperature > 1000 °C; iii) thermal efficiency between 50–90 %, and estimated cost of about 125 \$/kWt, which could be lower than molten salt receivers cost (Ho, 2016; Mancini et al., 2011). On the other hand, particle attrition is a critical issue that can be promoted in falling particle receivers. This technology seems to be scalable to 10–100 MWe power tower systems (Ho, 2016).

Several previous works have analyzed the main characteristics of falling particle solar receivers. Siegel et al.



developed a 2-MWt on-sun test of a falling particle receiver. The performance model indicated that an 80 W/cm² average flux will be required to achieve 900 °C given an inlet temperature of 600 °C (Siegel et al., 2010). When the particle mass flow is increased, the output temperature is decreased, albeit thermal efficiency is improved. A possibility to increase the particles' residence time is to recirculate the hot particles into the curtain (Christian and Ho, 2013; Ho et al., 2013). Another possible strategy to raise the particles' outlet temperature is to hinder the flow of falling particles by using chevron-like meshes (Mehos et al., 2017). Ho et al. (Ho et al., 2016) studied the performance of a 1-MWth high-temperature falling particle receiver in an on-sun test with continuous recirculation. Ceramic particles (with notably higher absorptance than $CaCO_3$) were used in the test. The peak particle temperatures reached were over 700 °C with a thermal efficiency of ~65 % (Ho, 2016).

Falling particles receivers have a promising future because of their scalability potential, good performance and lower complexity than other solar particle receivers. However, pilot-scale experiments using CaCO₃ particles are still being performed to properly evaluate the potential of these receivers for the CSP-CaL integration.

Centrifugal particle receivers

Since rotary kilns are currently used to carry out calcination on a very large scale, this technology is especially interesting for the CSP-CaL integration. Nevertheless, for its use as a solar receiver, the rotary kiln must be properly adapted to enable heating by concentrated solar irradiation.

The main advantages of rotary kilns for solar calcination are (Abanades and André, 2018): i) adjustable residence time of particles by controlling the tube rotational speed and tilting angle; ii) high temperatures achievable in the cavity; iii) solids conversion in continuous mode and in a controlled atmosphere; iv) uniform radial heating; v) good heat transfer thanks to the direct contact of the rotating particle bed with the hot tube walls; vi) possibility of operation in co-current or counter-current flow, which allows solids preheating by the exhaust gas. A calciner based on a solar rotary kiln technology was proposed as early as 1980 by Flamant, Badie et al. (Badie et al., 1980; Flamant et al., 1980). The reactor is almost horizontal, with an inclination of 5° to facilitate particle transport. These works highlighted the relevance of the radiative properties of the solar reactor. A thermal efficiency of 0.1-0.3 was achieved with a maximum calcination conversion of 0.6 by using a 2-kWt solar furnace reactor with a total absorptance of about 0.9-1 due to the cavity effect. Excellent transfer coefficients between the bed and the internal wall were reported. Meier et al. developed two 10-kWth solar reactors to investigate solar



Fig. 5 Conceptual schematic of an FB solar receiver with beam down technology. The concept was presented in Chirone et al., 2013.

calcination. One of them was directly irradiated (Meier et al., 2004) while the other one was irradiated indirectly (Meier et al., 2005). Maximum conversion efficiencies of 20 % and 38 % were achieved for directly and indirectly heated solar reactors, respectively, with a solar flux input of 2000 kW/m². For the directly irradiated reactor, the typical efficiency obtained in several tests reached 13 % while the maximum efficiency was about 20 % (Meier et al., 2004).

An indirectly heated reactor design seems especially interesting for the CSP-CaL integration since CO_2 emissions are avoided. The indirectly heated reactor proposed by Meier at al. (Meier et al., 2005) consists of a tilted cylindrical steel drum with ceramic insulation. In this case, an adequate gas conveying system is needed to ensure proper gas circulation across the receiver. Typical reactor overall efficiencies vary between 25.2 and 34.8 %, depending on the rotational speed (8–18 rpm), mass flow rate (2–8 kg/h), and particle size (2–3 mm) (Meier et al., 2005).

Main reactor energy losses are caused by re-radiation (13.6%), conduction (20.5%), and sensible heat of the products (20.2%), whereas the remaining losses (14.2%) are mainly due to loss of material and convection heat losses. In this case, an improved reactor design incorporating a recovery thermal energy system and minimizing heat loss by convection and conduction would raise efficiencies up to 70%.

Fluidized bed receiver

Fluidized bed (FB) reactors display higher thermal inertia than rotary kilns. Therefore, continuous operation is improved in the former, as the thermal regime can be maintained in the case of small fluctuations of solar radiation (Flamant et al., 1980). Both rotary kilns and FB reactors have the potential for rapid employment since the technologies on which they are based are already mature in the cement industry and FB-boiler manufacturing, re-

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spectively.

Flamant et al. (Badie et al., 1980; Flamant et al., 1980) proposed an FB reactor to carry out the CaCO₃ decomposition. The total absorptance of the fluidized bed depends on both the particle emittance and the bed physical properties (porosity, particle size, fluidization regime) (Flamant et al., 1980). Salatino et al. (Salatino et al., 2016) analyzed the thermal performance of a bubbling fluidized bed of sand particles to store energy from CSP in a sensible form. To evaluate the hydrodynamics of the process, a near-2D fluidized bed prototype was constructed (Migliozzi et al., 2017). The use of compartmented dense gas fluidized beds was proposed by Chirone et al. (Chirone et al., 2013) (Fig. 5). These compartments are: i) the receiver, located around the cavity through which concentrated solar rays enter by means of a beam-down technology; ii) the heat exchanger section, where the sensible heat of solids is released to a steam cycle; and iii) storage. Dynamic simulation results showed an overall thermal efficiency of up to 71 %. This study set the bases for the construction of a 100-kWt solar FB prototype within the SOLTESS project (Chirone et al., 2013).

A SOLTESS pilot-scale plant could be suitable to attain the calcination of limestone, since the achievable temperatures reached 900 °C. Using CaCO₃ instead of sand, or a mixture of both, would allow storing energy in both sensible and thermochemical form as proposed in Valverde, 2015.

Summarizing, in addition to particle size effects, the existence of thermal gradients and the uncontrollability of the flux profile across the reactor are important challenges to be solved in both solar and non-solar calciners. In particular, solar calcination has specific issues to scale up such as: i) transfer losses in the high-temperature solar receiver, particularly re-radiation losses; ii) heat transfer to particles by radiation and iii) problems derived from thermomechanical stresses imposed on the solar receiver.

4.2 Carbonator

A proper design of the carbonator reactor is critical to ensure an adequate reaction between CaO and CO₂, either to release the stored energy in TCES schemes or to capture CO₂ from the flue gas in non-renewable power plants. Unlike calcination, carbonation does not occur completely in the required short residence. Typically, limestonederived CaO conversion reaches a residual value after a few cycles below 0.1 at conditions for CO₂ capture (Abanades, 2002). Remarkably, CaO conversion is highly dependent on the reaction conditions (Benitez-Guerrero et al., 2017b) and the particles' residence time in the carbonator (Perejón et al., 2016a). This shows the importance of a correct sizing of the carbonator so that the particles can react appropriately during a certain time of residence,



Fig. 6 Conceptual schematic of a continuous CFB carbonator reactor. Reprinted with permission from Ref. (Charitos et al., 2011). Copyright: (2011) American Chemical Society.

which will enhance the efficiency of the reaction (Ortiz et al., 2015).

A large-scale carbonator must provide: i) enough residence time of the particles to reach the target temperature and allow for a satisfactory carbonation conversion; ii) small thermal gradients and non-homogeneous conversion; iii) homogeneous heat transfer to the reactor's wall; iv) small temperature differences between solids entering the reactor and the carbonator temperature to avoid reactor cooling and the consequent reaction stop, and v) low level of particle attrition and agglomeration.

Similarly to the calciner, most of the carbonators proposed are based on FB reactors (Hanak et al., 2015). **Fig. 6** shows a schematic of a typical CFB carbonator reactor. High carbonation efficiencies (~90 %) (Romano, 2012) are achieved due to the good mass and heat transfer coefficients achieved using fluidization. High-intensity acoustic fields could improve the carbonation efficiency (Valverde et al., 2013), allowing even fluidization of cohesive particles. This issue is analyzed, together with other assisting methods for fluidization in Raganati et al., 2018. Nevertheless, fluidization-assisting techniques for improving fluidization and carbonator efficiency have been tested on a lab scale. Additional effort is required to bring these options to large-scale FB reactors. The carbonator



on a large scale for post-combustion CO_2 capture is characterized by a large size (volume ~18 m³/MWe; solids inventory ~1300 kg/MWe (Romano, 2012)). In contrast, in a 100-MWth CSP-CaL plant, the carbonator size could be significantly reduced (128–234 kg/MWe) (Ortiz et al., 2018b) because of the enhanced kinetics and the higher multicycle CaO conversion at conditions for energy storage (Benitez-Guerrero et al., 2017a; Kyaw et al., 1998).

The use of entrained flow reactors has already been developed for carbonation on a pilot scale. This type of reactor is employed in the cracking industry (Chuachuensuk et al., 2013) with the possibility of handling fine particles that are difficult to fluidize in FB reactors. In the CSP-CaL integration, the use of fine particles would serve to achieve a notably higher CaO conversion under TCES typical conditions (high CO₂ partial pressure and high temperature at the carbonator) (Benitez-Guerrero et al., 2017a). In these conditions, carbonation is mainly limited by pore plugging, which hinders the multicycle conversion of CaO particles larger than about 50 µm (Benitez-Guerrero et al., 2017a). Moreover, an entrained flow carbonator could be more favorably integrated in cement plants due to the typical small size of particles used in the production of cement (Plou et al., 2019). CO₂ capture efficiencies obtained in a kW-scale prototype are over 90 % for a Ca/CO₂ molar ratio of 5 and solids residence times just lower than 5 s (Plou et al., 2019). On the other hand, the heat transfer coefficient in the entrained flow reactor would be in the range of 100–200 W/m²K (Ma and Zhu, 1999), which is remarkably low compared to FB reactors (500-800 W/m²K) (Li et al., 2016; Zhang and Koksal, 2006). Therefore the heat transfer between the cloud of gas and particles and the reactor wall has a critical relevance in this type of reactor that must be optimized. The heat transfer rate in the downer is closely related to the system hydrodynamics, the solids suspension density being the most influential factor (Ma and Zhu, 1999). Axial distribution of the average heat transfer coefficient of around 150 W/m²K was found in (Ma and Zhu, 1999). The higher the solids hold-up, the higher the heat transfer coefficient.

In a recently published work (Turrado et al., 2018), the carbonation was tested in a 6-m-long and 0.1-m-diameter downer reactor for CO_2 capture, where particles are injected at the top of the carbonator and move downwards together with the gas. Considering just 3 seconds for the solids residence time, the carbonation degree was around 0.06 under a 15 %v/v CO_2 atmosphere (typical concentration for post-combustion CO_2 capture). The authors found that the higher the CO_2 concentration, the higher the reaction rate, which is a relevant observation for CSP-CaL integration according to the proposed configuration in Ortiz et al., 2018b, where carbonation takes place under a pure CO_2 atmosphere. Researchers at the University of Ohio

tested a 120-kWth pilot plant in which the carbonator was an entrained bed operated at 450-650 °C (Wang et al., 2010). A test campaign was performed to assess the simultaneous capture of CO2/SO2 released by fuel combustion. The gas entering the reactor was preheated to the carbonator temperature by means of auxiliary heaters. Results showed almost 100 % CO₂ capture levels (Ca:C mole ratio of 1.6) by using particles of mass median diameter (D_{50}) of 3 µm. The capture efficiency was decreased using larger particles due to the lower reactivity (particles of sizes in the range 3-600 µm were tested). As expected, the higher the particle residence time, the higher the conversion. A similar carbonator configuration was tested at Cranfield University (Hanak et al., 2015). They also found that carbonation was enhanced as the particle size was decreased, which was attributed to the increase of the surface-to-volume ratio.

De Castilho and Cremasco compared the performance of downer and riser reactors (De Castilho and Cremasco, 2012). Downer reactors present a more uniform flow in both radial and axial profiles. At the entrance of the downer, the flow is less complex and more predictable in the center next to the solids feed (De Castilho and Cremasco, 2012). Particle velocities are higher in downer reactors and are more diluted (Bolkan et al., 2003), which has to be carefully assessed in the carbonator design. A 1D model of an entrained flow carbonator was proposed in Spinelli et al., 2018, and is currently being developed on a pilot scale within the SOCRATCES project (Socratces Project, 2018) to analyze the reactor behavior in the CSP-CaL integration.

Typically, carbonation reactors are tested/simulated at ambient pressure for post-combustion CO_2 capture (Dean et al., 2011). On the other hand, carbonation under pressure (3–5 bar) would improve the thermochemical energy storage efficiency by the direct integration with a CO_2 Brayton cycle (Chacartegui et al., 2016; Ortiz et al., 2017a).

4.3 Power cycle

The high enthalpy of the exothermic carbonation reaction and the high reaction temperature require optimizing the energy integration to maximize the process efficiency. In the carbonator, it is crucial to extract the carbonation heat released not only for enhancing power production but also for keeping the reactor at the desired temperature and avoiding its increase to the equilibrium temperature, which would stop the reaction (Ortiz et al., 2018b).

As usual in power block technology, the power cycle to be integrated with the CaL process should be characterized by: i) a high efficiency (~45 %), taking advantage of the high temperature heat source (650–1000 °C depending on both the CO₂ partial pressure and the absolute pressure

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in the reactor) (Alovisio et al., 2017); ii) the use of turbomachinery available on a commercial scale; iii) the integration of high-efficiency heat exchangers (even for solids-based configurations) to take advantage of the heat released during the CaL process; iv) minimum cooling and heating consumption from utilities, and v) water consumption for cooling to be as low as possible. Air cooling would be preferred in CSP-CaL integration.

A Rankine power cycle has been proven to be especially suitable for CaL-based CO₂ capture to take advantage of the heat released during carbonation (Perejón et al., 2016b). Rankine cycle technology is well known as it is the basic technology for both renewable and nonrenewable power production, which minimizes implementation risks. Moreover, the current Rankine cycle state of the art shares some synergies with the carbonator reactor. High efficiencies were reached by integrating a supercritical steam Rankine cycle (Stein and Buck, 2017), which is currently commercially used in fossil-based plants with capacities higher than 400 MWe. Several process schemes have been proposed to analyze the potential of integrating a Rankine cycle into the carbonator (Hanak and Manovic, 2017b; Martínez et al., 2011; Ortiz et al., 2016a; Romano et al., 2012; Romano, 2013).

A supercritical steam cycle integrated into the CaL process was proposed in Romeo et al., 2008, which achieved a thermal-to-electric efficiency as high as 40.4 % with a reduced energy penalty (4.5 %). A detailed pinch analysis on the retrofitting of a supercritical steam coal power plant was presented in Romeo et al., 2010. Recently, a supercritical CO₂ Brayton cycle was proposed to be integrated for the decarbonization of coal-fired power plants (Hanak and Manovic, 2016). It was possible to reduce the proposed supercritical CO₂ cycle by 1 % points of the energy penalty of the CO₂ capture process compared to the supercritical Rankine cycle-based-plants (Hanak and Manovic, 2016), although it must be taken into account that supercritical CO₂ technology has not yet reached commercial maturity.

In contrast with integrating the CaL process in nonrenewable power plants, in which the steam power cycle technology proposed is the same as in non-retrofitted plants, the integration of the CaL process in CSP plants as a TCES system could be compatible with a substantial change in the power cycle. Most of the commercial CSP plants are based on a sub-critical Rankine cycle process (Siva Reddy et al., 2013). Typical live steam operation conditions are (T < 540 °C; 100 bar) (NREL, 2017). This usually involves a cycle efficiency lower than 38 % (NREL, 2017), leading to an annual solar-to-electricity conversion efficiency in the overall plant below 20 % (Yogi Goswami, 1998). The power cycle efficiency can be enhanced by integrating high-temperature (> 650 °C) Brayton cycles, which requires higher heat temperatures in the thermodynamic cycle (Stein and Buck, 2017). In the case of the CSP-CaL process scheme, the most efficient configuration is by directly integrating a CO₂ closed cycle (Alovisio et al., 2017; Ortiz et al., 2017a). The CO₂ entering the carbonator in this case should be well above the stochiometric needs in such a way that the excess CO₂ exiting the carbonator passes directly by a gas turbine for power production. Thus, the heat of the carbonation reaction is directly delivered to the power cycle (gas turbine) by using CO₂ as HTF. According to Chacartegui et al., 2016, the optimum pressure ratio (carbonator to outlet turbine pressures) is around 3.2 bar by considering a carbonator temperature of 875 °C, which leads to plant efficiencies above 45 % (without considering solar receiver losses). Other potential power cycles were analyzed (Ortiz et al., 2017a), including direct and indirect integration of Rankine cycles, supercritical CO₂ cycles and combined cycles.

4.4 Solids storage

Material storage is a key element for the CaL process as a TCES. Previously proposed CSP-CaL integrations include at least three storage vessels for the streams coming from the calciner (CaO and CO₂ vessels) and for the admixture of solids (CaCO₃ and unreacted CaO) exiting the carbonator (**Fig. 3**). Moreover, the use of solids storage tanks in the CaL process integrated as a post-combustion CO₂ capture system could improve the plant efficiency and reduce CO₂ emissions by adapting the CaL operation to the power plant demand (Astolfi et al., 2019; Criado et al., 2017).

A proper sizing of the storage vessels plays a fundamental role in the CaL integration as a TCES system. A guideline about storage sizing can be found in Bayon et al., 2018. Depending on the energy release criterion, the plant can be configured as a peaker (< 6 h of storage), intermediate or baseload plant. Despite the fact that longterm energy storage is a key advantage of TCES systems (Pardo et al., 2014), it was possible to operate the energy storage at high temperatures (Ortiz et al., 2018a) with a similar solar multiple as in current molten salts-based power plants (Casati et al., 2015). High-temperature storage simplifies the CSP-CaL process scheme. Smaller storage tanks than in molten salts plants are expected due to the higher energy storage density in the CaL process. Regarding CO₂ storage, the preferred option is to store it at high pressure (up to 75 bar) in order to guarantee liquid CO₂ storage conditions (considering storage at ambient temperature), and therefore reducing the storage volume (Chacartegui et al., 2016). Recently, it has been proposed to store the CO₂ at atmospheric pressure (thus avoiding CO₂ compression and therefore increasing the process efficiency) in huge vinyl buildings (Muto and



Hansen, 2019).

On a large scale, the storage system should accomplish the following characteristics: i) storage size as small as possible (to reduce costs) while ensuring sufficient storage to meet the operating plant criteria; ii) proper filling regulation and safety operation of the CO_2 gas vessel; iii) minimum cooling consumption from utilities; iv) ensure an adequate atmosphere inside the CaO storage tank to avoid carbonation, which would reduce the energy released to the power cycle; v) high-temperature solids handling devices and lock hoppers if needed.

From a techno-economic perspective, the system must have the highest energy density possible, which allows maximizing storage capacity. In this regard, it is important to address the size of the vessels needed for solids storage, which determines capital costs. To this end, a recent work (Ortiz et al., 2018a) proposed an equation to estimate the energy density of the system considering the particles' porosity and their packing density, process characteristics (pressure and temperature in the reactors and storage vessels) and conversion efficiency.

Most important factors for the solids storage vessel are:

- Capacity: to cover the expected dispatchability of the plant.
- Discharge rate: the storage vessels must deliver the material to a downstream process (calcination/carbonation) at a required rate.
- Solids cohesiveness: prolonged contact between the stored particles under consolidation stresses possibly at high temperature and in the presence of moisture, which enhances interparticle attractive forces (Durán-Olivencia et al., 2020; Valverde, 2013b). Moisture migration, aging and recrystallization may lead to dramatic gains in cohesive strength, agglomeration of smaller particles into larger ones, or caking (Prescott and Barnum, 2000). External forces such as vibrations induced during transportation, expansion and contraction resulting from temperature changes can also significantly enhance consolidation. As a result, an increase of the solids cohesiveness can hinder discharge from the container due to arching or ratholing.
- Attrition: the porous CaO formed upon calcination results in a friable solid (Blamey et al., 2010). Attrition of particles must be properly addressed.
- Safety and environmental concerns: determine explosion or burning risks and adopt adequate explosion/ fire-protection measures. Determine whether contaminants, atmospheric gases, humidity, and temperature can adversely affect the material stored.

4.5 Solids conveying and separation

Solids conveying results are crucial for the CaL process feasibility due to the large amount of solids, in some cases



Fig. 7 OLDS elevator schematic (OLDS elevator, 2019). Copyright: (2019) Olds ElevatorTM.

at very high temperature and under reactive (CO_2) atmosphere, that must be moved in a large-scale plant. CaO particle transportation from the calciner to the storage tank and then to the carbonator is a key issue. Carbonation of the particles must be avoided outside the carbonator which requires a controlled atmosphere in both conveying systems and storage tanks. A solution is to replace the CO₂-rich atmosphere at the calciner exit by a nitrogen atmosphere (system inertization), allowing to reduce the temperature for storage without carbonation.

On a large scale, the solids and gas handling devices must: i) be effective, continuous and reliable, and ii) avoid particle segregation by size. Particles tend to congregate towards the middle, while larger ones fall to the outside (Maynard, 2013; Mehos and Maynard, 2009). Another key requisite is ensuring a low energy consumption. Typical values of consumed energy for the CaL process can be estimated in the range of 3–5 MJ/ton each 100 m (Mills, 2003).

Available technologies to transport high-temperature particles up and down the receiver include mine hoists, bucket elevators, pocket elevators, screw conveyors, pneumatic conveyors, conveyor belts, cleated conveyor belts, metallic belted conveyors, masses elevators, bucket wheels, linear induction-motor-powered elevators and

electromagnetic field conveyors (Ho et al., 2013). An OLDS elevator (**Fig. 7**) is a vertical screw conveyor which seems suitable to be integrated in the CaL process for high-temperature solids elevation, especially if the calciner is located at the top of a solar tower receiver.

Mechanical systems normally have a higher investment cost but a much lower operating cost than pneumatic transport systems (Schorcht et al., 2013). Pneumatic conveying is a well-known technology used in many applications such as the cement and lime industry (Mills, 2003). Therefore, it could expect to be feasible for the CaL process, even if fine particles are employed.

Belt conveyors are cost-effective only when there is a relatively high production rate and the transport distance is long (De La Vergne and Mcintosh, 2000). Many types of feeders exist for belt conveyors, but the most common is the vibrating feeder. Screw feeders have been proposed for the CaL process (European Commission, 2016; Hilz et al., 2017; Zhao et al., 2013), with particles size as small as ~30 µm. One of the key parameters to calculate the volumetric characteristic curve of the screw conveyor is the trajectory angle of particle motion, which affects the filling rate and the theoretical maximum mass flow rate. Several correlations, validated against commercial screw conveyors, predict the fill rate as a function of the rotation velocities and pitches, as well as the outlet mass flow rate as a function of the inclination angles, rotation velocities and pitches (Li et al., 2018).

Solids feeders (hoppers) are critical when using fines due to agglomeration (Turrado et al., 2018). Typical problems with solids hoppers when using cohesive particles are arching or ratholing (Maynard, 2013; Mehos and Maynard, 2009). These effects might give rise to the pulsed inputs of solids (erratic flow) instead of stable flows. According to Turrado et al., 2018, 50 µm is the minimum size of the particles that allows a continuous and controlled flow of solids to be fed into the drop-tube reactor. An option to improve the feeder performance could be to introduce a fluidizing gas at the bottom of the hoppers to ensure mass flow operation by avoiding core flow. Rotary airlocks are important for a dilute-phase system. They enable solids to be fed at a controlled rate into the gas stream (Mehos and Maynard, 2009). This system could be used in the calciner and carbonator to bring into contact both streams (gas and solid particles).

Since gas and solids are stored separately, a separation system must be considered in the plant. At the outlet of the calciner and carbonator, cyclone separators could be used as primary separation devices for relatively coarse particles, with a fabric filter downstream (depending on the particle temperature) in order to remove fine particles (< $20 \mu m$) from the CO₂ flow.

4.6 Heat exchangers

An efficient use of the heat from the different hot streams is critical for the process efficiency. In the case of the hot CO_2 stream exiting the calciner, a gas-gas heat exchanger as a heat recovery steam generator (HRGS) within a secondary steam cycle could be employed, which would generate enough power to carry out CO_2 compression (Ortiz et al., 2018a). Another possibility is to use solids-gas heat exchangers to release energy from the hot CO_2 stream for preheating the CaCO₃ particles entering the calciner (Chacartegui et al., 2016).

Suspension preheaters are well-known technology in the cement industry as gas-solids heat exchangers. The exhaust gases from the calciner flow through the cyclone stages from bottom to top. Particles are added to the exhaust gas just before the uppermost cyclone stage. They are separated from the gas in the cyclones and re-join it before the next cyclone stage (Schorcht et al., 2013). By using this solids-gas heat exchanger, the same exit temperature of the gas and solids streams is achieved from a co-flow arrangement with a considerably high contact surface. Suspension preheaters usually have between four and six cyclone stages, which are arranged one above the other in a 50-120-m-high tower (Schorcht et al., 2013). Due to high level of maturity of this technology, it seems an optimum choice to carry out both CaCO₃ particle preheating in the calciner side and particle cooling in the carbonator side.

The grate preheater is another well-known technique in the cement industry. Particles are fed onto a horizontal grate which travels through a closed tunnel. A fan draws the exhaust gas from the calciner into the top of the preheater. The temperature of the gas could be reduced from > 1000 °C to 150 °C while solids would be heated up to 700-800 °C (Schorcht et al., 2013). Another possible solids-gas direct heat exchanger was proposed by Shimizu et al. (Shimizu et al., 2004). This heat exchanger is an axial flow cyclone in which a quasi-counterflow heat exchange is realized to recover the heat carried by the particles. By using this design, an outlet gas temperature much higher than the particle outlet temperature could be attained. Fluidized bed designs are also a possibility to perform solids-gas heating with high heat transfer coefficients (up to $\sim 600 \text{ W/m}^2\text{-K}$), but have a higher parasitic power consumption and heat losses associated to fluidization (Ho et al., 2017).

Several solids-solids heat exchangers have been proposed to transfer heat between the CaO solids stream exiting the calciner and the CaCO₃/CaO mixture coming from the carbonator, such as a cyclonic preheater (Martínez et al., 2013) or a mixing seal valve (Martínez et al., 2014). To avoid recarbonation of CaO during the cooling process, which notably affects the multicyclic conver-



sion (Valverde et al., 2014), an indirect contact solids– solids heat exchanger with one intermediate heat transfer fluid recirculated within the bulk of both solids could be employed, although this equipment is not fully developed yet on a large commercial scale.

5. Next steps and remarks

The CaL process plays a central role in the nextgeneration post-combustion CO₂ capture technologies. The main improvements are related to enhance the multicyclic CaO conversion, ensure proper solids handling and efficiently recover the high-temperature heat released during the process. As shown in sections **2–3**, important advances have been accomplished and the technology has already been demonstrated on the MWt scale. No major technical barriers have been found for its employment on a commercial scale. Retrofitting coal-fired power plants with the CaL process is considered a viable and competitive technology (Abanades et al., 2015). Next research projects must aim at reaching a Technology Readiness Level (TRL) of 7–8, which implies a commercial demonstration at full scale (IEA, 2014).

The CaL process for energy storage lies at a lower level of maturity. Despite important advances to properly define and test the integration of the CaL process in CSP plants (sections 2–3), the solar calciner (particle receiver) remains as a major technological challenge. Current projects aim to reduce the technological risks progressing from a TRL-4 (technology validated in lab) to a TRL-5 level (technology validated in a relevant environment) (Flamant et al., 2018; Socratces Project, 2018). The huge interest for increasing dispatchability in CSP plants, the high technology development of the CaL process for CO_2 capture as well as the important efforts for developing solar particle receivers (Ho et al., 2017) should contribute to accelerating the employment of CSP-CaL integration on a commercial scale.

Acknowledgements

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727348, project SOCRATCES and by the Spanish Government Agency Ministerio de Economía y Competitividad (MINECO-FEDER funds) under contracts CTQ2017-83602-C2 (-1-R and -2-R).

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Authors' Short Biographies



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Assistant Professor at Universidad Loyola Andalucia. PhD in energy engineering (2018). His research activity is focused on the CaL process for both CO_2 capture and thermochemical energy storage applications. It comprises energetic and chemicals systems modelling. He has published over 25 papers mostly in Q1 journals with more than 600 citations.

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Industrial and biomedical engineer (Polytechnic University of Valencia) and PhD on thermal energy storage (University of Seville), with 4 years of experience in CSP. He currently works at the University of Seville (PSI) teaching heat transfer and thermal engineering.


Modulated Uniaxial Compression Analysis of Respirable Pharmaceutical Powders[†]

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Abstract

We describe a new instrument and method for measuring compressed bulk density of respirable pharmaceutical powders under low compression pressure: the modulated compression tester. The instrument modulates compression and decompression steps, allowing scrutiny of the overall compression response of samples. Compared to established methods for the determination of density and related parameters for pharmaceutical powders, this instrument has the capability of measuring smaller samples. The relative humidity can also be controlled in the instrument (3 % to 95 % RH), allowing assessment of the effect of moisture on compression response. We have used the instrument to determine the compressed bulk density of Trehalose, Leucine, Trileucine, and Mannitol powders of varying crystalline and amorphous compositions and particle size and size distribution, demonstrating that the new modulated compression tester is suitable for low pressure (< 1200 kPa) density measurement of respirable powders (< 10 μ m) and expensive active pharmaceutical ingredients available in limited quantities (typical sample mass requirement of < 100 mg). In addition, the modulation feature of the instrument allows the analysis of the transition from plastic to semi-elastic compression response. The outputs and features of this instrument are useful for formulation development, quality control measurements, discerning between different or similar powders due to differences in the compression response, and optimizing powder compression parameters for pharmaceutical applications.

Keywords: compressed bulk density, respirable powders, powder compression, powder elasticity, dry powder inhalers

1. Introduction

Evaluation of the compression response of fine and respirable pharmaceutical powders is of prime importance because of the implications it has on formulation development, manufacturing and quality of the final product. Adequate characterization of the bulk powder properties is needed through the entire product development lifecycle (de Boer et al., 2017; Sørensen et al., 2005). For solid dosage forms, knowledge of the particle density and powder bulk density are necessary for assessing the aerodynamic properties (Feng et al., 2011), dispersibility (Boraey et al., 2013; Weiler et al., 2010) and parameters that influence powder filling processes, such as flowability (Faulhammer et al., 2014; Osorio and Muzzio, 2013). In order to assess the quality of a final product, the properties of powdered excipients and active ingredients must be precisely and accurately characterized. It is therefore important to characterize the bulk density and compression response of powders for manufacturing and quality control of final pharmaceutical products.

Providing an unambiguous definition of powder density is not straightforward because of the presence of voids within particles and between neighboring particles in a powder. This fact gives rise to a family of density definitions for pharmaceutical powders: true density, particle density, bulk density and tapped density, among others. The true density of a solid object excludes internal and external voids that are not a fundamental part of the molecular packing; thus, true density can be measured reproducibly because it does not include pore volume in its determination (Brockhaus and Carlozzo, 1995). Particle density is the ratio of the particle mass over the volume of the particle with external and internal voids, also known as the hydrodynamic volume (Vehring, 2008). Bulk density is



[†] Received 30 May 2020; Accepted 8 July 2020 J-STAGE Advance published online 29 August 2020

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the mass of the powder in a column divided by its volume, where its volume is the hydrodynamic volume of the particle plus interstitial spaces between particles (USP, 2015). Tapped density is obtained by mechanically tapping the powder in a column at a specified frequency, duration and amplitude until no further volume change can be observed (USP, 2015).

Bulk density and tapped density are routinely used in the pharmaceutical industry to characterize powders (Sørensen et al., 2005). However, bulk density of a powder sample depends on how the sample was handled (USP, 2015). For instance, disturbing the powder sample can result in rearrangement of the particles and a change in the bulk density. In contrast, the tapped density technique deliberately disturbs the powder bed to improve sample packing so that more repeatable density measurements can be made. However, an inaccurate reading of the volume from the measuring cylinder can introduce errors. In addition, bulk and tapped density measurements usually require large amounts of powder, typically using tens of grams (Sørensen et al., 2005; USP, 2015). This becomes a major drawback if expensive, rare, limited-quantity or difficult-to-make samples require analysis. Furthermore, bulk and tapped density techniques are better suited for large particles and where the interparticle forces are small compared to inertial forces. This way, when the powder is handled or tapped, the particles can easily rearrange, and the powder can achieve a repeatable bulk density.

The compression response of fine and respirable powders, which have a mean particle size of less than 10 µm, is dominated by interparticle forces (Sarkar et al., 2017; Shamsaddini-Shahrbabak and Vehring, 2012). The interparticle forces influencing the bulk density of powders are also the interactions that interfere with powder flow (USP, 2015). Particle size and shape are also known to be important determinants of powder flow and compression response (Adeove and Alebiowu, 2014; Kaerger et al., 2004; McKenna and McCafferty, 1982; Patel et al., 2007). Assessing the compressibility of fine respirable powders is uniquely challenging given the increased influence of cohesive forces (Thalberg et al., 2004; Weiler et al., 2010) relative to inertial forces (Desai et al., 2001). The cohesive forces in fine powders may also be influenced by surface characteristics (e.g. rugosity, contact area), intermolecular forces (e.g. Van der Waals interactions), electrostatics, material properties and environmental conditions, in addition to particle size and shape (Baldelli and Vehring, 2016; Sarkar et al., 2017; Weiler et al., 2010). As a result, when compared to powders with larger particles, fine powders are typically more cohesive and display relatively poor flowability and dispersibility; thus, they are not well suited for bulk or tapped density measurements.

The cohesive nature of fine and respirable powders likewise holds implications for powder handling during

manufacturing as well as for delivery efficiency from inhalation devices (Elia et al., 2016; Rudén et al., 2018; Weiler et al., 2010). Powder products that are meant for inhalation (e.g. dry powder inhalers) are compressed at low pressures and packaged into capsules that require additional energy upon use to disperse them for inhalation (de Boer et al., 2017; Faulhammer et al., 2014; Prime et al., 1997). In such a case, it is important to use low compression pressures when packaging the powder product to achieve particle rearrangement, resulting in a loose powder compact. Utilizing low pressures when plastically compressing respirable powders can also mitigate the deformation or fracturing of the particles (Chen et al., 2017; Raut et al., 2016; Sørensen et al., 2005; Vu et al., 2020), preserving the aerodynamic properties of the particles, while minimizing the volume of powder needed for each capsule. As a result, single-value density measurements, such as bulk and tapped density, are unsuitable for relatively cohesive respirable powders, so new methods are required for accurate and reproducible Compressed Bulk Density (CBD) measurements.

For the overall compression response of fine powders to be described, they must be actively compressed, taking into consideration the entire compression curves and elasticity of the powders (Vu et al., 2020). Assuming there is no moisture, a powder column is mostly a two-phase system that consists of air and particles. Generally speaking, when a powder is subjected to a compression force, it will go through a series of either reversible or irreversible compression stages. The former occurs as a result of material elasticity and the latter is due to plasticity of the powder (Chen et al., 2017; Vu et al., 2020). The first stage of the compression process is seen as the displacement of the gaseous phase by the solid phase (powder packing and particle rearrangement) within the bulk as a result of the compression force, leading to the reduction of the bed volume (Klevan et al., 2009; York, 1978). After this stage, many air gaps between particles are filled, yet the particles themselves have not fractured or deformed. Once the bed has reached a sufficiently close packing, it starts showing elastic response to the applied force. At higher compression force, non-elastic materials or those elastic materials that have yielded may show permanent, plastic deformation, and particle fracture and further packing become possible. At very high pressures, the powder bed acts like a solid body.

A powder's compression response strongly depends on the way that particles pack together. When powder is subjected to an axial force, this external force brings the particles closer to one another and causes the volume to reduce. This stage may be referred to as the particle rearrangement stage (Bolhuis et al., 1996; Tousey, 2002; Vu et al., 2020; Yap et al., 2008). It is therefore possible, experimentally, to determine the pressure at which the powder is compressed and starts showing significant reversible response; this is



the transition pressure from plastic to elastic deformation.

In general, CBD measurements are based on uniaxially compressing a powder sample and measuring its density under a defined pressure. A number of studies involving low-pressure compression of pharmaceutical powders have been reported (Faulhammer et al., 2014; Heda et al., 1999; Kostelnik et al., 1968; Llusa et al., 2014; Nikolakakis et al., 1998; Podczeck and Lee-Amies, 1996; Sheikh-Salem and Fell, 1981; Sørensen et al., 2005, 2006). A previous report has also used a commercial compression instrument that can accommodate milligram powder quantities for bulk density measurements (Sørensen et al., 2005). While these studies have demonstrated the use of low-pressure compression for bulk density measurements and the use of small sample quantities, none has experimentally differentiated the compression response of respirable powders between densification due primarily to particle rearrangement, i.e. plastic deformation, from densification due to semi-elastic particle or powder deformation. The ability to experimentally identify these compression responses is only achievable at low pressures and is important for establishing suitable compression pressures for packaging or processing respirable powders. The instrument in this paper is similar to the commercially available Geopyc 1360 (Micromeritics, Norcross, GA), which can only handle larger sample masses, as well as the Texture Analyzer (Stable Micro Systems, Surrey, UK), which is designed for a variety of uses, but is not specifically for density measurements of fine respirable powders and does not have RH control capabilities.

We report here the development of a uniaxial low-pressure and modulated compression instrument for CBD measurements of fine and respirable pharmaceutical powders. The focus of this paper is to demonstrate the capabilities of the new instrument and its ability to differentiate between very similar respirable powders at low compression pressures. We also show details of the modulation compression technique and introduce a new parameter for powder elasticity, which can be used to easily distinguish between plastic and semi-elastic compression response.

2. Materials and methods

2.1 Materials

With the exception of crystalline Leucine (raw material), all powder samples used in this study were produced by spray drying and contain particles with mass median aerodynamic diameters (MMAD) in the respirable range ($\leq 10 \,\mu$ m). D-(+)-trehalose dihydrate (177,613, Fisher Scientific Co., Ottawa, ON, Canada), Trileucine (BCBP2254V, Sigma-Aldrich Corp., St. Louis, MO, USA), L-Leucine (AC125121000, Acros Organics, New Hampshire, NH), and D-mannitol (SLBH1429V, Sigma-Aldrich Corp., St. Louis, MO, USA) are pharmaceutical excipients and were used to produce the powder samples for this study. These excipients were chosen on the basis of their different effects on particle formation, cohesiveness and mechanical properties (Vehring, 2008).

Most of these excipients were spray-dried by themselves or in mixtures to produce the samples shown in **Table 1** and to allow CBD measurements of different formulations, particle sizes and particle size distributions. Monodisperse samples had a particle size distribution with a geometric standard deviation (GSD) of 1.1 while polydisperse

Table 1 Materials and formulations used for compressed bulk density tests, including fully crystalline and fully amorphous materials, different particle sizes and different particle size distribution. The Mass column shows the range of masses needed for a measurement; the geometric standard deviation (GSD) and mass median aerodynamic diameter (MMAD) columns correspond to the size distributions of the spray dried powders (note that the 100 % Leucine sample was the raw material and was not spray dried); and $\rho_{t mix}$ corresponds to the calculated true density of each material or mixture.

#	Trehalose [% w/w]	Leucine [% w/w]	Trileucine [% w/w]	Mannitol [% w/w]	Mass [mg]	GSD	MMAD [µm]	$ ho_{ m t,mix}$ [g/cm ³]
1		100			78.7–79.5	(raw material)		1.29
2	100				58.9–59.3	1.6	2.5	1.53
3	99.6		0.4		86.4–91.7	1.1	9	1.53
4	99		1		103.9–110.2	1.1	9	1.52
5	95		5		72.8–77.3	1.1	9	1.50
6	80	20			63.2-68.5	1.6	2.5	1.48
7	75	25			40.0-42.6	1.6	2	1.47
8	75	25			38.2-40.3	1.6	4.5	1.47
9	55	45			34.6–37.4	1.6	3.6	1.42
10				100	68.3–69.7	1.1	10	1.51
11				100	64.4-65.7	1.6	3.5	1.51



Fig. 1 SEM images of the materials and formulations tested and reported in this paper. The numbering of the images corresponds to the materials and formulations listed in **Table 1**. For direct comparison, all images are at the same magnification and show a scale bar of 2 μ m. An SEM image for sample #8 was not available; however, it was expected to have similar morphologies to those shown for sample #7 since the composition was the same and the size difference was small. These formulations show a range of particle sizes and morphologies ranging from spherical and smooth to highly rugose and wrinkled.

samples had a particle size distribution with a GSD of 1.6. The median sample mass of the materials and formulations listed in **Table 1** was 66 mg. All samples were stored at a relative humidity (RH) below 5 % and between 22 and 23 °C in a desiccator for several weeks before being used for measurements.

Field Emission Scanning Electron Microscopy (Zeiss Sigma FE-SEM; Carl Zeiss, Oberkochen, Germany) was used to assess particle size and morphology. Powder samples were mounted directly onto aluminum Scanning Electron Microscope (SEM) stubs (Product 16111; Ted Pella, Inc.; Redding, CA, USA). Subsequently, the samples were sputtered with a gold coating (Denton Vacuum Desk II; Moorestown, NJ, USA) to a thickness of 10 to 15 nm. Images ranging from magnifications of 500× to 20000× were taken at a working distance of 5.3 to 6.3 mm using an accelerating voltage of 3 to 4 kV. Scanning Electron

Microscope images of these samples are shown in **Fig. 1** to show the differences in particle sizes and morphologies.

The experimental set-up for monodisperse and polydisperse spray drying has been discussed elsewhere (Ivey et al., 2018b; Wang et al., 2019). The aerodynamic particle size distributions were measured in-line with the spray drying process using a time-of-flight aerodynamic particle sizer (3321, TSI, Shoreview, MN, USA) (Ivey et al., 2018a).

The solid phase of the powder samples was assessed using Raman spectroscopy to determine whether they were amorphous, crystalline or a mixture of the two. A custom dispersive Raman spectroscopy system was utilized for this purpose. The system included a 671 nm diode-pumped solid-state laser (Ventus Solo MPC6000; Laser Quantum, Stockport, UK). A detailed description of a similar apparatus has been published elsewhere (Wang et al., 2017).

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Samples were placed into a closed sample chamber under nitrogen to prevent moisture exposure. All spectra were measured at a temperature between 22 and 23 $^{\circ}$ C and at less than 5 % RH.

2.2 Methods

2.2.1 Modulated compressed bulk density instrument

The new powder compression apparatus consisted primarily of a linear actuator, a piston, a sample cavity and a load cell (shown schematically in **Fig. 2**). These components were housed inside an enclosure that allowed easy access for sample loading and unloading, servicing, alignment of the sample holder and cleaning. The linear actuator and the load cell were connected to a computer for control and data acquisition.

A powder sample was loaded into the sample holder (a stainless-steel die with a cylindrical cavity) which was then placed on top of the load cell and tared. Upon measurement, a piston coupled to a non-rotary, linear actuator (Physik Instrumente, M-229.26S, 25 mm, Karlsruhe, Germany) exerted an axial force on the sample. The diameter of the piston used for measurements was designed such that an engineering fit (sliding fit) was obtained with the sample holder cavity. The resulting clearance of 0.1 mm reduced the friction between the piston and the sample cavity while preventing the powder from flowing out of the sample cavity when compressed. The sample cavity had an internal diameter and height of 5 and 6 mm, respectively, which resulted in powder sample masses of usually less than 100 mg; this small sample mass requirement is useful for testing expensive, limited-quantity, rare or difficult-to-make samples.

A stepper motor controller (Physik Instrumente, C-663 Mercury Step, Karlsruhe, Germany) interfaced with the actuator and was controlled by a computer running custom software. The load cell (FuTeK, LRF400- FSH04041, Irvine, CA, USA), with a maximum load capacity of 44.5 N and a maximum load deflection of 0.117 mm, was



Fig. 2 Schematic of the instrument and its principal components.

used to measure the force being exerted on the powder bed during compression; the measured force was converted to pressure using the known geometry of the sample die. A USB controller (FuTeK, USB220, Irvine, CA, USA) was used to interface with the load cell.

The RH of a small volume of approximately 200 cm³ around the sample can be precisely maintained at 0 % or controlled in 1.0 % increments between 3 % and 95 % RH using a humidity generator (RH-200, VTI, Hialeah, FL). This feature is unique to this instrument and allows measurements under different environmental conditions depending on experimental requirements. Previous similar measurements on fine pharmaceutical powders lack the capability of density measurements under real-time and precise relative humidity conditions (Antikainen and Yliruusi, 2003; Kaerger et al., 2004; Nordström et al., 2009; Sørensen et al., 2005; Thalberg et al., 2004). For the measurements reported in this study, the RH control capabilities of the instrument were used to maintain 0 % RH.

2.2.2 Control and data acquisition

A custom program with a graphical user interface was developed using a system design platform (LabVIEW, National Instruments 2011, Austin, TX, USA) to simultaneously control the instrument and acquire its data. This program was also used to define the measurement criteria and automate each measurement, which simplified instrument operation and reduced operator-induced systematic errors. The program was used to modulate the displacement of the piston, resulting in compression and decompression cycles on the powder. Harmonic, sawtooth, triangular wave and other custom modulation profiles can be used to study powder compression.

2.2.3 Modulated compression profile

For the results discussed here, a triangular modulation mode was used for its simplicity. The triangular wave mode used consisted of a series of linear compression and decompression segments and was defined by specifying the velocity, acceleration and deceleration of the linear actuator, as well as the compression and decompression displacements for each segment of a compression cycle. These compression and decompression segments were repeated until the measurement limits or hardware limits of the instrument were reached. An example of a triangular modulation profile is presented in **Fig. 3** along with the pressure exerted on a powder during a measurement.

2.2.4 Modulated compressed bulk density (mCBD) measurement

A cylindrical stainless-steel die, which is the sample holder, was loosely filled with powder sample using a spatula. The spatula was used to level the surface of the powder so that it was flush with the top edge of the cavity.



The previously tared die was then placed on a weighing balance to determine the mass of the powder. The uncompressed sample volume was assumed to equal the volume of the sample holder's cavity. The die was then placed on the load cell, which was tared before commencement of a measurement. The position of the compressing piston was adjusted for each measurement and zeroed by carefully bringing the ram near the top of the sample cavity until it touched just off on the powder inside the cavity. The piston then advanced into the cavity at a rate defined by the user and compressed the powder. The parameters used for the density measurements discussed in this study were fixed at 0.01 mm/s for the velocity of the piston, 0.2 mm/s^2 for the acceleration and deceleration rates, a compression displacement of 0.06 mm per cycle and a decompression displacement of 0.02 mm per cycle. Based on these parameters, an individual compression and decompression cycle took approximately 8 seconds.

The position of the piston was logged continuously by the program and was used to determine the instantaneous volume of the sample. The force exerted on the sample was continuously measured with the load cell, and pressure was calculated by taking the ratio of the compression force measured to the cross-sectional area of the piston. For a crystalline Leucine powder (sample #1 from **Table 1**), **Fig. 3** shows a sample modulated displacement profile (solid black trace, left axis) and the changes in compression pressure changes over time (dotted red trace, right axis).

The modulated compression profile allowed for the observation of plastic compression due to particle rearrangement and semi-elastic compression of this sample. It can be seen that the compression pressure remains close to zero kPa upon decompression for the first ~250 seconds in the measurement, while it deviates away from zero kPa af-



Fig. 3 A sample modulated displacement profile is plotted (solid black trace) on the left axis as a function of time. The compression pressure exerted on the powder (calculated from the force measured by the load cell) is plotted (dotted red trace) on the right axis as a function of time. The compression pressure on the powder remains close to zero kPa upon decompression for the first ~250 seconds. Powder measured was crystalline Leucine (sample #1 from **Table 1**).

ter ~250 seconds (corresponding primarily to semi-elastic deformation of the powder).

The compressed bulk density was calculated at each step by dividing the sample mass by the instantaneous sample volume. At the end of a measurement, the data was combined into a graph that shows the compressed bulk density as a function of compression pressure (see **Fig. 5**).

2.2.5 Powder elasticity ratio

A parameter for powder elasticity was derived from the data to identify regimes of plastic and semi-elastic deformation during the compression process and to establish the transition point between the two. The calculation was based on the assumption that the powder compressed like a spring when behaving elastically. In this case, following Hooke's law, the force on the powder is linearly proportional to a small compression displacement by a stiffness constant. For a modulated compression displacement, and for perfectly elastic response, the stiffness constant will be the same when calculated for the decompression segment and the compression segment; the ratio of these two stiffness constants will be 1. However, for plastic or semi-elastic response, the two stiffness constants will be different, and the calculated ratio will be zero or less than 1, respectively.

The powder elasticity ratio was calculated from the compression pressures (obtained directly from the measured forces) and the displacements of the compression piston for each compression and decompression segment. The powder elasticity ratio was calculated as the ratio of the change in pressure between the start and end of an individual compression-decompression cycle, over a displacement ratio as follows:

$$E = \frac{1 - \frac{\Delta P_{\rm D}}{\Delta P_{\rm C}}}{1 - \frac{\Delta S_{\rm D}}{\Delta S_{\rm C}}} \tag{1}$$

where $\Delta P_{\rm C}$ is the change in pressure between the start and end of a compression segment, $\Delta P_{\rm D}$ is the change in pressure between the start and end of a decompression segment, $\Delta S_{\rm D}$ is the change in displacement between the start and end of a decompression segment, and $\Delta S_{\rm C}$ is the change in displacement between the start and end of a compression segment. The value of the powder elasticity ratio ranges from zero for completely plastic response, to one for completely elastic response.

Fig. 4 shows a plot of a subset of the compression displacement and compression pressure data for crystalline Leucine (sample #1 from **Table 1**) between 2.2 and 2.9 mm and up to 250 kPa, respectively, for the sample measurement shown in **Fig. 3**.

Fig. 4 shows that up to ~ 100 kPa and up to a displacement of 2.65 mm, the measured force between the powder and the compression piston returned to zero at the end of



each decompression segment; the calculated powder elasticity ratio was zero and the powder compressed plastically. However, as the pressure on the powder increased beyond ~100 kPa, the measured force between the powder and the compression piston was not zero at the end of each decompression segment. Hence, the calculated powder elasticity ratio was greater than zero and the powder compressed semi-elastically.

The powder elasticity ratio was calculated discretely for each cycle in the modulation profile. Because of this, the transition pressure from plastic to semi-elastic compression response was estimated at the mid-point of the two compression pressures measured at the end of two consecutive compression segments, where the first value corresponds to the maximum compression pressure measured during the last plastic cycle and the second value corresponds to the maximum compression pressure measured during the first semi-elastic cycle. The transition density was estimated by calculating the average value of the densities measured at the maximum compression pressures and the minimum decompression pressures and then finding the average density at the estimated transition pressure (see Fig. 5, top). The accuracy of the transition pressures and densities can be improved by using finer modulation profiles.

As can be seen in the amorphous Trehalose sample measurement shown in **Fig. 5** (bottom), the powder elasticity ratio clearly shows the transition from plastic to semi-elastic compression when compared to the smooth profiles of the CBD data (**Fig. 5**, top).

2.2.6 Data processing

The data collected from each measurement was processed to calculate the powder elasticity ratio, the compression pressure at which the powder transitions from the plastic to semi-elastic compression regime, and the corresponding powder density. Graphs were generated for the powder elasticity ratio and mCBD as shown in



Fig. 4 A subset of the compression displacement from 2.2 to 2.9 mm and compression pressure data up to 250 kPa for crystalline Leucine (sample #1 from Table 1) shown in Fig. 3. Plastic response is seen for pressures up to ~100 kPa; semi-elastic response starts at pressures $> \sim 100$ kPa.

Fig. 5, where the CBD profile was bound by the densities measured at the maximum and minimum displacements for each cycle in the modulation profile (labeled as Max Compression Pressure and Min Compression Pressure, respectively). An average density for the powder, calculated as the average of the maximum and minimum compression pressures was also included with the CBD data. Pressure data below 10 kPa were not plotted in the results as they were highly variable and had been determined to be strongly linked to previous powder handling (USP, 2015) as well as piston-die friction (measured to be below 0.1 N or 3 kPa when the instrument is aligned properly).

From the measurement of the powder elasticity ratio of 100 % amorphous Trehalose (sample #2 from **Table 1**) shown in **Fig. 5** (bottom), it can be concluded that the compression response was entirely plastic up to a pressure of ~80 kPa. In this range the compression overcame



Fig. 5 Sample data for spray dried 100 % amorphous Trehalose (sample #2 from Table 1). This sample measurement shows the outputs of the data processing, which includes powder density (yellow trace, top) and the powder elasticity ratio (black circles, bottom) as a function of compression pressure in a logarithmic scale to clearly show powder response at low pressures. Transition pressure denoting the change from plastic to semi-elastic compression response is indicated by the black solid vertical line. Average density (black dotted trace, top) is calculated from the densities at the maximum and minimum compression pressures and is used to estimate the powder density at the transition pressure.



frictional forces to rearrange the powder into closer packing. At higher pressures the powder showed partially elastic response, but in the entire range of the measurement the response remained partially plastic, indicating that rearrangement or irreversible deformation had still occurred.

3. Results and discussion

It was assessed whether the modulated compression instrument is capable of differentiating between similar respirable powders at low pressures. It was expected that changes in a powder's composition, particle size or particle size distribution result in different overall compression response, including different plastic or semi-elastic responses to compression, allowing quantified measurements to be used to tell different samples apart. Hence, the following cases were tested: 1) powders with the same chemical composition but consisting of different particle sizes or particle size distributions, and 2) the same particle sizes and particle size distributions but different composition.

3.1 Measurement repeatability

Repeatability of measurements is an important factor for compressed bulk density measurements in the low-pressure region. Powders may compact prior to the measurement during storage or handling. This problem is accentuated if only small sample masses are available such that friction effects during the measurement become more prominent. A successful technique must be able to identify the regions of the compression profile that are repeatable and independent of sample history. To assess this capability, three representative powdered materials were tested in duplicate (i.e. two replicates): 1) 100 % spray dried amorphous Trehalose as an example of a cohesive respirable powder, 2) 100 % raw crystalline Leucine as an example of a powder with larger particle size and 3) a spray dried mixture of 55 % Trehalose with 45 % Leucine as an example of a spray dried powder with a dispersibility enhancing excipient. These correspond to samples #2, 1 and 9 from Table 1, respectively and were chosen for their differences in composition, true density, particle size, particle morphology and solid state; they were expected to have different compression responses. The duplicate CBD measurements and powder elasticity ratios are shown in Fig. 6.

The CBD data (**Fig. 6**, top) show three pairs of distinct CBD profiles, with each duplicate pair closely overlapping in the region above 10 kPa. The profiles based on maximum and on minimum pressure are both reproducible where the replicate measurements are within 1 % from the average density of the two samples for each composition at any pressure above 10 kPa. The powder elasticity ratio data (**Fig. 6**, bottom) also shows three distinct profiles for each

duplicate pair, showing transitions to semi-elastic compression response at similar pressures for each pair (vertical lines) and reaching very similar final powder elasticity ratio values at the end of the measurement. CBD values at compression pressures below 10 kPa are also shown. At pressures much below the transition pressure, variability was high and the profiles were not reproducible.

As shown in Table 2, based on the powder densities at the transition between the plastic and semi-elastic regions, all duplicate measurements are within ~ 2 % of the average. Similarly, the transition pressures are within ~12 % of the average. The main source of error in the estimated transition values is the method by which the powder elasticity ratio is calculated. As discussed in the Methods section, the powder elasticity ratio is only known discretely and calculated once for each modulated compression cycle. Because of this, the spacing with respect to pressure between consecutive powder elasticity ratio values is directly linked to the frequency of the modulation profile. Although the experimental parameters chosen for this study demonstrate excellent measurement reproducibility as shown in Fig. 6 and Table 2, the accuracy of the transition values can be further improved by utilizing a finer modulation profile. Other error sources are small and most prominent at measurement pressures below 10 kPa. These include powder history or handling prior to measurement (random), changes in environmental conditions (random), piston-die friction (systematic), load cell measurement error (systematic), piston position control and knowledge (systematic) and mechanical hardware deflection (systematic). However, under proper sample preparation, instrument alignment, calibration, maintenance and operation, these additional errors do not contribute significantly to the overall measurements.

As seen in these duplicate modulated compression results, the low-pressure measurements made by this instrument show excellent repeatability and the resulting CBD and powder elasticity ratio curves can be used to differentiate between similar respirable powders. For the sake of clarity, the results presented in the following sections contain only a single measurement per sample tested and show only the average CBD.

3.2 Ability to discriminate between powders with the same composition but consisting of different particle sizes

To demonstrate the capability of the mCBD instrument for testing the compression response of small amounts of fine and respirable pharmaceutical powders and discriminating between them, samples with the same composition but different particle sizes were first measured. For instance, changes to the particle size will change the total number of contact points between particles in the





Fig. 6 Duplicate measurements of 100 % amorphous Trehalose, 100 % crystalline Leucine and a mixture of 55 % Trehalose and 45 % Leucine (samples #2, 1 and 9, respectively, from **Table 1**). The top figure shows the CBD profiles for each sample as a function of the maximum and minimum pressures reached from the modulated compression. The bottom figure shows the calculated powder elasticity ratio for each sample as a function of pressure. Pressure is shown in both figures on a logarithmic scale to clearly show powder response at low pressures. Vertical lines indicate the pressures at which the samples transition from plastic to semi-elastic compression response. Data from compression pressures below 10 kPa are included in the top figure to show the high variability at very low pressures.

Table 2Average transition pressures and densities from plastic to semi-elastic compression response for the duplicate measurements shown in Fig. 6.Standard deviation is also shown as a percentage of the average values.

Sample	Transition Pressure		Transition Density	
	Meas. 1 [kPa]	Meas. 2 [kPa]	Meas. 1 [kg/m ³]	Meas. 2 [kg/m ³]
100 % Amorphous Trehalose	77.2	81	770	788
100 % Crystalline Leucine	62.2	52.4	437	433
55 % Trehalose and 45 % Leucine	172	186	331	339

powder, affecting its overall cohesion and its compression response. This is important, for example, in formulation development to achieve certain powder characteristics (de Boer et al., 2017; Prime et al., 1997), as well as for quality control to confirm that powders meet manufacturing specifications, e.g. during scale-up. In either case, the mCBD instrument should be capable of measuring a difference in the compression response of two powders with the same



composition but different particle size distributions.

Shown in **Fig. 7** are two spray-dried powder samples of 100 % Mannitol. The first sample was polydisperse (sample #11 from **Table 1**; GSD of 1.6 and a MMAD of 3.5μ m), while the second sample was monodisperse (sample #10 from **Table 1**; GSD of 1.1 and an MMAD of 10 μ m). Both samples were found to be crystalline using Raman spectroscopy.

The mean mCBD measurements (**Fig. 7**, top) and the powder elasticity ratio curves (**Fig. 7**, bottom) show two very distinct compression profiles. Although the chemical composition and solid phases were the same for both samples, the compression responses were different. On the other hand, the transition from plastic to semi-elastic response was very similar at ~99 kPa and ~475 kg/m³ for the polydisperse sample and ~101 kPa and ~468 kg/m³ for the monodisperse sample. The polydisperse sample can achieve higher compressing less elastically than the monodisperse sample. Since the polydisperse sample consists of



Fig. 7 Comparison of two powders of 100 % crystalline Mannitol but with different particle size distributions. Semi-logarithmic profiles of the average mCBD (top) and powder elasticity ratios (bottom) vs. compression pressure show two different compression responses. The pressures at which the powders transition from plastic to semi-elastic compression response are indicated by vertical lines in both plots.

particles of different sizes, these differences in compression response might be attributed to the smaller particles filling the interstitial spaces, resulting in a reduction in the void space in the powder bed and higher bulk density (York, 1978). This can also be seen in the powder elasticity ratio curves (**Fig. 7**, bottom), where after the transition point, the elasticity of the polydisperse powder increased less sharply, indicating that some of its particles can continue to rearrange as the pressure increases. Conversely, the sharper increase in the powder elasticity ratio for the monodisperse powder is an indication that most particle rearrangement has already occurred.

In this specific example, there was also a sudden decrease in the elasticity of the polydisperse powder at ~300 kPa of pressure. This decrease corresponds to a release of stress in the powder that could be due to particle deformation or fragmentation (Chen et al., 2017; Vu et al., 2020), or could also be due to breakage of bridges or other structures formed by the particles and which were previously held in place by interparticle forces. This is further indication that the polydisperse powder may be undergoing further rearrangement as the pressure increases, although it is not currently possible to decouple this from particle damage in the semi-elastic response region.

A second example shown in **Fig. 8** compares the mean mCBD measurements for a two-component formulation (75% Trehalose and 25% Leucine) spray dried into two separate polydisperse powders with GSD of 1.6 and MMAD of 2 μ m and 4.5 μ m, respectively (samples # 7 and 8 from **Table 1**). In both samples Trehalose was fully amorphous and Leucine was fully crystalline under Raman spectroscopy.

As can be seen in Fig. 8 (top), the sample with the smaller particle sizes (MMAD of 2 µm) achieved higher densities than the sample with larger particle sizes (MMAD of 4.5 µm); similarly to the previous example shown in Fig. 7, these higher densities could be attributed to the smaller particles being better at filling any interstitial spaces as the powder is compressed. From the particle morphologies shown in Fig. 1, it can be seen that the particles were not spherical and had a significant external void fraction. Even though the compositions were the same and the overall morphologies for particles from both samples were very similar, the surface features of the smaller particles had sharper curvatures, which may lead to smaller contact points between particles, reducing particle cohesion (York, 1978). An alternative explanation to the CBD of these two samples is that particles with a larger MMAD have a lower particle density because Leucine takes a longer time to crystallize (Baldelli et al., 2016), resulting in an overall lower density powder. In either case, whether it is the difference in particle density or the change in the particle cohesion due to the changes in particle size, the CBD profiles are different for both samples, with the larger particle size



resulting in an overall lower bulk density at any pressure.

Furthermore, the pressures and densities at which the powder transitions from plastic to semi-elastic response were different, with the sample composed of the smaller sized particles reaching semi-elastic compression response at higher pressures: ~91 kPa and ~422 kg/m³ for the smaller particle size versus ~48 kPa and ~370 kg/m³ for the larger particle size vs. for the smaller particle size. This is further indication of increased particle cohesion during plastic deformation and particle rearrangement for the larger particles; however, as can be seen in the powder elasticity ratio curves (**Fig. 8**, bottom), both traces converge quickly in the semi-elastic regime, which is an indication that higher pressure was needed to overcome the increased cohesion between larger particles.

In both examples, it is clear that the instrument can detect differences in the compaction profiles that are directly or indirectly caused by changes in the particle size distributions.



Fig. 8 Comparison of two polydisperse powders of 75 % Trehalose and 25 % Leucine but with different MMAD. Semi-logarithmic profiles of the average mCBD (top) and powder elasticity ratios (bottom) vs. compression pressure show two different compression responses. The pressures at which the powders transition from plastic to semi-elastic compression response are indicated by vertical lines in both plots.

3.3 Ability to discriminate between powders with the same particle sizes but different compositions

It is expected that the compression response of powders is also a function of their composition and not just of the particle sizes and distributions. For instance, the presence of different materials on the surface of a particle can make them more or less cohesive (Vehring, 2008). Again, the degree of cohesiveness plays an important role in formulation development to achieve certain powder characteristics such as dispersibility or flowability (de Boer et al., 2017; Prime et al., 1997), as well as in quality control to assess adherence to manufacturing specifications. In either case, the mCBD instrument should be capable of measuring a difference in the compression response of powders with different compositions but the same particle sizes.

The following measurements compare monodisperse powders containing Trehalose and Trileucine with small increments in the amount of Trileucine. It has been shown that Trileucine, a surface-active amino acid, can be used as a shell former in particle formation to achieve particles with low cohesion and low density (Lechuga-Ballesteros et al., 2008). It is expected that this will affect the compression response of these powders by allowing the particles to slip past one another and rearrange more easily. All samples had the same GSD (1.1) and MMAD $(9 \mu m)$. The following measurements compare the mean compression response of 99.6 % Trehalose with 0.4 % Trileucine, 99 % Trehalose with 1 % Trileucine, and 95 % Trehalose with 5 % Trileucine (samples #3, 4 and 5 from Table 1, respectively). From the SEM images shown in Fig. 1, it can be seen that an increase in Trileucine content resulted in an increase to the rugosity of the particles. This increase in rugosity is expected to lower the cohesive forces between the particles (Baldelli and Vehring, 2016).

Because of the different formulations, the mean bulk densities in these measurements are normalized by the true density of the particles in order to make meaningful comparisons between the density profiles. From this normalization, a value of 1 would correspond to a bulk density that equals the true density of the material, meaning that the compressed powder would be absent of any voids. Conversely, this normalized density can be used as a measure of the void space in a powder sample and of the packing of particles within a compressed bulk.

Comparing these measurements with the particle morphologies in the SEM images shown in **Fig. 1**, it can be seen that increasing Trileucine from 0.4 % to 1 % had a small effect on the particle morphology, making the particles more rugose and with more external voids; however, it is likely (Lechuga-Ballesteros et al., 2008) that this increase in Trileucine resulted in a more dispersible (and more flowable) and less cohesive powder that can achieve



higher densities upon compression more easily.

A further increase in Trileucine to 5 % resulted in an even clearer difference between the mean compression response of these powders as shown in Fig. 9 (top), where a difference in the mCBD and powder elasticity ratio curves can be easily observed. However, increasing Trileucine from 1 % to 5 % resulted in a decrease in powder density upon compression. Comparing these measurements to the SEM images shown in Fig. 1, it can be seen that such an increase in Trileucine caused a strong change to the particle morphology. The particles were much more rugose at 5 % Trileucine and the increased number and size of external voids resulted in lower particle density. While the transition pressures and densities calculated for both powders were very similar, the increase in Trileucine (from 1 % to 5 %), and the corresponding change in the particle morphology, resulted in a lower final powder elasticity ratio (Fig. 9 bottom). This means that the reduction in compressed bulk density of the powder with 5 % Trileucine is not entirely due to changes in particle cohesion but to a decrease in particle density caused by the increase of external void space in the more rugose particles.

A similar comparison of two polydisperse powders with the same particle size distributions and particle diameters (GSD of 1.6 and an MMAD of 2.5 μ m), 100 % Trehalose versus 80 % Trehalose and 20 % Leucine, is shown in **Fig. 10**. Similar to Trileucine, Leucine is also a surface-active amino acid used as a shell former in particle formation to achieve particles with low cohesion and low density (Feng et al., 2011). From the comparison of these two powders, it is expected that the sample containing Leucine will have enhanced powder dispersibility and reduced particle cohesion.

From these measurements, the mean compression response of both samples (**Fig. 10**, top) can be quantitatively distinguished, where the presence of Leucine resulted in an



Fig. 9 Comparison of three monodisperse powders (GSD 1.1) with the same particle sizes (MMAD 9 μ m) of 99.6 % Trehalose with 0.4 % Trileucine, 99 % Trehalose with 1 % Trileucine and 95 % Trehalose with 5 % Trileucine (samples #3, 4 and 5 from **Table 1**, respectively). Semi-logarithmic profiles of the average mCBD normalized by true density (top) and powder elasticity ratios (bottom) vs. compression pressure show different compression responses. The pressures at which the powders transition from plastic to semi-elastic compression response are indicated by vertical lines in both plots.



Fig. 10 Comparison of two polydisperse powders (GSD 1.6) with the same particle sizes (MMAD 2.5 μ m) of 100 % Trehalose and 80 % Trehalose with 20 % Leucine (samples #2 and 6 from **Table 1**, respectively). Semi-logarithmic profiles of the average mCBD normalized by true density (top) and powder elasticity ratios (bottom) vs. compression pressure show different compression responses. The pressures at which the powders transition from plastic to semi-elastic compression response are indicated by vertical lines in both plots.



increase in the powder's bulk density at a given pressure and also resulted in an increased transition pressure and transition density. The Leucine-containing powder is easier to compress. This is an indication that powder dispersibility is enhanced and particle cohesion is reduced, as expected.

Overall, the measurements show that small amounts of different respirable powders can be differentiated reliably using the modulated compression technique. The compression behavior is determined by a variety of competing factors including size distribution, cohesiveness and rugosity of the particles and their particle density. Being able to assess both bulk density and elasticity of the powder under low pressure aids in the interpretation of the results.

4. Conclusions

Using modulated compression, this new density tester is capable of distinguishing whether a compression step is reversible or irreversible and is therefore useful in revealing the compression response of fine and respirable pharmaceutical powders under low applied pressures. By using modulated compression, bulk density measurements can reveal transitions between plastic and semi-elastic compression responses, something not possible with non-modulated or entirely linear compression methods.

Quantification of this transition can be used to determine a pressure at which it can be assumed that the powder handling history has been erased and reproducible results can be obtained, e.g. for the purposes of selecting a suitable level of compaction for powder filling operations. Additionally, the ability to identify the transition point between these two regimes can aid in making modifications to a powder's formulation (e.g. adding a dispersibility enhancer to improve flowability) so that the resulting powder can achieve a desired bulk density at a given pressure before the physical integrity of the particles is compromised. This is especially important for fine pharmaceutical powders with a mean particle size smaller than 25 μ m and in particular for respirable powders with a mean particle size < 10 μ m.

Selected tests presented in this paper demonstrate that the instrument can be used to easily discriminate between similar fine and respirable powders with slight changes in composition, particle size or particle size distribution, based entirely on their compression response. This capability is particularly useful in quality control applications where defined product attributes need to be maintained, or in formulation development where certain properties need to be achieved.

The instrument, the control software and data processing have been designed and implemented such the tester produces repeatable and reproducible measurements at low pressures. The small sample mass requirement of typically less than 100 mg is particularly useful in early product development for performing CBD measurements of expensive, limited-quantity, and rare or difficult-to-make powders.

Acknowledgements

The authors acknowledge the support of AstraZeneca, the Canada Foundation for Innovation, Alberta Advanced Education and Technology, and the Natural Sciences and Engineering Research Council of Canada. The authors thank Isobel Tetreau for help with producing the final figures.

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Authors' Short Biographies



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Authors' Short Biographies



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Dr. David Lechuga-Ballesteros, Research Fellow at AstraZeneca, is a leading scientist in the area of pharmaceutical material sciences and particle engineering. Dr. Lechuga has co-authored over 100 publications including peer-reviewed articles, book chapters and abstracts, co-edited a special issue on respiratory and nasal drug delivery, and a book on drying technologies for biotechnology and pharmaceutical applications. Dr. Lechuga is named as an inventor in over fifteen patents describing new drug crystal forms, novel formulations, or specialty particle engineering processing equipment. Dr. Lechuga currently serves in the Editorial Advisory Board of several leading Journals in the area of Pharmaceutics.



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Authors' Short Biographies



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Effects of Powder Vibration and Time Consolidation on Soft and Hard Wheat Flour Properties[†]

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Abstract

Consistency and reliable flow are of great concern during the handling and processing of flour. In this study, wheat flour was consolidated by normal stress and vibration, and rheological factors including bulk solid compressibility, Warren-Spring cohesion strength, permeability, and wall friction were evaluated. Soft red winter (SRW) and hard red spring (HRS) wheat flours were vibrated for 5 and 10 minutes and compressed under 10 and 20 kPa for 12 and 24 h. After vibration, wall friction increased from 10.87° to 14.13° for SRW flour and decreased from 11.00° to 7.10° for HRS flour, and the permeability decreased for both the flours. Consolidation time and stress had a significant effect (P < 0.05) on wall friction and compressibility. The HRS Carr index increased from 25.77 to 38.48 when consolidated under 20 kPa for 24 hours, but the SRW Carr index decreased slightly from 46.60 to 44.24. The SRW flour permeability decreased significantly (P < 0.05) when compression pressure was increased from 10 to 20 kPa. while HRS permeability was less affected by consolidation. The consolidation and vibration effects on bulk flour properties differed likely due to inherent differences in the composition and hardness of HRS and SRW.

Keywords: flour, time consolidation, plastic-elasticity, storage, vibration

1. Introduction

Wheat flour is one of the most important food products in the world. The bulk powder properties of wheat flour, including cohesiveness, flowability, wall friction, and permeability, are important for processing and handling, such as silo unloading and pneumatic transportation. These properties are highly dependent on particle size, shape, surface roughness, and composition (Molerus and Nywlt, 1984). The U.S. has differentiated wheat into 6 classes based on its composition and hardness. The flours from different wheat classes differ in particle size, surface fat and protein contents (Bian et al., 2015). Soft wheat flour has less protein and more fat content, and smaller particle size. Therefore, soft wheat flour is always cohesive than hard wheat flour (Bian et al., 2015). Studies also have found that the soft wheat flour shows higher cohesiveness than hard wheat flour due to the particle's rough surface characteristics (Kuakpetoon et al., 2001). Due to

* Corresponding author: Kingsly Ambrose; Add: 225 S University St, West Lafayette, Indiana 47907, USA E-mail: rambrose@purdue.edu TEL/FAX: +1-7654946599 flour particle size and compositional differences, soft and hard wheat flours could behave differently under similar consolidation or vibration conditions. During storage and transportation, minor changes in particle property contribute to significant changes in bulk powder properties. Besides environmental conditions such as humidity and/ or temperature changes causing consolidation, stress applied to the particle will affect bulk flour properties. Consolidation caused by the powder's own weight has been found to reduce flowability (Teunou and Fitzpatrick, 2000). During consolidation, with the variable of time and deformation rate, particle surface contact and deformation can be distinguished as reversible elastic, irreversible plastic deformation, and viscoelastic deformation (Tomas, 2000). Many studies have reported that these bulk powder property changes are mainly due to interparticle force changes (Domian and Poszytek, 2005; Teunou and Fitzpatrick, 2000).

Discrete taps, or vibration, always exists during transportation or handling, which could lead to the segregation of granular materials (Jain et al., 2013). Studies have shown that in particulate systems which are made of coarse and fine fractions, the coarse powder fraction shifts upwards and fine powder fraction shifts downwards during vibration. The particle size distribution affects the



Received 2 February 2020; Accepted 2 March 2020
 J-STAGE Advance published online 29 April 2020



segregation tendency in particulate systems (Kawakita and Lüdde, 1971; Parsons, 1976). A decrease in bulk volume is also found after vibration (Podczeck and Sharma, 1996). But, there are lack of studies that quantify this effect of segregation in wheat flour on their bulk characteristics. Furthermore, the vibration of cohesive powder could result in self-agglomeration (Kahrizsangi et al., 2016). Both particle segregation or self-agglomeration are undesirable for flour processing and handling. However, the effects of vibration on flour properties are unexplored. In addition, hard wheat flour and soft wheat flour differ in cohesiveness and particle size distribution.

In this study, we have used different techniques to determine the important wheat flour handling and processing properties. Tests like compressibility (including Hausner ratio, compressibility index, Carr index), permeability and Warren-Spring cohesion were used to assess flowability of the flour samples.

Goal of this manuscript was to study the vibration and time consolidation effects on soft and hard wheat flours bulk properties. Flour compressibility, Warren-Spring cohesion, permeability, and wall friction after consolidation and vibration treatments were tested, in order to provide a reference for bulk flour property changes after storage and transportation.

2. Materials and methods

2.1 Sample preparation

Soft red winter (SRW) and hard red spring (HRS) flours were obtained from The Mennel Milling Company (Fostoria, OH, USA). The moisture content was determined using AOAC method 925.10 (AOAC, 2006), by drying 2–3 g of flour at 130 °C for 2 h. The moisture contents of SRW and HRS were 12.71 ± 0.07 and 12.45 ± 0.02 % w.b., respectively. SRW contains 7.6 % protein (14 % m.b.) content and HRS contains 12.8 % protein (14 % m.b.) (Miller and Hoseney, 1997; Bian, et al., 2015). Flour particle size and shape factors were measured in

two replicates using the Morphologi G3-ID instrument (Malvern Panalytical, Inc., Westborough, MA, USA). SRW had a mean particle circularity equivalent (CE) diameter of $11.97 \pm 0.11 \,\mu\text{m}$ and a circularity mean of 0.83 ± 0.03 , while HRS had a particle CE diameter of $16.91 \pm 0.76 \,\mu\text{m}$ and a circularity mean of 0.78 ± 0.02 (Figs. 1, 2).

For consolidation, 50 g of flour was compressed using a vented piston on an Anton Paar rheometer (MCR 502 series, Anton Paar, Graz, Austria) under 10 and 20 kPa for 12 and 24 h before testing. These compression pressures were chosen to approximate stresses encountered during flour storage (Domian and Poszytek, 2005). To mimic handling, 50 g of flour was vibrated for 5 and 10 min using a tapped density tester (Agilent Technologies, Santa Clara, CA, USA) before property measurements. All the experiments were performed in triplicate to gauge for statistical significance. The complete design of experiment is presented in **Table 1**.

2.2 Flour rheology tests

Bulk flour properties including compressibility, Warren-Spring cohesion strength, permeability, and wall friction were determined before and after consolidation and vibration treatments using built-in test methods on the Anton Paar MCR-502 rheometer.

Compressibility: Compressibility is a measure of the



Fig. 1 Particle size number distribution of SRW and HRS flours.



Fig. 2 Images of HRS (left) and SRW (right) flour particles.



	Treatment					
Sl. No	Sample	Vibration (min)	Time-consolidation		Parameters measured	
		vibration (mm)	Consolidation time (h)	Pressure (kPa)		
1	SRW	5, 10	12, 24	10, 20	Carr index, WS cohesion strength, Permeability, Wall friction	
2	HRS	5, 10	12, 24	120, 20	Carr index, WS cohesion strength, Permeability, Wall friction	

Table 1 Summary of experimental parameter values used in the study.

relative volume change when a pressure (normal stress) is applied and represents the density change under the applied normal stress. Carr index was used as an indicator to describe the compaction mechanism in this study. Low Carr index indicates low compressibility and a freeflowing powder. The Carr index is a characteristic of a powder's compressibility and is often used as an indication of a powder's flowability and is defined by the powder density before compression (ρ_0) and after compression (ρ_t):

$$Carr Index = \frac{\rho_t - \rho_0}{\rho_t}$$
(1)

Flour was compressed to 50 N. A Carr Index of 1 indicates an incompressible bulk solid ($\rho_t = \rho_0$). This is interpreted as the best possible flowability a granular material can have. The larger the value of Carr Index, the poorer the flowability of the material (Abdullah and Geldart 1999). In this study, the Carr index was obtained at 50 N (25 kPa) load in order to mimic the normal load in a flour storage silo.

Warren-Spring (WS) cohesion strength: This measurement is used to determine the cohesion of powders as a function of applied normal stress. A homogenous powder bed is created by consolidation at different normal stresses of 3, 6 and 9 kPa using a vented piston and then the Warren-Spring geometry was used to measure the torque at a very small rotational speed of 0.1 rpm. The cohesion strength can be derived from the torque (M) via a simple moment balance by correlating the shear resistance to the torque measured (Mohammed et al., 2011):

WS Cohesion Strength =
$$\frac{3M}{2\pi (R_0^3 - R_i^3)}$$
 (2)

where R_i and R_0 are the radius of Warren-Spring geometry shown in **Fig. 3**. The maximum cohesion strength obtained during the rotation of probe is known as Warren-Spring cohesion strength.

Permeability: Permeability is defined as the resistance of fluid (air) through a compacted bed of powder. The permeability was determined by measuring the pressure gradient of air across a packed bed of length (L) at an airflow velocity (U) using the powder cell accessory at-



Fig. 3 Schematic diagram of a Warren-Spring geometry.

tached to the rheometer (Mishra et al., 2020) and is given by Darcy's law (Whitaker, 1986):

$$Permeability = \frac{U \cdot \eta \cdot L}{\Delta p}$$
(3)

where Δp is the pressure drop in the compacted powder bed, and η is the air dynamic viscosity. Consolidation of flour reduces the porosity; thus, permeability is an important factor when developing unloading strategies for wheat flour. Flour permeability was tested under 3, 6, and 9 kPa pressure by measuring the resistance to airflow at 0.15 L/min.

Wall friction: This property measures the resistance between powder and the container wall material. In this study, the wall friction of flour on stainless-steel was measured. A stainless-steel probe was used to measure the wall friction at a rotational speed of 0.05 rpm under 3, 6, and 9 kPa pressure. Normal stress (σ) and shear stress (τ) were used to calculate the wall friction angle (Bian et al., 2015):

Wall Fricition =
$$\tan^{-1}(\frac{\tau}{\sigma})$$
 (4)

2.3 Data analysis

Each test used fresh samples and all the measurements were conducted in triplicate. One-way ANOVA was used



to determine the effect of vibration on powder properties and two-way ANOVA was used for determining the effect of consolidation on powder properties as influenced by consolidation pressure and time. Statistical analysis was performed by Statistical Analytical System software (SAS Institute, Cary, NC, USA). P-values less than 0.05 were considered significant difference.

3. Results and discussion

3.1 Effects of vibration on flour bulk properties

During wheat flour transportation, bulk flours undergo vibration inside the moving truck. The normal force applied to the flour particle during vibration is not as high as inside a storage bin, but particles rearrange depending on their differences in size and shape.

The Carr index (Table 2) reflects the percentage of volume change during compression, which is a good indicator of compressibility and powder flowability (Prescott and Barnum, 2000). HRS flours did not exhibit a significant difference in the Carr index values when vibration time was increased from 5 to 10 min. Both HRS and SRW flours were not significantly affected by vibration. But, the Carr index of HRS flours was much lower than SRW in similar to the observation by Bian et al. (2015). This indicated that vibration history did not affect the compressibility of the wheat flours. Though this study was limited to tapping of 10-min in a lab-scale, the results indicate that the flour compressibility is mainly affected by its own particle properties and moisture content. Furthermore, this study was limited to the lab-scale tapping for 10 min in maximum with 50 g of flour, it was not possible to fully monitor the real transportation scenario where the wheat flour could be subjected to several hours of vibration.

The wall friction angle decreased after vibration of HRS flours but increased with vibration for SRW flours (**Table 3**). The differences in results could likely be due to

the differences in flour particle hardness. During the measurement of wall friction angle, the probe only touched the top surface of the bulk flour. During vibration, HRS particles might have been rearranged with large particles moving to the surface (Knight et al., 1993), without formation of agglomerates. Thus, the wall friction decreased with increase in particle size at the surface of bulk flour (Iqbal and Fitzpatrick, 2006). This mechanically induced effect due to vibration is also called granular convection, or more commonly, the Brazil nut effect, in which mechanical agitation of a granular medium segregates the particles, such that the largest particles end up on top (Ehrichs et al., 1995). For SRW, on the other hand, some agglomerates were observed during vibration. Selfagglomeration of cohesive powder may occur during vibration (Kahrizsangi et al., 2016). The agglomerates formed with the highly cohesive SRW flour particles, during vibration, resulted in cohesive particles accumulating on the bulk flour surface. During the wall friction test measurement, the SRW flour agglomerates on the top of the surface were deformed when in contact with the wall friction probe. This potentially could have crumbled the loose agglomerates formed on the surface which in turn would have exposed the cohesive powder fraction to the probe which led to an increase in wall friction angle.

Significant differences in permeability were not observed for both HRS and SRW flours, except for the SRW flour tested at 6 and 9 kPa load (**Table 4**) where a statistical change was observed. Overall the result corresponded well to the Carr indices, that compressibility is not affected by vibration. Though the results did not reveal significant changes, permeability decreased with vibration, which indicated that rearrangement has some effect, but not a major effect, on permeability.

Both HRS and SRW flours exhibited changes in WS cohesion strength after vibration (**Table 5**) with an increased effect on SRW cohesiveness than the HRS flour. Even at 5 min of vibration, the WS cohesion strength increased for both HRS and SRW flours but was not

Fable 2 Carr index of wheat flour at different vibration tin

	Vibration time	Carr index
HRS	Control	36.95 (2.01) a
	5 min	37.76 (1.24) a
	10 min	36.99 (0.19) a
SRW	Control	46.60 (0.39) a
	5 min	45.26 (1.07) a
	10 min	46.79 (0.95) a

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW. Table 3 Wall friction of wheat flour at different duration of vibration.

	Vibration time	Wall Friction (°)
HRS	Control	11.00 (0.40) a
	5 min	7.03 (0.19) b
	10 min	7.10 (0.63) b
SRW	Control	10.87 (0.83) a
	5 min	11.43 (0.71) a
	10 min	14.13 (1.04) b

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

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Vibration time		Permeability (10^{-12} m^2)				
		3 kPa	6 kPa	9 kPa		
HRS	Control	16.75 (0.70) a	13.03 (0.48) a	11.82 (0.38) a		
	5 min	15.92 (0.86) a	12.81 (0.55) a	11.59 (0.39) a		
	10 min	15.78 (1.13) a	12.93 (0.64) a	11.62 (0.45) a		
SRW	Control	9.56 (0.43) a	5.64 (0.13) a	4.54 (0.29) a		
	5 min	8.63 (0.53) a	4.79 (0.32) b	3.69 (0.16) b		
	10 min	8.68 (0.46) a	4.90 (0.28) b	3.78 (0.08) b		

Table 4 Permeability of wheat flour at different vibration times.

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

Table 5	WS cohesion	strength of	f wheat flour	as influenced	d by th	e duration	of vibration.
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Vibration time		WS Cohesion strength				
		3 kPa	6 kPa	9 kPa		
HRS	Control	0.70 (0.26) a	0.91 (0.09) ab	1.08 (0.10) a		
	5 min	0.81 (0.05) a	1.02 (0.06) a	0.97 (0.05) a		
	10 min	0.63 (0.22) a	0.87 (0.01) b	1.00 (0.10) a		
SRW	Control	0.70 (0.13) a	2.26 (0.09) a	3.41 (0.57) a		
	5 min	0.94 (0.08) a	2.49 (0.05) a	3.63 (0.32) a		
	10 min	0.66 (0.18) a	1.50 (0.24) b	2.95 (0.26) a		

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

statistically different than the control samples. The WS measurement probe penetrated 10 mm into the top of the compressed powder bed before applying a torque to induce failure in the powder bed. This was approximately about one third the volume of the powder bed. Vibration which would have caused; granular convection of larger particles to the top could potentially explain the drop in Warren-Springs cohesion due to presence of higher sized particle fractions at the top. The limited number of agglomerates formed in SRW did not affect the cohesion strength measurement unlike the wall friction angle. High standard deviation of WS cohesion strength is found for SRW control sample at 9 kPa consolidation which could be due to the high cohesiveness of the SRW powder.

3.2 Effects of time consolidation on flour properties

During storage, the flour gets consolidated in the bin and the bulk properties change, influenced by both consolidation time and stress. During consolidation, flour may become gradually more compact when submitted to compression stress over storage time (Teunou and Fitzpatrick, 2000). Large compression stress may result in

 Table 6
 Carr index of wheat flours as affected by time consolidation.

	Time (h)	Pressure (kPa)	Carr index
HRS	Control		35.77 (0.85) a
	12	10	35.45 (0.44) a
	12	20	35.83 (0.58) a
	24	10	37.68 (0.88) ab
	24	20	38.48 (0.72) bc
SRW	Control		46.60 (0.39) ab
	12	10	46.28 (0.67) ab
	12	20	45.38 (2.14) ab
	24	10	47.95 (0.22) b
	24	20	44.24 (0.67) a

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

more compacted powder, which increases the particle contact surface and further affects the bulk powder properties.

SRW flour contains less protein than HRS, thus the SRW particles are expected to be softer than HRS and the



particle deformation scenarios will be different. During consolidation, the effects of time and stress had a positive effect on the Carr index as shown in **Table 6**.

For HRS flour, the Carr index was mainly affected by consolidation time, and the values increased with time of consolidation. This could be due to the irreversible plastic deformation of HRS particles due to time consolidation and the smaller particles filled into the voids when conducting the Carr index measurements. However, for SRW flour, the Carr index did not change significantly except at compression duration of 24 h at 10 kPa load. The SRW flour particle is soft and could elastically deform (reversible) during time-consolidation, therefore, the particle reverted to the original shape when the load was removed, and the compressibility value did not change. The inconsistency in Carr index values at 10 kPa load when consolidated for 24 h could potentially be because of transient effects in that the particle did not return to its original shape.

For both HRS and SRW flours, when comparing 10 and 20 kPa pressure for the same consolidation time, the wall friction angle significantly increased with increased pressure (**Table 7**). However, with increased consolidation time, the wall friction angle decreased significantly for SRW, from 12.93° to 11.40° under 20 kPa, while increased from 9.45° to 11.07° for HRS flour.

Flour particles compressed under high consolidation stress could cause particle shape deformation and the increased surface contact area between the probe and bulk flour could result in increased interparticle force between particles and the wall. Therefore, the wall friction increased with the increase in pressure from 10 to 20 kPa for both HRS and SRW flours.

The consolidation time, on the other hand, showed in-

Table 8 Permeability of wheat flour as affected by time consolidation.

consistent results for both HRS and SRW flours. Domian and Poszytek (2005) and Tomas (2000) found that the angle of internal friction decreased with increasing consolidation time. The same trends were found for SRW and HRS flours under 10 kPa. HRS's wall friction at 24 h and 20 kPa, in particular, increased from 12 h, which could be because that the HRS was more affected by compression.

As expected, consolidation affected flour permeability (**Table 8**). With increased consolidation time and pressure, permeability decreased significantly for SRW flours. For HRS, on the other hand, the lowest permeability was observed under 20 kPa pressure compressed for 12 h and then increased with consolidation time. This could be due to the differences in cohesiveness and particle size distri-

 Table 7
 Wall friction angle of wheat flour as affected by time consolidation.

	Time (h)	Pressure (kPa)	Wall F	Friction (°)
HRS	Control		11.00	(0.40) a
	12	10	8.11	(1.16) c
	12	20	9.45	(0.39) ab
	24	10	7.26	(0.31) c
	24	20	11.07	(0.29) ab
SRW	Control		10.87	(0.83) a
	12	10	10.27	(0.46) ab
	12	20	12.93	(0.59) c
	24	10	9.31	(0.09) b
	24	20	11.40	(0.62) ab

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

Time (h)		Pressure (kPa)	Permeability (10^{-12} m^2)					
			3 kPa		6 kPa		9 kPa	
HRS	Control		16.75	(0.70) a	13.03	(0.48) a	11.82	(0.38) a
	12	10	13.23	(1.00) bc	12.35	(1.08) ab	11.60	(0.97) ab
	12	20	11.92	(1.03) c	10.41	(0.69) b	9.81	(0.86) ab
	24	10	12.89	(2.02) bc	11.67	(1.33) ab	11.02	(1.24) ab
	24	20	15.89	(0.78) ab	13.13	(0.47) a	11.86	(0.46) a
SRW	Control		9.56	(0.43) a	5.64	(0.13) a	4.54	(0.29) a
	12	10	8.73	(0.23) ab	5.17	(0.20) ab	3.90	(0.07) ab
	12	20	3.19	(0.54) c	2.94	(0.53) c	2.66	(0.60) c
	24	10	7.79	(0.74) b	4.86	(0.18) ab	3.80	(0.04) b
	24	20	2.95	(0.27) c	2.52	(0.34) c	2.16	(0.19) c

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.



Time (h)		Pressure (kPa)	WS Cohesion Strength					
			3 kPa	6 kPa	9 kPa			
HRS	Control		0.70 (0.26) a	0.91 (0.09) a	1.08 (0.10) a			
	12	10	0.98 (0.42) a	1.14 (0.04) a	1.18 (0.14) a			
	12	20	1.17 (0.30) a	1.18 (0.17) a	1.18 (0.10) a			
	24	10	1.08 (0.40) a	1.11 (0.19) a	1.04 (0.15) a			
	24	20	0.78 (0.04) a	1.04 (0.10) a	1.08 (0.06) a			
SRW	Control		0.70 (0.13) a	2.26 (0.09) a	3.41 (0.57) ab			
	12	10	0.91 (0.05) a	2.58 (0.16) a	4.66 (0.18) a			
	12	20	0.86 (0.36) a	2.33 (0.36) a	4.10 (0.37) ab			
	24	10	0.55 (0.07) a	1.96 (0.66) a	3.25 (0.79) b			
	24	20	0.72 (0.26) a	1.98 (0.40) a	3.66 (0.23) ab			

 Table 9
 WS cohesion strength of wheat flour as affected by time consolidation.

Values in parentheses are the standard deviations. Values followed by the same letters are not significantly different when compared within HRS and SRW.

bution of the flours. SRW is softer and more cohesive than HRS, thus under consolidation, the bulk density increased, and bonding occurred between particles (Bian et al., 2015). With increasing bulk density and fewer voids between particles, the permeability decreased. HRS particles are harder than SRW particles, thus the voids during consolidation remained, and the effect of pressure was not significant.

Table 9 shows the WS cohesion strength values after consolidation. Only SRW flour, after 24 h of consolidation at 10 kPa pressure, exhibited a significant difference. This indicated that consolidation has a limited effect on WS cohesion strength. Similar to permeability, the SRW bulk properties are more affected by consolidation because of the flour particle's own properties, and after 12 h and 10 kPa consolidation, cohesiveness increased significantly. This result agrees with Iqbal and Fitzpatrick (2006), that the time consolidation does not have an effect on flour's effective angle of internal friction, which represented the cohesiveness of the powder.

4. Conclusions

HRS and SRW have different compositions, therefore consolidation and vibration effects on the bulk flour properties differed. Vibration rearranges the particles inside the container and helps cohesive flour powder form agglomerates, thus the compressibility, cohesiveness, permeability, and wall friction changed. After vibration, smaller particles filled the interparticle voids and formed a denser bulk with decreased permeability. Wall friction demonstrated significant changes before and after vibration. Thus, rearrangement and uniformity of the flour after transportation are attention-worthy. The rearrangement possibly changed the particle size at the location where WS cohesion strength was measured, which resulted in a decreased WS cohesion strength for SRW flours. With vibration, segregation of flour can cause inconsistency of flour quality for downstream processing. But the effect of vibration time on flour segregation is still an unexplored area of research.

Time consolidation increases interparticle interactions. Due to the differences in flour hardness, the effect of time and pressure were not the same for SRW and HRS flours. SRW flour was affected by pressure change while HRS flour was affected by storage time. Because SRW flour is softer and more cohesive than HRS, the flour particles tended to deform, and SRW flour was more compacted under high pressure.

Particle size and shape, as well as surface chemical composition, could also have changed after consolidation, thus further studies on single-particle changes are needed in order to better understand the bulk property changes under time consolidation.

Nomenclature

CE	Circular equivalent
HRS	Hard red spring flour
L	Packed bed of length
М	Torque by Warren-Spring geometry
Q	Airflow rate
$R_{\rm i}$	Inner radii of WS geometry (Fig. 3)



 R_0 Outer radii of WS geometry (**Fig. 3**)

- WS Warren-Spring
- σ Normal stress
- τ Shear stress
- Δp Pressure drop in the compacted powder bed
- η Air dynamic viscosity
- ρ_0 Powder density before compression
- $\rho_{\rm t}$ Powder density after compression

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A Semi-Automated DEM Parameter Calibration Technique of Powders Based on Different Bulk Responses Extracted from Auger Dosing Experiments[†]

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Abstract

Discrete Element Method (DEM) proved to be an essential tool to optimize the industrial auger dosing process for pharmaceutical powders. During the DEM parameter calibration process of a certain powder, several parameter combinations might lead to a similar bulk response, which could also vary for other bulk responses. Therefore, a methodology is needed in order to narrow down the number of combinations and be at once close to reality representation. In this study, a vertical auger dosing setup is used as a standard calibration device to extract three different bulk responses, i.e., angle of repose, bulk density, and mass flow rate. Simulations using LIGGGHTS software package are performed based on Design of Experiments (DoE) by varying four input factors, i.e., auger speed, particle-particle and particle-wall static friction coefficients, and particle-particle rolling friction coefficient. The successful application of multivariate regression analysis (MVRA) results in predicting the bulk behavior within the studied ranges of parameters. In this regard, clustering the different predicted behaviors of the three responses together allows to dramatically reduce the admissible parameter combinations. Consequently, an optimized set of calibrated DEM parameters is chosen, where the simulation results accurately match the experimental reference data. This simple dynamic calibration tool proves to strongly verify and predict the flowability of free-flowing bulk materials.

Keywords: discrete element method, design of experiment, auger dosing, mass flow rate, multivariate regression analysis, calibration

1. Introduction

Screw conveyors are utilized extensively in process engineering as mechanisms to transport bulk materials (e.g., granular materials). As the screw rotates, bulk materials are dispensed from the container and conveyed along the screw casing. Although the mechanical system is quite simple, understanding and controlling the material behavior towards an optimal process might be challenging (Moysey and Thompson, 2005; Owen and Cleary, 2009; Roberts, 1999). In fact, several problems might be experienced if the machine is not designed properly in connection with the conveyed material's nature and mechanical behavior (Clearly, 2007; Owen and Cleary, 2009). These problems can be defined, for instance, as surging and unsteady flow rates, inhomogeneity of the product, inaccurate metering and dosing, product degradation, high start-up torques, excessive power consumption, high equipment wear, variable residence time, and segregation.

1.1 Screw feeding and DEM

Particle simulation is a popular approach to model and predict the behavior of bulk materials involved in different systems. These systems may include several applications such as storing, transporting or processing granular materials, for instance, sand, semolina, pigments, pharmaceutical powders, crystallized products such as ammonium sulfate, fertilizers, polyethylene powder, harvest products or other bulk materials in food, chemical, mining or pharmaceutical industries. In this study, the DEM (Cundall and Strack, 1979) is utilized to model granular flow at the particle level. DEM has proven to be an effective and wellestablished approach to study stress and motion of particulate systems (Börner et al., 2016). In fact, DEM is applied to simulate particle systems in different industrial applications (Zhu et al., 2008) as e.g., in connection with screw feeding process. In particular, DEM is used to model



Received 20 December 2019; Accepted 26 March 2020
 J-STAGE Advance published online 30 May 2020

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the behavior of particles flowing in screw feeders in several studies leading to a number of valuable findings (Fernandez et al., 2011; Moysey and Thompson, 2005; Owen and Cleary, 2009). Different responses obtained from DEM modeling of screw conveyor process showed a good agreement with analytical and experimental reference results. These responses include mass flow rate, required screw power, and particle transfer velocity (Owen and Cleary, 2009, 2010; Shimizu and Cundall, 2001). Pezo et al., 2015 studied the influences of screw length and different screw design types on the performance of screw conveyor-mixer during material transport. In this, DEM modeling and experimental validation were performed, where it was shown that the modified screw conveyor geometry leads to better mixing quality.

In order to decrease the computation time in DEM, a scaling-up principle based on coarse-graining method is implemented by increasing the size of particles introduced in the system while maintaining the size of the system geometry (Bierwisch, 2009; Ciantia et al., 2016; Sinnott and Cleary, 2016; Wang et al., 2016). This leads in reducing the computational costs of the DEM simulations. In this, the number of particles is decreased dramatically, i.e., by a scaling factor of S^3 . It is important to notice that the upscaling should not affect the velocity of the moving geometries and the gravitational acceleration.

1.2 Calibration approaches

Notwithstanding the wide range of applicability of DEM, choosing a set of micromechanical parameters sufficient for representing the macroscopic behavior of granular material lacks always a calibration process. Therefore, many research works can be found in the literature and are dedicated to this aim. The conventional calibration approach is the "trial and error", where in many cases, one factor is changed at a time to reach a certain relation between the inputs and outputs of the system. A comprehensive review that addressed to the angle of repose (AoR), measurements techniques, suitable applications and the role of several parameters are presented by Al-hashemi and Al-amoudi, 2018. As an assessment for the improvement of DEM calibration approaches, Coetzee, 2017 addressed various calibration approaches, which covered over 25 years of related studies. Roessler et al., 2018 developed a standard calibration scheme for the DEM parameters of free-flowing bulk materials using a modified drawdown test to solve the problem of ambiguity. In a sandpile test, Zhou et al., 2002 investigated the impact of particle-particle as well as of particle-wall coefficients of friction, i.e., static and sliding on the angle of repose. They were able to establish a power-law relationship between the extracted AoR and the input parameters and revealed that all friction coefficients followed a positive dependency, whereas particle

size followed an opposite one. Aside from the DEM, other methods, for instance, macroscopic porous media mechanics, can be implemented to obtain the behavior of granular materials on larger scales and realize important behaviors such as fracturing and consolidation (Heider et al., 2018; Obaid et al., 2017; Pillai et al., 2018). However, these methods postulate the continuity of the material and don't explicitly describe the interactions between the particles. For that reason, our underlying study will focus mainly on the DEM approach.

More efficient approaches are being recently following systematic data analysis such as Design of Experiments (DoE). Based on DoE, El Kassem et al., 2018 calibrated the AoR value of a pharmaceutical powder by varying the coefficients of rolling friction and restitution. In an advanced study, El Kassem et al., 2020 developed a systematic numerical approach, using DoE and multivariate regression analysis (MVRA), to efficiently study the influence of different DEM input parameters on various bulk responses. The statistical prediction model of the AoR and porosity, of free-flowing and cohesive powders, accomplished a good quantitative agreement between DEM simulation and experimental data results. In a roller compaction process application, Souihi et al., 2013 utilized an orthogonal partial least squares (PLS) regression to study the outcomes of a reduced central composite face-centered design in DoE. Yan et al., 2015 employed a parametric multi-level sensitivity approach to analyze the influence of DEM input parameters, namely coefficients of friction and restitution, and Young's modulus (Y), on AoR and particle flow rate in a discharge system from a flat bottom cylindrical container. Principal component analysis (PCA) is used to weight the contributions and sensitivity of each parameter on the bulk responses. The study showed the significant effect of the coefficient of static friction and the insignificant impact of the particle restitution coefficient and Y. The reduction in Y values showed insignificant impact, where this is complied with (Lommen et al., 2014), in such, decreasing the shear modulus' value (e.g. from 107 and 1011 Pa) has no influence on the DEM results. Relying on experimental measurements, Johnstone, 2010 applied DoE to perform various calibration and validation techniques.

1.3 Scope of this work

The existence of a large number of parameter combinations outputting the same bulk behavior in simulations is considered a bottleneck for many DEM users. In this study, a novel semi-automated DEM calibration approach that focuses on the ambiguity problem is developed. An auger dosing application is used to output three different bulk responses, namely angle of repose, mass flow rate, and bulk density. Unlike most of the studies involving screw conveying machines, a vertical-oriented micro auger



is used in this work to represent an auger dosing process of free-flowing pharmaceutical powder. The objective of this research work is first to perform a parametric study and then to calibrate free-flowing powder using DoE and MVRA. A quadratic D-Optimal design model is used to setup an optimized number of combinations to be simulated. A simulation tool is realized by an open-source software LIGGGHTS® (Kloss et al., 2012), where the simulations were carried out in parallel computing toolbox. An analytical mass flow rate test for dynamic powder discharge using an auger is derived and verified by our DEM simulations and experiments. The auger dosing performance is studied in dependence on auger speed, particle-particle coefficients of static and rolling friction and particle-wall static friction coefficient. Although the coefficient of friction between particles and boundaries is a significant affecting parameter, it is not widely included in the literature. This work extended the scope of previous studies by including this factor into the parametric studies. In this study, the level of effectiveness of these coefficients is investigated to check how they impact four studied responses, i.e., mass flow rate, angle of repose, bulk density, and translational kinetic energy. Meanwhile, as it is almost impossible to measure the energy output on the single-particle scale experimentally, the energy dissipation of the particles is only identified through DEM.

In this work, the DEM parameter combinations are reduced efficiently to reach an almost solitary combination of parameters by superimposing three output prediction contour plots. Calibrations are done based on the bulk behaviors obtained from the experiments and thus the regression analysis model is validated. By this, it is well clarified that using multiple calibration tests lead to more accurate and realistic results and thus reduce the ambiguity. As a result, the simple auger dosing machine can be considered as a standard calibration device for advanced industrial applications.

2. Materials and methods

2.1 Sample description and characterization

In this research work, a pharmaceutical crystalline lactose monohydrate powder, called SpheroLac 100, produced by the German company MEGGLE Wasserburg GmbH & Co. KG was used. It is a typical dry non-cohesive (free-flowing) powder used in different applications, such as in capsule filling, blends, premixes, sachets, and trituration. In the following, methods used to characterize the powder with its particle size, shape and density are discussed. These will be used later on in the setup and analysis of the DEM simulations. The characterization tests were repeated three times to ensure repeatability and accuracy of the results.

2.1.1 Particle size and shape description

Dynamic image analysis of particle size and shape by means of Camsizer XT from Retsch Technology GmbH was performed. It measured the volume moment mean (D[4,3]). The D[4,3] identifies around which central point (center of gravity) of the frequency the volume/mass distribution would rotate. Compared to other particle sizes calculation methods, the above-mentioned method is characterized in such a way that it does not demand the number of particles in its estimation. In addition, the Camsizer XT assists in estimating the particle shape, where the particles are outlined in two-dimensional images in terms of the minimum and maximum Feret diameters (Femin, Femax). In this, Fe_{\min} and Fe_{\max} are the length of the minor and of the major axis, respectively. Based on ratio of Fe_{\min} with respect to Fe_{max} one computes the aspect ratio (ASR), where values in the range [0, 1] reflects the elongation of a particle and, thus, the deviation from a spherical shape. In particular, small values represent elongated particles and higher values represent spherical particles.

According to Li et al., 2002, the circularity or roundness (Ro) is a further factor that determines to what degree a particle possesses a spherical shape. This factor is estimated based on the projected area (A) of the particle and the total perimeter of the projection (P) as

$$Ro = \frac{4 \times \pi \times A}{P^2} \,. \tag{1}$$

2.1.2 Density

The particle (material or true) density (ρ_p) was determined using the Ultrapyc 1200e, Automatic Density Analyzer from Quantachrome Instruments (USA). In this, a pycnometer measures the material density of the powder samples using an inert helium gas. It measures the volume by applying the principle of Archimedes of displacement and the technique of gas expansion according to Boyle's law.

2.2 Experimental investigation

2.2.1 Bulk density

In order to visualize the height of the powder bed and compare the DEM simulation with the experiment, a simple test using a transparent glass tube of an inner diameter 24 mm and a total height of 94 mm was utilized. Initially, a mass of 6 g of SpheroLac 100 was filled inside the tube where then the volume was recorded and thus the bulk density (BD) was obtained.

2.2.2 Auger dosing

An auger powder container with an inner diameter of 64 mm and a total height of 224 mm was used in running the mass flow rate (\dot{m}) experiments of SpheroLac 100 powder.



It consists of a cover, a funnel, an opaque cylindrical glass tube, a shaft connected to a rotational motor, and an auger. The geometry and the dimensions of the auger, including the inner and outer diameters, the pitch and the auger filling volume per 1 revolution, which is used to conduct the experiments, are illustrated in **Fig. 1**. Theoretically, the auger filling volume represents the maximum volume a material, which could be filled in one complete rotation.

The auger dosing container encloses a stainless-steel funnel (1.4404) with an upper diameter of 63 mm, a lower opening diameter of 6 mm and an inclination angle of 45°. The auger is connected directly to the drive shaft of an overhead stirrer rotating motor RZR 2102 control from Heidolph Instruments (Germany). A laboratory weighing balance XPE 204 from Mettler Toledo (Germany), used as a catch scale, is placed under the outlet of the auger dosing container to record the powder mass flow every 0.2 s. The dosed powders are collected in a container made of borosilicate 3.3 glass (**Fig. 2**). The XPE 204 is placed on a Regupol sound 17 isolation pad to avoid the transmission of any external vibration into it. The XPE 204 has readability down to 0.1 mg and a capacity up to 220 g. HTerm software is used on a computer to record the values of mass



Fig. 1 Illustration of the auger geometry used in the tests.



Fig. 2 Experimental setup of the auger dosing tests in (a) front CAD view and (b) laboratory equipment setup.

flow over time. In addition, an ionization device Static Line LC is used to neutralize electrostatic charges. The container was placed at a distance of 80 mm from the bottom of the catching container, where, initially, was loosely filled with 6 g of the tested powder.

The volumetric mass flow rate (*m*) is calculated using the difference in mass (Δm) obtained from the XPE 204 divided by the difference in time (Δt) between consecutive weighing balance measurements:

$$\dot{m}(g/s) = \frac{\Delta m(g)}{\Delta t(s)}.$$
 (2)

To ensure repeatability, the test was repeated three times at three different auger rotational speeds, i.e., 400, 600 and 800 rpm, where an average of the obtained *m* was considered as an experimental reference value at each speed. After dosing, the formed AoR inside the catching container was measured. The AoR prescribes the slope of a discharged conical heap of loose bulk solid material (Marigo et al., 2014). It represents a cohesiveness characteristic of a powder (Zhou and Qiu, 2010). It is widely a familiar method to characterize powders according to their flowability (Krantz et al., 2009; Lumay et al., 2012). It is frequently applied to calibrate DEM simulation parameters as the angle of the heap formed upon the settlement of the powder depends on the strength of the inter-particulate friction.

2.3 Design of experiment (DoE)

DoE is an efficient optimized tool to design a matrix of experiments (in our case simulations) to be executed and consequently generate a reliable process model. It is mainly used to identify the cause-effect relationship between factors and responses in a studied system or process (Sundararajan, 2018). The DoE methodology was implemented to examine the effects and interactions of DEM input parameters on the output bulk responses. This approach helped in facilitating the DEM calibration procedure. To acquire the maximum quantity of information from the minimal number of simulations, D-Optimal design, based on the least square method (Eriksson et al., 2008), with a quadratic model type, was adopted using Cornerstone 6.1.1.1.

2.4 Multivariate regression analysis (MVRA)

MVRA is a statistical approach used to evaluate the variation of several response variables and hence build a regression model. In the underlying study, this approach was used to examine and interpret the variation and effect of various DEM input parameters on the studied bulk responses. By employing Cornerstone, the collected data values from the experiments are standardized in such a way that the original variables are scaled to have a mean value of of 0 and



a variance of 1. The standardization step is initially done since one of the investigated parameters has a different measurement unit than the others. The coefficient of determination (adjusted R^2) was used to describe the goodness of fit of the model which in turn represents the proportion of the variability of the data explained by the model. A high level of confidence (±95 %) was considered in the DoE analysis. As a representation of the effect of each input parameter on the studied bulk responses, an adjusted response graph was used. The response values are tuned to average out the effects of the other input parameters. Moreover, a Pareto graph is applied to figure out the relative range of effect of each particular studied DEM input parameters. It shows the orthogonally-scaled effects of the parameter on the studied responses. In particular, applying orthogonal scaling to the values of a parameter α_i yields scaled values β_i in the range [-1, 1]. This is defined as $\beta_i := (\alpha_i - M_s)/(1 + 1)$ $R_{\rm S}$ with $M_{\rm S} = (\alpha_{\rm max} + \alpha_{\rm min})/2$ and $R_{\rm S} = (\alpha_{\rm max} - \alpha_{\rm min})/2$, see, e.g., (Triefenbach, 2008). Moreover, a prediction model based on the regression analysis was built, which helped in predicting and figuring out the best-optimized combination between the parameters studied.

Fig. 3 illustrates the general flowchart followed in the systematic calibration approach. From the auger dosing experiments, the results of the bulk responses to be studied are considered as the reference targets. The DEM input parameters are varied according to DoE design model and studied in the following regression analysis. The prediction model is then used to calibrate the parameters by selecting an optimized parameter combination, where a good fit is obtained between the simulation results and the experimental data.

3. DEM simulations

3.1 Contact models

In our DEM simulations, the particles are considered as rigid bodies, where they have translational and rotational degrees of freedom assigned to their center of mass. In this, particle interactions are modeled using Newton's equations of motion, contact laws for force and overlap relationships. In this study, the soft-particle approach, originally proposed by Cundall and Strack, 1979 is followed, where the particles are allowed to overlap with each other (small deformation) when coming in contact. Consequently, the elastic and plastic deformations and the frictional forces between the particles can be determined (Zhu et al., 2007). Various interactions, i.e., forces and torques due to gravity, deformations under collisions, and static and rolling frictions might take place as two particles *i* and *j* endure contact. In this study, Hertz-Mindlin contact model (Hertz, 1882; Mindlin, 1949) was applied to calculate these resulting forces. Translational and rotational equations of motion of a particle *i* are expressed by the following equations:

$$m_i \frac{\mathrm{d}\boldsymbol{v}_i}{\mathrm{d}t} = \sum \left(\boldsymbol{F}_{ij}^{\mathrm{n}} + \boldsymbol{F}_{ij}^{\mathrm{t}} \right) + m_i \boldsymbol{g} , \qquad (3)$$

$$I_i \frac{\mathrm{d}\boldsymbol{\omega}_i}{\mathrm{d}t} = \sum \left(\boldsymbol{R}_i \times \boldsymbol{F}_{ij}^{\mathrm{t}} - \boldsymbol{\tau}_{ij}^{\mathrm{r}} \right), \tag{4}$$

where m_i , g, I_i , v_i and ω_i are the mass, gravity vector, moment of inertia, translational velocity and rotational velocity of particle *i*, respectively. The interplay between two particles *i* and *j* at time *t* results in normal and tangential forces, i.e., F_{ij}^n and F_{ij}^t , respectively. R_i refers to the vector between the particle *i* center and the contact point, where F_{ij}^t is applied. Moreover, τ_{ij}^r represent the torque resulting from the rolling friction between the two particles.

In this regard, the rolling friction in DEM is utilized as a correction parameter that allows to use spherical particle



Fig. 3 General flowchart of the calibration process.

shapes instead of representing the real shapes of the particles (Iwashita and Oda, 2000; Wensrich and Katterfeld, 2012). To represent the rolling friction in our study, the alternative elastic-plastic spring-dashpot (EPSD2) rolling resistance model was used, which is initially proposed by Ai et al., 2011 and extended by Iwashita and Oda, 2000. The mentioned model is implemented to compute the torque $\tau_{i,t+\Delta t}^{r}$ at an incremental time step as

$$|\boldsymbol{\tau}_{ij,t+\Delta t}^{\mathrm{r}}| \leq \mu_r \boldsymbol{R}^* |\boldsymbol{F}_{ij}^{\mathrm{n}}|, \qquad (5)$$

where μ_r is the rolling coefficient and R^* is the equivalent radius. In this model, the damping torque is disabled for simplicity.

For the purpose of having a stable integration scheme, the time step (Δt) was set to a value less than 20 % of the critical time step (Rayleigh time, $T_{\rm R}$). $T_{\rm R}$ is calculated based on the Rayleigh wave propagation, where the elastic wave propagation from one particle to the adjacent contacting particle can be computed according to the following equation (Li et al., 2005).

$$\Delta t < T_{\rm R} = \frac{\pi R \sqrt{\frac{\rho}{G}}}{0.1631\nu + 0.8766} \,. \tag{6}$$

In this, R, ρ , G and v are the particle's radius, density, shear modulus and Poisson's ratio, respectively.

3.2 Simulation procedure and parameters

3.2.1 Simulation setup

The DEM numerical simulations were carried out using LIGGGHTS[®] -Premium 4.X, which is an open-source software from DCS Computing GmbH (Linz, Austria). They were conducted on an eight-node high-performance cluster that uses 64 CPUs (Intel Xeon 2.60 GHz). The post-processing of the simulations was carried out using the open-access ParaView software, version 5.4.1 64-bit from Kitware Inc. (New York, NY, USA). Solid-Works version Premium 2016 from Dassault Sysèmes (Vélizy-Villacoublay, France) was used to model the 3D CAD parts applied in the DEM simulations. Thereafter, the 3D models were spatially discretized using the open-access Gmsh, version 3.0.6 (Geuzaine and Remacle, 2009).

3.2.2 Simulation conditions and input parameters

The Young's modulus and Poisson's ratio values of the funnel and the auger, as they are considered stainless steel, and the catching container (borosilicate 3.3 glass) were selected from the literature (Geuzaine and Remacle, 2009; MakeItFrom, 2019a). Following the recommendations (Govender et al., 2015; Marigo and Stitt, 2015), Young's modulus for the particle was reduced within a certain per-

 Table 1
 The considered DEM input parameters throughout the study.

Material parameter/con- tact model	Symbol	Unit	Value
Young's modulus funnel and auger ^a	Y _F	GPa	200
Young's modulus catching container ^b	Y _C	GPa	67.8
Young's modulus particle	Y _p	GPa	0.026
Poisson's ratio funnel and auger ^a	v		0.28
Poisson's ratio catching container ^b	v		0.21
Poisson's ratio particle	v		0.3
Particle diameter (after coarse-graining)	$d_{\rm p}$	μm	690
Contact law parameters			
Coefficient of restitution particle-particle	$e_{\rm pp}$		0.2
Coefficient of restitution particle-wall	$e_{\rm pw}$		0.2
Coefficient of rolling friction particle-wall	$\mu_{\rm r,pw}$		0.2
Coefficients of restitution and friction wall-wall			0.2
Factory settings			
Filling mass		g	6
Number of particles			22705
Simulation time step		S	$2.62 imes 10^{-6}$
Acceleration due to gravity	g	m/s^2	9.81

^a (MakeItFrom, 2019a), ^b (MakeItFrom, 2019b)

missible limit in order to reduce computational costs. The boundary conditions, like coefficients of restitution and rolling friction between the particle and the walls (stainless steel and glass) were assumed to be constant throughout the simulations. The particle size was scaled-up six times using the coarse-graining method identified by Bierwisch et al., 2009. **Table 1** presents the applied DEM input parameters in the auger dosing DEM simulations.

On the other hand, one process parameter and three-particle properties were varied (**Table 2**) in the context of the DoE: auger rotational speed (ω), coefficient of static friction ($\mu_{s,pp}$) and coefficient of rolling friction ($\mu_{r,pp}$) between particle-particle and coefficient of static friction ($\mu_{s,pw}$) between particle-wall. Three values were selected for each of the parameter, which include a low, a center, and a high value, see, (Roessler and Katterfeld, 2019; Wilkinson et al., 2017) for reference. Based on the DoE, only 20 simulation runs were required.





3.2.3 DEM studied responses

Four main factor responses were studied in this work, i.e., angle of repose (AoR), bulk density (BD), mass flow rate (\dot{m}), and the overall translational kinetic energy (TKE). The BD was determined inside the funnel after the insertion and settlement of the particles. After opening the funnel, \dot{m} and the average of TKE were computed and then normalized (NA-TKE) over the total time of dosing (DT) of the particles. The AoR was determined in the catching container after the particles were settled down at the end of the dosing process. **Fig. 4** shows a cross-sectional view of

 Table 2
 List of the parameters varied in the DoE simulations related to the auger dosing.

Parameter	Symbol	Unit	Value
Auger rotational speed	ω	rpm	400, 600, 800
Coefficient of static friction (par-par)	$\mu_{\rm s,pp}$		0.3, 0.55, 0.8
Coefficient of static friction (par-wall)	$\mu_{\rm s,pw}$		0.1, 0.25, 0.4
Coefficient of rolling friction (par-par)	$\mu_{\rm r,pp}$		0.1, 0.4, 0.7

the initial state of the funnel filled with 6 g of powder using ParaView software.

Table 3 presents the DoE matrix followed in performing the parametric and calibration study. The results cover the dosing of 5.2 g, which is the common linear steady state of the particle flow (dosing) for all the simulations. This is because of having big mass flow fluctuations at the end of the dosing due to the very low amount of powder left inside the funnel.



Fig. 4 Illustration of the initial state of particles filled inside the funnel.

Table 3DoE matrix and DEM results for the considered 20 simulations.

Run	ω (rpm)	$\mu_{ m s,pp}$	$\mu_{ m s,pw}$	$\mu_{\rm r,pp}$	AoR (°)	BD (g/cm ³)	ṁ (g/s)	NA-TKE (µJ/s)	DT (s)
1	400	0.3	0.1	0.1	29.3	0.764	0.3995	0.0340	13.0
2	400	0.3	0.1	0.7	35	0.761	0.3712	0.0267	14.0
3	400	0.3	0.4	0.1	29.3	0.767	0.2585	0.0135	20.2
4	400	0.3	0.4	0.7	34.5	0.753	0.2520	0.0107	20.8
5	400	0.55	0.25	0.4	37	0.742	0.2689	0.0112	19.2
6	400	0.8	0.1	0.1	33.5	0.748	0.3780	0.0283	13.8
7	400	0.8	0.1	0.7	40.3	0.730	0.3346	0.0265	15.6
8	400	0.8	0.4	0.1	33.5	0.752	0.2471	0.0139	21.2
9	400	0.8	0.4	0.7	39.5	0.724	0.2301	0.0138	22.8
10	600	0.55	0.4	0.1	32.8	0.759	0.3677	0.0362	14.2
11	600	0.8	0.1	0.4	36.4	0.733	0.4872	0.0594	10.6
12	600	0.8	0.25	0.7	40	0.723	0.3796	0.0352	13.8
13	800	0.3	0.1	0.7	38.4	0.757	0.6674	0.0992	7.8
14	800	0.3	0.25	0.4	36.8	0.759	0.5538	0.0663	9.4
15	800	0.3	0.4	0.1	30.2	0.767	0.4946	0.0778	10.6
16	800	0.55	0.1	0.1	32	0.753	0.6782	0.1102	7.6
17	800	0.55	0.4	0.7	41.5	0.734	0.4523	0.0616	11.6
18	800	0.8	0.1	0.7	40	0.729	0.5974	0.1095	8.8
19	800	0.8	0.25	0.1	33.8	0.754	0.5458	0.0694	9.6
20	800	0.8	0.4	0.4	36.2	0.735	0.4482	0.0689	11.6



4. Results and discussion

4.1 Material characterization

In this section, the results obtained from the experimental tests are summarized. In particular, **Table 4** presents the results of the particle size, shape and density of the Sphero-Lac 100 powder. The particle shape in LIGGGHTS was set as spherical since the powder has high ASR and *Ro* values.

4.2 Experimental results

4.2.1 Bulk density

Since the funnel used in the auger dosing experiment is not transparent, the exact height of the powder inside the funnel cannot be determined. Therefore, a transparent glass tube was used instead. After filling 6 g of powder inside the glass tube, the average powder height inside the tube was 17.5 mm (**Fig. 5**). As a result, the average calculated BD in the experiment is 0.758 g/cm^3 .

4.2.2 Mass flow rate

The results of the \dot{m} tests of SpheroLac 100 at the three rotational speeds are illustrated in **Fig. 6**. A linear regression of the mass curves (with capital M) was done, where the coefficient of determination (R^2) of the linear

Table 4Particle size, shape and density of SpheroLac 100 powder.

	D[4,3] (µm)	ASR	Ro	$\rho_{\rm p}({\rm g/cm^3})$
SpheroLac 100	115	0.746	0.891	1.5361



Fig. 5 The BD experimental result.



Fig. 6 The results of the \dot{m} tests at three different auger rotational speeds.

regression of the mass curves was equal to 1 in all the experiments. The slopes of these linear curves represent \dot{m} , namely 0.2568 g/s, 0.3744 g/s and 0.5074 g/s at speeds of 400, 600 and 800 rpm, respectively. The left graph column represents the mass M (g) and the right graph column represents \dot{m} (g/s) where both are plotted over time (s).

4.2.3 Angle of repose

After the dosing was completed, the powder collected in the catching container formed a heap. For each experiment, the AoR was determined by considering the average value between the left and right angles, i.e., θ_1 and θ_2 , respectively.

Table 5 summarizes the results of \dot{m} and the AoR from the auger dosing experiments. The values of \dot{m} at the three different speeds and the averaged AoR, besides the BD, are the macroscopic reference values, which were used in the DEM calibration simulations by validating the prediction models (explained in section 4.4). It is also worth mentioning, that it was not possible for us to measure the TKE experimentally. Therefore, TKE will be discussed in the DEM parametric study but it was not considered as a parameter in the calibration process.

4.3 Parametric study

In this section, the effect of the studied parameters on multiple bulk responses will be discussed in terms of manner and extent. **Fig. 7** illustrates the effects on the studied responses in an adjusted response graph. Each of the given box plots (row-wise) corresponds to a bulk response, and each of them (column-wise) coincides with a DEM input parameter. The data points shown in **Fig. 7** represent the points obtained from the simulations and the effect drawn (curve) from them. These data points are adjusted to average out the effects of the other factors included in the model.

The regression models of the four responses have shown high adjusted R^2 values, which indicates very good fits to the determined data points. **Table 6** lists the values of the adjusted R^2 of the four studied responses.

4.3.1 Factors affecting the angle of repose

As can be seen from **Fig.** 7(a), all the studied parameters have a significant effect on the AoR but with varying levels of effectivity. For a more comprehensive illustration

 Table 5
 Summary of the experimental results of the AoR and m.

ω (rpm)	AoR (°)	<i>ṁ</i> (g/s)
400	33.2	0.2568
600	33.4	0.3744
800	33.2	0.5074





Fig. 7 Adjusted response of the (a) AoR, (b) BD, (c) \dot{m} and (d) NA-TKE as a function of the four varied DEM input parameters.

Table 6Outline of the adjusted R^2 values related to the four responses'models.

	AoR	BD	'n	NA-TKE
Adjusted R^2	0.975	0.983	0.998	0.986

of the individual and interactive effects of these parameters, Pareto chart is developed in Fig. 8. It shows the orthogonally-scaled effect of the input parameters on the AoR. The bars being above the 0-axis signify the positive effect (proportional) of the corresponding parameters, and the ones being below it signifies negative effect (antiproportional). The factors are distributed in descending order according to the level of positive or negative effects from left and right, respectively. Consequently, it can be clearly seen that $\mu_{r,pp}$ is the most affecting factor on the AoR in our system, where its increase increases the angles of the heap. This is contradictory to most of the literature, where it is stated that the biggest impact on the AoR is the $\mu_{s,pp}$. This can be explained by that the introduction of the rotating micro-auger in the system caused more a rotational motion of the particles around their center. The auger speed has a small effect on the AoR. Moreover, it is important to notice the almost negligible effect of $\mu_{s,pw}$, which can be neglected from the list of affecting parameters on the AoR.

4.3.2 Factors affecting bulk density

Fig. 9 illustrates the orthogonally-scaled effects on the BD. According to the parametric study, $\mu_{s,pp}$ and $\mu_{r,pp}$ can be considered the only effecting parameters on the BD in this study while the $\mu_{s,pw}$ has an insignificant effect. The interactions between $\mu_{r,pp}$ and both of $\mu_{s,pp}$ and $\mu_{s,pw}$ have



Fig. 8 Orthogonally-scaled effects of the model factors on the AoR.



Fig. 9 Orthogonally-scaled effects of the model factors on the BD.

a negative impact on the BD, where, as they increase, the BD decreases.

4.3.3 Factors influencing the mass flow rate

Similarly, the orthogonally-scaled effects on the \dot{m} are shown in Fig. 10. It is evident how the ω has the



largest positive significance on \dot{m} , whereas $\mu_{s,pw}$ has the largest negative impact on it. As the particle-wall friction increases, the tendency of particle flow decreases dramatically leading to low mass output. It is important to notice that although the major effect $\mu_{s,pw}$ is having on \dot{m} , it has not been considered before as a calibration parameter in many other studies which now reveals its importance to be more widely studied.

4.3.4 Factors influencing the kinetic energy

In Fig. 11, the influence of the studied DEM input factors on the NA-TKE, is demonstrated in a Pareto graph of effects. Once more, ω has the highest positive significant effect followed by $\mu_{s,pw}$, which has the largest negative impact on the NA-TKE. It is noticeable that the $\mu_{s,pp}$ is showing a negligible effect on the NA-TKE. The reason for this is that the particles are basically being exposed to a rotary motion by the auger, therefore, the translational contact between the particles was almost not existing. Moreover, the rotation of the auger caused the particles to rotate around themselves, rather than rotating around one common axis. This can be seen by the presence of $\mu_{r,pp}$ as having some impact. Although the particles are not showing a translational relative motion with respect to each other, the $\mu_{s pw}$ is still proven to be a very affecting parameter on the NA-TKE. This means that the particles



Fig. 10 Orthogonally-scaled effects of the model factors on the m.



Fig. 11 Orthogonally-scaled effects of the model factors on the NA-TKE.

are sliding on the boundary during dosing. Therefore, it is important to draw attention to the importance of calibrating the roughness of the boundaries in DEM. Moreover, as the NA-TKE basically represents the dynamics of the particles, the AoR was measured when the NA-TKE reached the value of 0. This is because the AoR should be measured when the particles get in rest (Qi et al., 2019).

4.4 Experimental validation of predictive models

A prediction model, based on the MVRA results, is built and used to validate the robustness of the model. As $\mu_{r,pp}$ and $\mu_{s,pp}$ have the highest significant impact on the AoR and the BD, the contour plots were illustrated based on these two parameters (**Fig. 12a** and **Fig. 12b**). Although, as explained in subsection 4.3.3, ω and $\mu_{s,pw}$ have the highest impact on the *m*, but due to the aim of finding the optimal parameter combination between the calibrated parameters by superimposing three contour plots together, $\mu_{r,pp}$ and $\mu_{s,pp}$ were varied on the predicted contour plot of the *m* (**Fig. 12c**) as well. As an illustration example to find out the best optimized DEM parameter combination, the predicted contour plots were generated at $\omega = 800$ rpm and $\mu_{s,pw} = 0.347$ (as an optimized value resulting from the optimization algorithms in Cornerstone) as fixed values.

As can be seen from the above figures, wide ranges of combinations between $\mu_{r,pp}$ and $\mu_{s,pp}$ in each response lead to delivering the experimental reference values which are the underlined values in the graphs. Therefore, considering a single experimental bulk behavior highlights the problem of ambiguous parameter combinations in the calibration process. Consequently, the three predicted contour plots in Fig. 12 were superimposed. By this, the number of admissible combinations is dramatically minimized, where a very small intersecting region between the reference target values was found (see Fig. 13). Taking into account the minimized area of permissible combinations, the valid range for $\mu_{r,pp}$ is between 0.1 and 0.2 combined with $\mu_{s,pp}$ between 0.34 and 0.5. For more clarity, the intersecting contour lines away from our reference target values are blurred in the graph. The contour lines of the BD and the \dot{m} evidently intersect, whereas the contour line of the AoR (33.2°) is shifted around 0.3° ahead, which is accepted and within the range of the prediction model. In the context of the superimposing approach, one of the problems that may occur is the non-intersection between the contour lines (Derakhshani et al., 2015). Roessler et al., 2018 added that the measurement error needs to be taken into consideration to enable a significant overlap of the test results.

Cornerstone software offers an integrated optimization algorithm to select an optimal unique set of parameters combination that predicts the response values based on the experimental reference target values. Based on the optimization feature algorithm, that aims to match the


target values with minimum deviation errors, a simulation at 800 rpm was executed to validate our prediction model (confirmation run). In addition, two more simulations, at speeds 400 rpm and 600 rpm, took place similarly based on their prediction models as well which are not explained here. **Table 7** lists the different considered combinations and related bulk responses.

Fig. 14 compares the experimental AoR and the simulation ones. The results show a very close matching between the simulated heaps and the reference ones.

Using the selected optimized DEM input parameters, a



 $\begin{array}{c} 0.3 \\ 0.1 \\ 0.14 \\ 0.18 \\ 0.22 \\ 0.26 \\ 0.3 \\ 0.34 \\ 0.38 \\ 0.42 \\ 0.46 \\ 0.5 \\ 0.54 \\ 0.58 \\ 0.62 \\ 0.66 \\ 0.7 \\ \mu_{r,pp} \end{array}$

Fig. 12 Predicted contour plots of the (a) AoR, (b) BD and the (c) \dot{m} by varying $\mu_{s,pp}$ and $\mu_{r,pp}$ and having ω and $\mu_{s,pw}$ fixed.

DEM simulation is performed to calibrate the BD with the experiment. **Fig. 15** represents the powder height of the BD test in the experiment compared to that of the DEM simulation, where they both show the same height (17.5 mm) and thus the determined BD was matching (0.758 g/cm³).

Fig. 16 represents the m graphs of the three prediction simulations, where the results of the DEM clearly matches with the experimental findings. This enhances as an



Fig. 13 Superimposed contour plot showing the permissible combinations of the AoR, BD, and \dot{m} that fulfill the experimental reference values.



Fig. 14 Comparing the AoR of the (a) experiments and the (b) DEM simulations.



Fig. 15 The BD results in experiment (a) and in the DEM simulation (b).

 Table 7
 DEM parameter combinations of the prediction model and the bulk responses.

Run	ω (rpm)	$\mu_{ m s,pp}$	$\mu_{ m s,pw}$	$\mu_{ m r,pp}$	AoR (°)	BD (g/cm ³)	<i>ṁ</i> (g/s)	NA-TKE (µJ/s)	DT (s)
21	400	0.523	0.375	0.1	33.1	0.757	0.2542	0.0119	20.6
22	600	0.313	0.36	0.32	33.8	0.758	0.384	0.0313	13.6
23	800	0.51	0.347	0.1	33.5	0.757	0.5053	0.0692	10.4



Fig. 16 Validating the \dot{m} of the DEM with the experiments at speeds (a) 400 rpm, (b) 600 rpm and (c) 800 rpm.

additional validation to our systematic MVRA using the auger dosing as a standard calibration device. It is shown in the \dot{m} graphs, especially with speeds 600 rpm and 800 rpm that, at the beginning of the powder flow, there is a small deviation between the experiment and the simulation. In fact, this is due to the acceleration of the motor until the auger filling volume is full with powder.

As it has been pointed out, the regression prediction models qualitatively and quantitatively predicted the results of the three experimental calibration tests. **Table 8** summarizes the results from the validation process and compare them with the experimental reference values.

The maximum deviation is 2.86 % (in the case of the DT), where the overall mean deviation of the whole responses (12 results listed in **Table 8**) is 0.87 %.

Compared to (Roessler et al., 2018), our approach seems to be more efficient and reliable, where we ran only 20 simulations (instead of 384 in their case) to reach the same accuracy of the results. Thus, our systematic approach is an optimized procedure that saves time and money using DoE and MVRA.

Table 8Evaluation of the calibrated parameter combinations of thesimulation results compared to that of the experiments.

ω (rpm)	Bulk behavior	Experiment	Simulation	Deviation (%)
400	AoR (°)	33.2	33.1	-0.3
	BD (g/cm ³)	0.758	0.757	-0.13
	<i>ṁ</i> (g/s)	0.2568	0.2542	-1.01
	DT (s)	20.4	20.6	0.98
600	AoR (°)	33.4	33.8	1.2
	BD (g/cm ³)	0.758	0.758	0
	<i>ṁ</i> (g/s)	0.3744	0.384	2.56
	DT (s)	14	13.6	-2.86
800	AoR (°)	33.2	33.5	0.9
	BD (g/cm ³)	0.758	0.757	-0.13
	<i>ṁ</i> (g/s)	0.5074	0.5053	-0.41
	DT (s)	10.4	10.4	0

5. Conclusions

In this work, a standard calibration method for calibrating non-cohesive powders by tremendously reducing the ambiguity of the DEM parameters selection is established. It is based on an auger dosing principle, which calibrates three bulk material properties at the same time, namely AoR, *m* and BD in relation to the auger speed, particleparticle beside particle-wall static friction coefficients and particle-particle rolling friction coefficient. The study analysis was done through a highly systematic statistical approach using MVRA. With only 20 simulations, a parametric study of DEM input parameters on the bulk behaviors was performed followed by generating very robust prediction models. This parametric study explained how the aforementioned bulk behaviors depend highly on the particle level interactions and properties. The simulation results used to build a prediction model showed how a high number of different parameter combinations can lead to the same bulk responses. This study proved that using the superimposing principle by combining the prediction contour plots of the bulk responses evidently lead to a very narrow region that matches greatly with the experimental reference values. One optimized solution combination of DEM parameters through the prediction model was selected, where their results agreed significantly with the experimental data. A number of conclusions extracted from this study can be summarized as follows:

- Individual calibration tests are not sufficient to calibrate a material in DEM where the ambiguity for the admissible parameter combinations is high.
- · The auger dosing machine can be used to extract three



reference bulk responses, i.e., AoR, BD, m.

- Using the D-optimal design model, the superimposing principle of three predicted contour plots from the MVRA and the optimization algorithm in Cornerstone proved to be a robust approach to eliminate ambiguity.
- $\mu_{r,pp}$ was shown to have an overwhelmed effect over $\mu_{s,pp}$.
- Using the presented auger dosing machine, a unique optimized parameter combination was identified and experimentally validated.

For the future work, process optimization should be carried out by studying and validating more material properties and bulk behaviors. In addition, the study should be extended to cover cohesive powders.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-forprofit sectors.

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The Properties of Kaolin from Different Locations and Their Impact on Casting Rate[†]

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Abstract

It has been well known that mineral samples from different locations and origins can exhibit a significant shift in their properties and behavior. The present study of three samples of kaolin from a wide set of origin of deposits, composition, and ceramic properties, provided an important and perhaps a unique opportunity for investigating the interdependence of mineralogy, chemical composition, particle morphology, and surface property with their rheological behavior in ceramic applications such as casting rate. The X-ray diffraction patterns of kaolin samples #2 and #3 suggested low crystallinity with Hinckley Index (HI) ranging between 0.78 and 0.8. On the other hand, kaolin sample #1 was highly ordered with HI of about 1.21, and it had higher quartz content. This free quartz could enhance the permeability and hence increase the casting rate. The abundance of divalent ions (Ca^{2+} and Mg²⁺) in samples #2 & #3 could result in the collapse of the electrical double layer and reduction of zeta potential, consequently, coagulation of the particles leading to an increase of viscosity and dispersant demands. The morphology study suggested the platelet particles in samples #2 & #3 would lead to slower dewatering, thus, lower casting rate than that of the blocky (lower aspect ratio and narrower size distribution) particles in sample #1.

Keywords: kaolinite, kaolin, clay, powder, particles, casting

1. Introduction

Kaolin has a global market with an estimated value of 5.42 billion USD in 2018 (Kumar S., 2019). The market size is expected to grow continuously due to the increasing demand of ceramic products in a wide variety of applications (Dondi M. et al., 2008), such as whiteware (Sanz A. et al., 2018), paper (Frías M. et al., 2015), construction (Heah C. et al., 2011), paint (Ahmed N.M., 2013), drilling fluid (Au P.-I. and Leong Y.-K., 2013), etc. Furthermore, kaolin has great potential to be tailored for more innovative products including rapid-casting clays, engineered paper with kaolin coating, and nanocomposites (Dondi M. et al., 2003; Murray H.H., 2000). These advanced applications require more in-depth knowledge of the structure-property-behavior relationship of kaolin, which is not fully understood. In fact, it is difficult to comprehend the complexity because kaolin samples ex-

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hibit different particle size, size distribution, shape, chemical composition, surface chemistry and charge due to their diverse geological conditions and processing parameters.

The main scope of the present study is to investigate the kaolin properties that impact the rheological behavior. The key characteristics of the kaolin samples include mineralogy, the degree of kaolin crystallinity, chemistry, morphology, particle size, size distribution, shape and shape distribution, surface chemistry, interfacial properties, and the interaction with various deflocculants or dispersants.

2. Materials and methods

2.1 Materials

Three kaolin samples #1, #2, and #3 were carefully selected. Sample #1 was coarse-grained kaolin that had been engineered to achieve improved casting rate. This kaolin is currently commercialized by an American kaolin producer. The original geological source of the primary kaolin was from Georgia (USA). Sample #2 was wet-processed kaolin from Colombia, South America.



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Received 11 April 2019; Accepted 9 May 2019 J-STAGE Advance published online 2 November 2019

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KONA

The raw material for this sample was primary kaolin. Wet processing of this raw material resulted in a kaolin slurry which, in turn, was filter pressed to obtain the kaolin represented by Sample #2. Sample #3 was produced from the mechanical processing of Sample #2.

2.2 Methods

X-ray diffraction (XRD). The phase of each kaolin sample, as well as the crystallinity, was characterized using Panalytical X'Pert Powder with a 1400 W Cu X-ray tube.

Thermal gravimetric analysis (TGA). The weight loss due to dehydroxylation, phase transition, or thermal decomposition of each kaolin sample was measured and analyzed using TGA/SDTA851e.

Scanning electron microscopy (SEM). The texture, particle morphology of the kaolin sample was analyzed using the micrographs obtained by Hitachi S3000 SEM.

The zeta potential of kaolin particles was measured using Zeta Reader Mark 21.

The casting rate was measured following the protocol described by Eygi et al. (Eygi M.S. and Ateşok G., 2008)

3. Results and discussion

3.1 Mineralogical composition

The X-ray diffraction patterns of the three kaolin samples are illustrated in **Fig. 1**. Samples #2 and #3 were observed to be disordered and poorly crystalline and contained traces of quartz and very sparse mica (illite). Their Hinckley Index (HI)—a measure of crystallinity of



Fig. 1 XRD patterns of kaolin samples #1, #2, and #3. Sample #1 showed very sharp and narrow reflections lines and almost very smooth background revealing the high degree of crystallinity Ka = kaolin; Qz = Quartz, II = Illite. Samples #2 & #3 showed broad, asymmetrical peaks towards low 2θ value, which suggested an average smaller crystallite size based on the increased width of the diffraction peaks.

kaolin ranged between 0.78 and 0.8. Kaolin was indicated by its characteristic reflection peaks at 7.14 Å (001), and 3.56 Å (002), quartz (SiO₂) at 3.33 Å and illite at 10 Å.

Sample #1 was highly ordered with HI of almost 1.21 and characteristic peaks at 7.14 Å (001) and 3.56 Å (002), which suggested higher quartz content compared with samples #2 and #3.

The measurement of HI (degree of crystallinity of kaolin) is shown in **Fig. 2** using the range of 2θ 19–22° of kaolin samples. The calculated I (020)/I (1Í0) ratios of studied kaolin samples were 0.63, 1.09 and 1.10 for samples #1, #2, and #3, respectively. The smaller the value, the higher the crystallographic order of kaolin (Qiu X. et al., 2014). The average flake thickness of kaolin along the *c*-axis was calculated using the Debye-Scherrer equation,

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

in which *L* is the crystallite size; *K* is the Scherrer constant that depends on the shape and size distribution of the crystal; λ is the wavelength of incident X-ray; β is the full width at half maximum (FWHM); θ is the Bragg angle. The estimation of crystal size using FWHM of (001) peak is shown in **Fig. 3**. **Table 1** summarizes the calculated results of kaolin samples from XRD patterns. According to the FWHM (001) data of the three kaolin samples, the average flake thickness along the *c*-axis of samples #1, #2, and #3 were 517 Å, 160 Å, and 152 Å, respectively (as shown in **Table 1**). It was evident that sample #1 had thicker flakes than samples #2 and #3, which is supported by the SEM images.

From the XRD patterns of kaolin samples, it was clear that sample #1 was highly ordered kaolinite with HI of 1.21 and average flake thickness along the *c*-axis of 517 Å; while kaolin samples #2 and #3 had HI of 0.8-0.76 and an average flake thickness along the *c*-axis of 152–160 Å, respectively. Moreover, the narrow and sharp (001)



Fig. 2 XRD patterns at 2θ 19–22° of kaolin to measure the degree of crystallinity of kaolin (Hinckley Index, HI) and crystallographic order using I (020)/I (110) ratios.





Fig. 3 The FWHM measurement of the (001) XRD peak revealed the crystallite size of kaolin particles.

Table 1 Calculated results of kaolin samples.

	Sample #1	Sample #2	Sample #3
HI	1.21	0.80	0.76
I(020)/I(1Í0)	0.63	1.09	1.10
FWHM (001)	0.151°	0.334°	0.32°
Crystallite Size	517 Å	160 Å	152 Å
Number of Unit Layer	76	28	32

diffraction peak with an FWHM of 0.15° was characteristic of sample #1. Whereas the FWHM (001) of samples #2 and #3 was about 0.33°. Poor crystallinity of samples #2 and #3 kaolin resulted in irregular morphology and subsequently in poor rheological behavior.

3.2 Thermal gravimetric analysis (TGA)

3.2.1 Low-temperate endothermic region

The peak observed in TGA curves of samples #2 and #3 at 53 °C could be due to dehydration of poorly crystallized kaolin (#2 and #3) or due to the loss of adsorbed water ($\Delta m = 2.211\%$). It could also be due to the trace of hydrated halloysite (its characteristic peak at 10 Å overlapped with illite peak).

However, low-temperature endothermic peak at 252 °C in DTA curves of samples #2 and #3 could be attributed to amorphous materials–goethite FeO(OH) or gibbsite Al(OH)₃ ($\Delta m = 0.941\%$). Samples #2 and #3 seemed to be stained with iron. Also Fe₂O₃ content of these samples was higher than in sample #1. Generally, highly crystal-line goethite is known to produce a maximum at 280 °C. However, low crystalline goethite is known to produce a peak at 250 °C in TGA curves (**Fig. 4** and **5**).

Additionally, sample #1 had shallow losses below



Fig. 4 Differential thermal analysis of kaolin samples.



Fig. 5 Derivative thermos-gravimetric curves of the samples.

200 °C ($\Delta m = 0.585\%$) as compared to samples #2 and #3. This could be the result of a reasonable degree of crystallinity, in the case of sample #1, whereas the weight losses observed in the other samples could be attributed to the presence of less ordered kaolinite, halloysite and/or amorphous materials.

3.2.2 Medium-temperature-endothermic region

The DTA curve for kaolinite showed an endothermic





Fig. 6 Thermo-gravimetric curve of kaolin Sample #1.

peak in the range 400-600 °C due to the dehydroxylation of samples #2 and #3. These peaks were associated with a weight loss of 11 % contaminated kaolinite (Fig. 6). In the case of sample #1 kaolin, the dehydroxylation peak temperature ranged between 440-700°C and a 9.6 % weight loss. The dehydroxylation of sample #1 compared with that of samples #2 and #3 could be attributed to the difference in the degree of crystallinity as well as the degree of substitution of Al in the octahedral sheet by Fe in various samples. Low degree of crystallinity and the relatively higher degree of structurally substituted Fe caused a low dehydroxylation temperature of samples #2 and #3. Sample #1 was distinguished mainly by the decrease in peak intensity around 530 °C indicating lower kaolinite content. Also, the peak was broader and more curved to the right for samples #2 and #3. These characteristics could be attributed to the higher thickness of the crystals and/or the higher degree of crystallinity.

3.2.3 High-temperature-exothermic region

The main difference was observed at the exothermic peak around 1000 °C (**Fig. 4**). This peak was wider and less pronounced in samples #2 and # 3 than that for Sample #1. Besides, it developed at a temperature of 10–15 °C lower than for Sample #1. One possible explanation for this difference in DTA behavior would be a higher degree of crystallinity and, eventually, a larger crystallite thickness for Sample #1 in comparison to samples #2 and #3. The dehydroxylation of kaolinite occurred between 600–700 °C along with the formation of metakaolin. The phase was further transformed into either γ -alumina or aluminum-silicon spinel with the presence of amorphous silica.

The major loss in mass was observed in the temperature range from 400 to 900 °C indicated by an endothermic peak in **Fig. 4**. The total mass loss observed on the TG curve was 11.035 % for sample #1 (**Fig. 6**). DTG and DTA curves of sample #1 showed that the temperature at the maximum mass loss was 533 °C. On the other hand, the mass loss of samples #2 and #3 was 12.3455 % that occurred at 520 °C. The mass loss for samples #2 and #3 was higher compared with that of sample #1 and could be correlated to the higher percentage of kaolin in samples #2 and #3 (90.18 %) as compared to 80.5 % for sample #1. The metakaolin was a disordered layer structure with some hydroxyls present (1/8) and probably had the same Al/Si as kaolinite plus the vapor phase which was considered to be pure H₂O (Roy R. et al., 1955). Metakaolin eventually becomes amorphous with additional heating (Brindley G. and Nakahira M., 1959).

The conversion of quartz during the calcination of kaolin was masked by the big and very broad dehydroxylation peak of clay minerals generally within the same temperature range. So, the calculation of quartz and illite associated with kaolin of studied samples should be based on XRD patterns.

3.3 Phase and chemical analysis

The chemical analysis of the investigated samples given in **Tables 2 & 3** agreed with the mineralogical composition of the samples determined by the X-ray diffraction (**Figs. 1–3**) and DTA-TG (**Figs. 4–6**) analysis, as well as confirmed by the SEM micrographs (**Figs. 9–11**). Based on the normal weight loss at 400–700 °C corresponding to dehydroxylation of kaolinite, the kaolin/halloysite content ranged between 78–80 % for sample #1 as compared with 87–89 % for samples #2 and # 3. The higher quartz and illite content in sample #1 may explain the lower content of kaolin in sample #1.

On the other hand, samples #2 and #3 had higher Fe_2O_3 , TiO_2 , CaO, MgO compared with sample #1. Generally, Fe could be located in two forms: 1) Fe- substitution in octahedral and tetrahedral sheets of kaolin, or 2) as amorphous iron (staining iron). Also, the Fe had a significant influence on the rheological properties of kaolin. High $K_2O\%$



Component (%)	Sample #1	Sample #2	Sample #3
SiO ₂	52.9	45.8	45.6
Al_2O_3	33.1	37.0	36.8
Fe ₂ O ₃	1.20	2.17	2.18
TiO ₂	0.37	0.58	0.58
CaO	0.00	0.02	0.01
MgO	0.07	0.15	0.16
Na ₂ O	N.D	N.D	N.D
K ₂ O	0.74	0.47	0.46
BaO	0.01	< 0.01	0.01
P_2O_5	0.01	0.01	0.01
MnO	0.02	0.02	0.03
SO ₃	N.D	N.D	0.001
PPI de 110 °C a 1000 °C	11.7	13.9	14.2

 Table 2
 Chemical composition of kaolin samples.

 Table 3
 Mineralogical composition of kaolin samples.

Minorala	% (Semi-Quantification)					
Willerais	Sample #1	Sample #2	Sample #3			
Quartz (Qz)	10-12	1–3	1–3			
Mica/Illite	7–9	4-6	4-6			
Gibbsite (G)	N.I.	1–2	1–2			
Kaolinite/Halloysite	78-80	87–89	87–89			
Others (Fe, Ti oxides/ Fe hydroxides)	< 1	1–2	1–2			

in sample #1 compared with the other two samples revealed the presence of mica mineral. Illite impurity was indicated in XRD patterns of kaolin.

The presence of divalent ion in terms of Mg followed by Ca in abundance in samples #2 and #3 kaolin could result in the compression of the electrical double layer resulting in the lower zeta potential of these samples. Low zeta potential would result in higher interaction between clay particles and an increase of viscosity and finally, the flocculation of clay particles.

3.4 Zeta potential

The zeta potential of the three kaolin samples was measured at specific pH to obtain the isoelectric point (IEP) as plotted in **Fig. 7**. The IEP of all three samples were interpolated to be 3~4, which agreed with the literature values (Au P.-I. and Leong Y.-K., 2016). Sample #1 exhibited a slightly higher isoelectric point as compared to samples #2 & #3. This could affect the interaction between clay particles in aqueous suspension, thereby influencing their flocculation properties.

3.5 Physical properties

3.5.1 Particle sizes and size distribution

The particle size distribution of the three samples is summarized in **Table 4**, which did not reveal any significant differences.

3.5.2 Specific surface area (SSA) and cation exchange capacity (CEC)

The higher SSA and CEC (methylene blue index, MBI) of samples #2 and #3 could be attributed to the imperfectly stacked poorly crystallized kaolin with a lot of curly, rough and eroded edges compared to sample #1 (well-crystallized books of kaolin). High CEC of samples #2 and #3 using MBI could be attributed to the exposure of more charged sites for the exchange to occur. The SSA and CEC of kaolin appeared to increase with a lower degree of crystallinity as refer to **Table 4**.

3.5.3 Morphological Analysis

SEM micrographs (Figs. 8-10) revealed the



Fig. 7 Zeta potential of the Kaolin samples.

Table 4Physical properties of kaolin samples.

Sample	#1	#2	#3
SSA (m^2/g)	8.5	26.3	24
MBI (meq/100g)	1.6	7.1	6.7
DV 10 (µm)	0.37	0.35	0.35
DV 50 (µm)	2.3	2.21	3.57
DV 90 (µm)	15.67	11.34	13.06
% Coarse (100–9.21) µm	18.8	15.1	20.2
% Medium (9.21–0.96) µm	50.8	48.8	55.4
% Fine (0.96) µm	30.4	36.1	24.4





Fig. 8 The SEM image of kaolin sample #1 showed blocky particles with relatively low aspect ratio, which exhibited faster dewatering and high casting rate.



Fig. 9 The SEM images of sample #2 showed the thin-platelet with a high aspect ratio, which was responsible for slow dewatering and casting processes.



Fig. 10 The SEM images of sample #3 showed the thinplatelet with a high aspect ratio, which was responsible for slow dewatering and casting processes.

morphological characteristic of kaolin samples.

Kaolin sample #1 had revealed more regular pseudohexagonal edges smooth surface, thicker flakes, and smaller diameter to thickness ratio (**Fig. 8**). During the grinding process, these particles tended to become more rounded, resulting in better packing. This blocky mor-



Fig. 11 Casting rate of different kaolin samples.

phology could have enhanced the dewatering and casting rate of sample #1.

The morphology of samples #2 and #3 (Figs. 9–10) was different from sample #1. This morphology revealed the poorly crystalline structure of these samples. The platelets had curly, rough, highly eroded edges with high aspect ratios. The eroded edges revealed the partial dissolution of this kaolin and explained the presence of amorphous materials that covered the platelets. These surface defects were strongly associated with the adsorption characteristic of this kaolin. The packing of plate-like particles (samples #2 & #3) could result in a lower casting rate of the samples than that of the sample with blocky particles (lower aspect ratio). The densely-packed platelets of samples #2 and #3 would lie flat in the casting mold, thereby slowing down the dewatering process.

3.6 Slip casting performance

The present investigation offered a good opportunity to study the property-performance relationship of kaolin. It was observed that the slip casting rate of kaolin sample #1 was significantly higher as compared to samples #2 & #3 (**Fig. 11**) in which the particles were more platy (higher aspect ratio) and exhibited lower crystallinity. The low casting rate of kaolin samples #2 & #3 also could be attributed to the high slip viscosity and the abundant divalent cations. For these reasons, kaolin samples #2 & #3 were less suitable for most of the traditional applications unless they are further treated or modified specifically.

4. Conclusions

Three kaolin samples from different geological origins were characterized and the relationship between their properties and slip casting performance was studied. Overall, it was found that kaolin sample #1 exhibited a significantly higher slip casting rate than the other two samples. Characterization showed that kaolin sample #1 had the highest crystallinity among the three samples studied, and its particles exhibited the most globular



shape as compared to the other samples. The globular shape of the particles could be one of the key elements that were beneficial to the dewatering process leading to faster slip casting. The thermal gravimetric analysis confirmed that kaolin sample #1 exhibited less weight loss in low to medium temperature endothermic regions than the other two samples. It could be due to less moisture content of sample #1 and thus less dehydroxylation due to a higher degree of crystallinity. Nevertheless, further investigation is needed to fully understand the complex nature of different kaolins and their rheological behavior.

Acknowledgments

The authors acknowledge the financial support from the Center for Particulate and Surfactant Systems (CPaSS) at the University of Florida, National Science Foundation (NSF Grant No. 1362060) and the industrial partners of CPaSS. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation/Sponsors.

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Authors' Short Biographies



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Fabrication and Characterization of Prussian Blue-Derived Iron Carbide-Iron Oxide Hybrid on Reduced Graphene Oxide Nanosheets[†]

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Abstract

This work demonstrates the fabrication of a nanoporous iron carbide-iron oxide/reduced graphene oxide (IC-IO/ rGO) hybrid via a controlled one-step thermal treatment of Prussian blue (PB)/GO hybrid at 450 °C under N₂ flow. The PB/GO hybrid is initially prepared through the in-situ deposition of PB nanoparticles on the GO sheets through electrostatic interactions. The morphological analysis of the hybrid reveals the uniform coverage of the rGO sheets by IC-IO nanoparticles and the even distribution of carbon (C), oxygen (O), and iron (Fe) on the rGO nanosheets. As a result of the hybrid composition and controlled morphology, the surface area of the obtained IC-IO/rGO hybrid (~40 m²/g) is significantly enhanced compared to those of the calcined GO sheets and PB nanoparticles (without GO).

Keywords: metal-organic frameworks, porous coordination polymers, metal oxides, metal carbides, graphene oxide

1. Introduction

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have attracted significant interest as porous materials because of their high surface area, large pore volume, controllable composition and pore size, etc. (Wang Z.-L. et al., 2018; Salunkhe R. R. et al., 2016; Kaneti Y. V. et al., 2017). Prussian blue (PB) and its analogues (PBAs) exhibit several attractive characteristics, such as open framework structures, high thermal stability, and good redox activity. These CPs have been employed in numerous applications, including drug delivery (Lin W. et al., 2009), energy storage (Paolella A. et al., 2017), sep-

[†] Received 27 May 2020; Accepted 21 July 2020 J-STAGE Advance published online 29 August 2020

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aration (Bureekaew S. et al., 2008), and so on (Doty F. et al., 2009; Ishizaki M. et al., 2013). Nevertheless, the poor conductivity and low chemical stability of PB presents major challenges for their practical applications (Salunkhe R. R. et al., 2015). Therefore, extensive efforts are needed to enhance the stability and conductivity of PB and its derived materials. To date, PB and PBAs have been employed as novel precursors for obtaining various transition metal compounds, including metal oxides and metal carbides (Azhar A. et al., 2019a). Generally, the calcination of PB in air produces iron oxide (IO) as a result of the removal of the cyano-group and the oxidation of the iron species. Our group previously synthesized PB and completely transformed it into nanoporous iron oxide hybrids (Azhar A. et al., 2019b), such as β -Fe₂O₃ (Machala L. et al., 2013), and mixed crystalline phases of iron oxide (α , γ and β - phases) (Roy X. et al., 2011). On the contrary, when pure PB was heated under inert atmosphere, the formation of metallic iron and iron carbide (IC) (Fe₇C₃, Fe₂C, and Fe₃C) was observed (Zakaria M. B. et al., 2016). Very recently, pure nickel carbide (Ni₃C) was successfully prepared from



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cyano-bridged CPs through a thermal treatment under inert atmosphere at 450 °C (Zakaria M. B. et al., 2019). Despite some progress, the construction of PB-derived metal carbide/carbon hybrids are still rarely reported.

Recently, carbonaceous materials, such as graphite, graphene oxide (GO), reduced graphene oxide (rGO), and carbon nanotubes (CNTs) have been widely used to enhance the functional performance of PB-based materials (Daneshvar F. et al., 2018; Azhar A. et al., 2018). The oxygen-containing functional groups on the surface of the two-dimensional (2D) GO nanosheets can serve as excellent sites for the in-situ growth of PB nanostructures (Lee T. et al., 2015). Our group has demonstrated the fabrication of several cyano-bridged CPs grown on GO nanosheets by a variety of methods (Zakaria M. B. et al., 2019). Herein, we report the synthesis of a hybrid material combining GO sheets with PB nanoparticles which can be subsequently transformed into a nanoporous IC-IO/rGO hybrid under nitrogen atmosphere at 450 °C. The obtained IC-IO/rGO hybrid has been thoroughly characterized in terms of its composition, morphology, thermal decomposition behavior, and textural properties.

2. Experimental

2.1 Chemicals

Sodium ferrocyanide(II) decahydrate $(Na_4[Fe(CN)_6] \cdot 10H_2O, \ge 99\%)$ was purchased from Sigma-Aldrich (Japan). The sulfuric acid solution $(H_2SO_4, 98\%)$ was obtained from Nacalai Tesque (Japan). Potassium hydroxide (KOH), sodium nitrate $(NaNO_3, \ge 99\%)$, and ferric chloride hexahydrate $(FeCl_3 \cdot 6H_2O, \ge 98\%)$ were sourced from FUJIFILM Wako Corporation (Japan). Graphite nanoplatelets (N008-100-N, thickness ~100 nm) were obtained from Angstron materials (USA). Potassium permanganate (KMnO_4, $\ge 99\%$) and hydrogen peroxide solution $(H_2O_2, 30 \text{ wt.}\% \text{ in } H_2O)$ were utilized as received without further purification.

2.2 Preparation of GO nanosheets

The thin GO nanosheets were fabricated by employing the modified Hummer's approach (Tanaka S. et al., 2017). In the first step, 0.33 g of graphite powder and 0.17 g of NaNO₃ were mixed together and stirred. Following this, 7.67 mL of concentrated H_2SO_4 solution was slowly poured into this suspension and then stirred for 1 h. Next, 1.0 g of KMnO₄ was added into the mixture solution which was placed in an ice bath below 20 °C. The mixture was subsequently stirred at 35 °C for 2 h and distilled water (83 mL) was added into this mixture solution under strong stirring. After that, 1.67 mL of aqueous H_2O_2 solution (30 % w/w) was added into the suspension. The final GO suspension was washed a number of times with a diluted HCl solution and distilled water. Finally, this GO suspension was sonicated in distilled water to exfoliate the GO sheets. The GO sheets were collected by centrifugation and subjected to repeated washing with distilled water, before being dried at ambient temperature, followed by a final drying in vacuum at 60 °C overnight. The as-prepared GO powder was dispersed in water to prepare an aqueous GO solution (2 mg mL⁻¹) to be used in subsequent steps.

2.3 In-situ deposition of PB nanoparticles on GO nanosheets (PB/GO hybrid) and conversion to iron carbide-iron oxide/rGO hybrid

Typically, 40 mL of 0.299 mM FeCl₃·6H₂O solution was poured into the GO solution (20 mL, 2 mg mL⁻¹) and stirred for 0.5 h. The mixture solution was slowly mixed with 40 mL of Na₄[Fe(CN)₆]·10H₂O solution (0.358 mM) and stirred for further 0.5 h, before being aged for two days. The product was isolated via centrifugation and washed multiple times with water and ethanol, and finally dried at room temperature. The porous IC-IO/rGO hybrid was achieved by calcining the PB/GO hybrid at 450 °C for an hour under nitrogen (N₂) flow with a ramping rate of 5 °C min⁻¹. For comparison, pristine PB nanoparticles without GO sheets were also prepared and heated under the same conditions.

2.4 Characterization

The purity and compositions of the samples were checked by X-ray diffraction (XRD) with a Rigaku RINT 2500X diffractometer utilizing Cu Ka (1.5406 Å) radiation. Nitrogen sorption isotherms were collected using a Quantachrome Autosorb at 77 K. To dehydrate the samples, they were subjected to degassing at 250 °C for 16 h prior to the BET measurement. Morphological observations of the products were conducted using both scanning electron microscope (SEM, Hitachi SU8000) and transmission electron microscope (TEM, JEOL JEM-2100F). The infrared (IR) spectra of the samples were collected using a Thermoscientific Nicolet 4700 spectrometer (Waltham, MA, USA). Raman spectroscopy measurements were performed using a Horiba-Jovin Yvon T64000 Raman spectrometer. Thermogravimetry (TG) measurements were carried out with a Hitachi HT-Seiko Instrument Exter 6300 under N₂ atmosphere from 30 to 550 °C at a ramping rate of 5 °C min⁻¹.





Fig. 1 (a, b) SEM images of (a) GO nanosheets and (b) PB nanoparticles. (c) SEM and (d) TEM images of the as-synthesized PB/GO hybrid.



Fig. 2 Wide-angle XRD patterns of GO, PB, PB/GO hybrid and IC-IO/ rGO hybrid. For comparison, the XRD pattern of calcined PB without GO is also shown.

3. Results and discussion

The PB/GO hybrid was obtained by the in-situ deposition of PB nanoparticles on the GO sheets (Azhar A. et al., 2019b). First, the GO sheets were synthesized by the exfoliation of graphite based on the modified Hummer's method (Tanaka S. et al., 2017). The SEM image of the prepared GO sheets (**Fig. 1a**) shows a two-dimensional (2D) crumpled sheet-like structure. The zeta potential measurements reveal the change in the surface charge of the GO sheets from negative to positive charge after the modification with PB nanoparticles. The morphology of the PB/the GO hybrid is depicted in **Fig. 1c**, which shows the wrapping of the PB nanoparticles by the GO sheets (i.e., the surface of the GO sheets is bumpy.). The TEM image further shows that the PB nanoparticles are successfully deposited on the surface of the GO sheets

(**Fig. 1d**). For comparison, pristine PB without GO sheets was also prepared (**Fig. 1b**). **Fig. 2** shows the XRD pattern of the PB/GO hybrid which reveals the diffraction peaks belonging to face-centered cubic (fcc) phase of PB (JCPDS No. 73-0687) (Cao L. et al., 2010). Importantly, after the modification with PB, the primary diffraction peak belonging to the GO nanosheets disappears, possibly due to the nearly complete surface coverage of the GO sheets by the PB nanoparticles (Islam M. N. et al., 2018).

Further compositional analyses of the PB nanoparticles, GO sheets, and PB/GO hybrid were carried out using fourier-transform infrared (FTIR) spectroscopy. The FTIR spectrum of the PB/GO hybrid (**Fig. 3a**) shows the presence of strong bands belonging to the cyano (CN) group of PB (Fe²⁺-CN-Fe³⁺) (Ge C.-X. et al., 2018). The peaks originating from oxygen-containing functional groups (Vermisoglou E. et al., 2014) on the GO surface is significantly reduced following the modification with PB nanoparticles, indicating the complete reduction of GO to reduced graphene oxide (rGO) (Ren S. et al., 2012) and the formation of PB on GO sheets.

The thermal degradation of PB under nitrogen flow was studied by TGA (**Fig. 4**). The TG curve of pure PB shows multi-step weight loss (Sun D. et al., 2019). In the first stage, lattice water and adsorbed water molecules in the structure are removed at temperatures between 30 and 210 °C. The second weight loss (210–420 °C) can be attributed to the loss of the cyano (CN) group present in the PB nanoparticles, and the final weight loss above 420 °C is correlated to the formation of IC. The thermal stability of the pure GO nanosheets under inert atmosphere was also investigated by TG measurements (**Fig. 4**). The evaporation of adsorbed water molecules and the removal of labile oxygen functional groups occur at ~250 °C and no further





Fig. 3 (a) FTIR spectra of GO, PB, PB/GO hybrid, and IC-IO/rGO hybrid. (b) Raman spectra of GO and IC-IO/rGO.

weight loss is observed (Park S. et al., 2011).

As depicted in **Scheme 1**, the thermal treatment of the PB/GO hybrid at 450 °C under N₂ atmosphere results in the formation of the IC-IO/rGO hybrid. The crystal structure of this hybrid after calcination was examined by wide-angle XRD (**Fig. 2**). Some peaks are assignable to iron carbide (Fe₃C, IC) (Fletcher D. et al., 2019), while the other peaks at 35.5° and 62.9° can be attributed to iron oxide (γ -Fe₂O₃) (Zhu K. et al., 2018), suggesting the presence of multiple iron phases after the heat treatment. Compared to the calcined PB (without GO), the relative intensity of the IO peak in the IC-IO/rGO hybrid is increased, which may be due to the reaction of iron species with oxygen functional groups of GO sheets.

Fig. 5a displays the SEM image of the IC-IO/rGO hy-



Fig. 4 TGA data of (a) PB and (b) GO. The measurement was carried out in N_2 atmosphere.

brid, which is composed of irregular and porous structures due to the removal of the organic group after calcination. Also, some IC-IO hybrid nanoparticles can be observed on the surface of the GO nanosheets. The TEM image clearly reveals the uniform decoration of the rGO sheets by IC-IO nanoparticles (**Fig. 5b**). The corresponding elemental mapping images in **Fig. 5c–f** confirm the uniform distribution of carbon (C), oxygen (O), and iron (Fe) on the rGO nanosheets.

The N₂ sorption isotherms of the calcined PB and the IC-IO/rGO hybrid are given in **Fig. 6**. The specific surface area of the IC-IO/rGO hybrid (38.7 m²/g) is significantly larger than those of the calcined GO sheets (1.25 m²/g) (Zakaria M. B. et al., 2019) and calcined PB (18.2 m²/g). This is likely due to the presence of IC-IO nanoparticles which may serve as effective spacers between the GO sheets, thus preventing the stacking of the GO sheets during the thermal treatment.

The FTIR spectrum of the IC-IO/rGO hybrid (**Fig. 3a**) clearly shows the disappearance of many oxygencontaining functional groups, which suggests the successful reduction of GO sheets to reduced GO (rGO) (Liu H. et al., 2015). Additionally, a weak IR band belonging to the CN group is also observed. Raman spectra of the GO sheets before and after the thermal treatment are compared in **Fig. 3b**. The *D* and *G* bands are clearly observed. However, the positions of the *D* and *G* bands are shifted after the



Scheme 1 Schematic illustration of the in-situ growth of PB nanoparticles on GO sheets (PB/GO hybrid) and the subsequent thermal decomposition to IC-IO/rGO hybrid.





Fig. 5 (a) SEM and (b) TEM images of the IC-IO/rGO hybrid obtained by the thermal treatment of the PB/GO hybrid at 450 °C for 1 h under N₂ atmosphere. (c) HAADF-STEM image of the IC-IO/rGO hybrid and (d-f) the corresponding elemental mapping for (d) carbon, (e) oxygen, and (f) iron.



Fig. 6 (a) N_2 adsorption-desorption isotherms of PB calcined at 450 °C and the IC-IO/rGO hybrid. (b) SEM image of calcined-PB nanoparticles.

thermal treatment. Compared to the I_D/I_G value of pure GO (1.02), the I_D/I_G value of the IC-IO/rGO hybrid is higher (1.12), suggesting the increase of structural defects in the GO sheets after calcination.

4. Conclusions

In summary, we have successfully achieved the in-situ deposition of PB nanoparticles on the surface of GO sheets through the interaction of PB with the oxygen-containing functional groups of GO nanosheets. This PB/GO hybrid can be converted to the IC-IO/rGO hybrid via a one-step thermal treatment at 450 °C under N₂ flow with well-retained morphology. This finding indicates that the presence of rGO during thermal treatment helps to promote the formation of iron carbide at high temperatures. The surface area of the obtained IC-IO/rGO hybrid (~40 m²/g) is superior to those of the calcined GO sheets and the calcined PB without GO. This hybrid material composed of multiple compositions may have many potential applications in supercapacitors and oxygen reduction reaction (ORR).

Acknowledgements

This work was conducted at the Queensland node of



the Australian National Fabrication Facility (ANFF-Q), a company established under the National Collaborative Research Infrastructure Strategy to provide nano and microfabrication facilities for Australian researchers. S.M.A., T.A., and Y.Y. thank Researchers Supporting Project Number (RSP-2020/6), King Saud University, Riyadh, Saudi Arabia.

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Polymer-Particle Enhanced Visible Light Range Photocatalytic Activity on Textile Applications[†]

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Abstract

Extension of photocatalytic activity within the visible light range has an immense importance on the ability of manufacturing self-cleaning textiles that are active indoors. This study focuses on assisting problems, which have delayed the commercialization of the photo-catalytically active textiles by following innovative technological developments in nanotechnology. Polymeric additives are utilized to prepare composite photocatalytic particles with the ability of extending light absorption in the visible light range. Techniques are introduced to avoid the deterioration of the composite particles during their application on textiles in addition to uniform coating strategies to enable an optimized concentration for improved photocatalytic efficiency. It is demonstrated that the titania (TiO₂) particles in anatase form extended absorption in the visible light range in the presence of branched titania particles. Correspondingly, an optimized dip coating process is evaluated for textile manufacturing, providing a systematic methodology to enable the production of self-cleaning textiles to be able to manufacture them with commercialization potential.

Keywords: self-cleaning textiles, visible light range photocatalytic activity, polymer titania composites

1. Introduction

Increasing environmental pollution, inevitable mass consumption of raw materials and, the most recently faced challenges in hygiene standards due to the Covid-19 pandemic keep forcing societies to make smart use of resources, including textiles. Notably, the high ecological cost of the conventional cleaning methods utilized for textiles encourages the market to introduce new and more technologically smart products. Photocatalytically active materials are known for their efficiency in self-cleaning, and their implementation can promote fast sanitization in the cases of efficient cleaning as well as sanitization against the spread of diseases (Saunders-Hastings et al., 2017). One fundamental challenge remains to be promoting the photocatalytic activity in the visible light range to enable applications indoors through understanding nano-technology principles and the photocatalytic activity of the selected additives.

Catalysts are substances that can accelerate reactions

Received 19 April 2020; Accepted 9 June 2020
 J-STAGE Advance published online 17 July 2020

through lowering the free activation enthalpy of the reaction (Wubbels, 1983). Accordingly, photocatalysis can be defined as a photoreaction in the presence of a catalyst where a chemical modification of one molecular entity results from the initial absorption of radiation by another molecular entity called a photosensitizer. The catalyst might speed up the photoreaction by interaction with the substrate in its ground state or with a primer photoproduct (Castellote and Bengtsson, 2011). The nature of photocatalysis is based on solid-state chemistry and knowledge on the crystal structure. Hence, nonstoichiometric and any other alternative imperfections such as impurities that can act as dopants that change the electronic properties affect the photocatalysis functionality of materials (Castellote and Bengtsson, 2011). The most commonly utilized photocatalytic materials are zinc oxide (ZnO), cadmium sulfide (CdS), iron(III)oxide (Fe₂O₃), tungsten trioxide (WO₃), tin oxide (SnO₂), zinc sulfide (ZnS) and titanium dioxide (TiO₂) (Cerhan et al., 2018; Dumitrescu et al., 2015). It is also common to use blends of these primary compounds in manufacturing. Among all the alternatives, titanium dioxide (TiO₂) is the most commonly used photocatalyst for the textiles due to its superior performance and light color that is the most suitable for the manufacturing of the optic white textile products (Patra and Gouda, 2013). TiO₂ has three polymorph forms varying in crystal structures as rutile,



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brookite, and anatase. When considering the enhancement of the photocatalytic activity, surface structure, composition, atomic and molecular scale surface dynamics, as well as the electronic properties play an important role. It is necessary to evaluate the adsorption and bonding of atoms and molecules on the surfaces to understand the mechanisms of self-cleaning ability. Among the polymorphs of titanium dioxide, anatase is the most thermodynamically stable form of titania amid the three nanocrystal types. The anatase powders with higher crystallinity are favored for photocatalysis since higher crystallinity provides a smaller quantity of defects acting as recombination sites in the middle of photogenerated electron and hole combination (Filippo et al., 2015). It is more active than the rutile phase as a photocatalyst, although its band gap value, 3.27 eV, is higher than the rutile's bandgap, which is 3.05 eV (Filippo et al., 2015; Hümmelgen, 2012; López and Gómez, 2012). Anatase powders tend to agglomerate despite the high photocatalytic performance (Kiwi and Rtimi, 2016; Qiu et al., 2012). The commercial Degussa-P25 powder contains anatase and rutile forms blended in a ratio of 3:1 and has a bandgap energy of 3.26 eV (López and Gómez, 2012). P-25 titania is commonly used as a benchmark for photocatalysts (Ohtani, 2008; Rui et al., 2014).

The challenge of standard photocatalytic semiconductor activity is known to be the fact that it takes place in the ultraviolet light range. In order to enhance the photocatalytic activity into the visible spectrum the formation of bonds between photocatalytic particles and pure elemental dopants or synthesized particles are needed. Beyond the standard dopants (Cerhan et al., 2018; Dumitrescu et al., 2015) advanced particles are introduced in this study named as branched particles with controlled synthesis and particle size distribution. The core-shell particle decorated with polymeric branches can actively control the binding event by pairing ion, metal complex recognition, and hydrogen-bond recognition (Randazzo et al., 2012).

Application of the visible light range photocatalytic activity enhancing nano-systems on textiles requires modifications to the textile manufacturing processes. Manufacturing of self-cleaning textiles at an industrial scale requires the integration of the selected photocatalytic system to the standard coating processes. Traditionally, this will be performed by following two steps; (i) development of photocatalytic additives that can be added into the selected finishing solutions without settling and, (ii) enabling their effective and homogeneous coating on the textiles at the optimized dosages. It is agreed that self-cleaning textiles with photocatalytic activity should maintain high-quality textile standards with the application of functionalized films promoting the increase in the potential market applications and meeting the variations in demands. Self-cleaning textiles decorated with photocatalytic materials possess the self-cleaning property, and hence they can actively clean themselves without a need for conventional laundry. This attribute provides significant benefits concerning the prevention of environmental pollution and cost savings in addition to the spontaneous active cleaning of the textiles even throughout their utilization before and after washing. Consequently, many scientific studies conducted on the textiles are linked to the desire to produce eco-friendly photocatalysis reactions. Although there are potential solutions proposed to widen the diversity of applicable photocatalytic materials, there is still room to perfect the applications due to the variation in the demand and the limitations in the activity within the visible light range (Kiwi and Rtimi, 2016).

In this study, photocatalytic materials and self-cleaning textiles are evaluated in the context of composite nanoscale additives promoting secondary bonds to adjust initial energy levels for enhanced photocatalysis action. Titanium oxide particles in anatase crystalline structure were made into composite photocatalytic agents through polymeric additives names as branched titania were coated on textiles in DI-water as well as standard finishing solution to support the implementation of the final combination suitable for self-cleaning textile standards. A commercial titania (Degussa P25) coating was compared to the anatase with and without the polymeric branching at various selected concentrations to optimize photocatalytic activity, particularly under visible light. The branched titania particles were synthesized and characterized for particle size and stability in addition to optimization of the most effective coating concertation for photocatalytic activity by analyzing absorbance and stain removal ability in solutions as well as post coating on textiles.

2. Experimental approach

2.1 Materials

The procedure for the synthesis of branch titania particles is adapted from an earlier study by S.A. Simakov and Y. Tsur. The technique is based on the hydrolysisprecipitation procedure, by using TiOSO₄•2H₂O as a precursor and water as a hydrolyzed preparation medium. Diethylene glycol monomethyl ether (DEGME) was used as a surface modifier to form the desired branches utilized for stability as well as an enhanced attachment onto the textile surface. The necessary chemicals were obtained from Sigma-Aldrich and used as received to conduct the particle synthesis reactions.

The advanced textiles utilizing nanotechnology in the coating processes, including the self-cleaning textiles, are generally preferred to be manufactured from either cotton or elastin type fibers and their blends (Akbar and Bahar Basim, 2019). Thus, the textile was selected



to be a blend of 35 % elastin and 65 % cotton for the coating procedure. In addition, a hydrophobic finishing solution was preferred by the manufacturer's recommendation based on its common implementation in textile production. The selected finishing solution is composed of Setasil KF 1320 (amino-functional micro silicon emulsion) Setas Chemicals, Serisoft 210 (non-ionic softener) Serboy Chemicals, Walline PE (polyethylene) Geochem Chemicals and acetic acid (Sigma-Aldrich for pH balance) at a total concentration of 2.7 % (w/v) in DI-water and measured pH of 3.52 (Akbar et al., 2017). These polymeric and polyethylene structures provide holding on the textile surface for additives by crosslinking (Andrienko, 2015).

2.2 Methods

2.2.1 Synthesis and particle size characterization of branched titania particles

Branched titania preparation procedure was carried out in a continuously stirred closed glass flask at room temperature by adding 20 g of TiOSO₄•2H₂O powder (≥29 % Ti Sigma-Aldrich) to 180 ml of diethylene glycol monomethyl ether solution (\geq 99 % Sigma-Aldrich) and 40 ml of DI-water. After mixing for 90 hours, the solution pH was increased by the dropwise addition of a dilute NH₄OH solution diluted from ammonium hydroxide solution of 26 % (Sigma-Aldrich) to pH 10. The addition of the NH₄OH solution changed the mixture into a white color suspension, and the resulting precipitates were separated by centrifugation. Following the separation by centrifugation, particles were washed three times with a diluted NH₄OH solution followed by DI-water to avoid creating bonds with the counter-ions of the salt used as a ligand structure (SO₄⁻²). The suspension was centrifuged after each washing step to separate the precipitates without significant loss of synthesized particles and to remove the counter-ions and ligand structure within the remaining solution. Finally, the precipitates were dried at 80 °C, and a white powder was obtained (Simakov and Tsur, 2007).

The baseline and synthesized branched titania particle size was measured using two methods; (i) static light scattering technique by Coulter LS 13 320 and, (ii) using an atomic force microscope (AFM). Commercially obtained anatase powder and the laboratory synthesized branched titania particles were prepared as dilute suspensions in DIW and finishing solution separately at 0.1 wt % by mixing 0.01 g powder in 100 ml DIW or solution. Since the powders are prone to agglomeration (Simakov and Tsur, 2007) suspensions were ultrasonicated multiple times until all the agglomerated particles were suspended in the solution. Consecutive particle size distribution analyses were performed by Coulter LS 13 320 until a single peak was observed on the size distribution curve, verifying that the stabilization of the suspension was achieved. Furthermore,

AFM based size analyses were also conducted by further dilution of the particles in DI water and drying a drop of sample on a freshly cleaved mica surface. After drying the suspensions on the cleaved mica substrate, samples were analyzed by AFM (Nanomagnetics Ambient AFM) in contact mode by scanning $5 \times 11 \,\mu\text{m}$ and $3 \times 5 \,\mu\text{m}$ size images to determine the individual particle size. Particle size measurements obtained from the two techniques are compared to evaluate stability as well as the relationship to the performance on the photocatalytic activity.

2.2.2 Evaluation of photocatalytic cleaning

2.2.2.1 Optimization of photocatalytic activity of particle suspensions

In order to evaluate the photocatalytic efficiency of various particulate systems, initial experiments were conducted by preparing suspensions and measuring their stain bleaching ability under the UV light. 10 ml solutions of photocatalytic components were prepared and mixed with 2 ml methylene blue dye (MB⁺) solution to make a 2×10^{-4} M concentration of the active dye. The prepared suspensions were exposed to 365 nm UV light for 5 minutes to observe the discoloration of methylene blue by the degradation of the methylene blue as a function of time. The solutions were compared for the change in color by taking pictures before and after the UV light exposure at 365 nm. The absorbance spectrums of the solutions were also attained as a function of time by using a Shimadzu UV1280 UV-visible spectrometer as methylene blue degradation occurs.

2.2.2.2 Evaluation of photocatalytic activity on textiles

ISO 10678:2010 standard "Determination of the photocatalytic activity of surfaces in an aqueous medium by the degradation of methylene blue" was used to determine the photocatalytic particle concentration efficiency on cleaning (Mills, 2012). This standard method requires the measurement of the rate of photocatalytic bleaching of MB⁺ in aqueous solution via UV/VIS spectrometry (Mills and McFarlane, 2007). The ISO 10678 standard was used to evaluate the absorbance performance of the coated textiles by measuring the efficacy methylene blue degradation in the presence of the coated textiles in solutions as they are exposed to UV light. The textiles samples treated with different coatings were cut into 10 cm² and dipped into a beaker filled with a 2×10^{-4} M MB⁺ solution followed by UV exposure. A sample of the solution was collected every 20 minutes, and the absorbance values were measured to evaluate the efficiency of photocatalytic degradation as a function of time.

In addition, stain tests were performed on the coated textiles by cutting them into 10 cm^2 pieces and dipping into a 2×10^{-5} M methylene blue solution for 20 seconds. The stained textiles were dried in an oven at 36 °C and exposed

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to UV light at 365 nm wavelength for a week. The stain bleaching was evaluated by taking pictures on daily basis. The UV light at 365 nm wavelength (Philips Fluorescent Light Bulb TL-D F15T8) was utilized during the analyses.

2.2.3 Zeta potential measurement of coated textiles

The zeta potential of the baseline and coated textile samples were measured by using Electro-kinetic Analyzer (Anton Paar SurPASS) as a function of pH of the circulating electrolyte. The textile samples were placed in a cylindrical cell with supporting disks, which have holes to allow the liquid flow. After the placement of the textile sample into the cylindrical cell, the cylindrical cell was placed in between the electrodes to bind to mobile pistons to allow variation in the distance between the electrodes and adjusting pressure applied to the sample specimen. The liquid flow was provided with a 1 mM KCl solution and the pH titration was performed by adding 50 mM HCl solution at each time interval, as directed by the Attract 2.0 software data analyzer of the SurPASS instrument. The isoelectric points of the coated textiles, which is the pH value where the zeta potential of the materials is zero, was determined based on the data attained from Attract 2.0 software. The data is plotted as a scatter graph of zeta potential as a function of pH is fitted to a polynomial correlation by utilizing MS Excel software. The isoelectric points were determined through placement of zero value for pH in the equations for each individual textile sample.

2.2.4 Bandgap energy determination

To determine the bandgap of the photocatalytically active samples, solutions prepared with anatase and branched titania concentrations in finishing solution were deposited on the glass slides. The glass slide was used in place of textiles to benefit from transparency of the glass for spectroscopy as the textiles cannot be analyzed as substrates due to their inhomogeneous opaque structure. The chemical bath deposition method was used to deposit the prepared solutions on the ultrasonically cleaned glass substrates, and the glass substrates were dried in glass Petri dishes at room temperature. The transmittance and absorbance measurements of the deposited thin films were obtained by Shimadzu UV1280 UV-visible spectrometer. The graphs were evaluated by using OriginLab software for the thickness and bandgap energy of the films.

The light energy which initiates a photocatalytic reaction must be at least equal, or higher, than the energy bandgap. The band energy plays a role as the threshold energy for the photocatalytic reaction. The absorption method is used for the identification of forbidden band energy, simply known as the bandgap energy. In this method, specification of the forbidden band energy is evaluated from the relation between the absorption coefficient and the forbidden band energy, as given in Eq. (1).

$$(ahv)^n \approx (hv - E_g) \tag{1}$$

where, *h*, *v* and α represent the Planck constant, the frequency, and the absorption coefficient, respectively. In this method, a graph of $(\alpha hv)^n$ versus *hv* is drawn. The energy value, $[(\alpha hv)^n = 0]$, is determined by Tauc plot through plotting to the linear portion of *hv* representing the bandgap energy of examined material against $(\alpha hv)^n$ (Godet et al., 1991). When the *n* value in the Eq. (1) is chosen to be 2, direct bandgap energy of material can be determined. If the *n* value is 1/2, the determined value is defined as the indirect bandgap value of the material (Akaltun et al., 2011; Astam, 2016; Cerhan-Haink and Basim, 2020).

$$n_{\rm f} = \left[\left(\frac{n_{\rm s} (2 - T_{\rm m}) + 2n_{\rm s} (1 - T_{\rm m})^{\frac{1}{2}}}{T_{\rm m}} \right) \right]^{1/2}$$
(2)

$$t = \left(\frac{(\lambda_1 \lambda_2)}{2(n_{f_2} \lambda_1 - n_{f_1} \lambda_2)}\right)$$
(3)

The maximum or minimum peak of the transmittance graph was obtained from the UV-VIS spectrometer and was used for the analysis of thin film thickness evaluation according to Eq. (2) and Eq. (3). $T_{\rm m}$, λ , t are the maximum peak parameters of transmittance, wavelength corresponding to maximum peak center, and thickness of the film, respectively. The thickness of the thin films was calculated by substituting amplitude of the first maximum peak, $T_{\rm m1}$, and amplitude of the second maximum peak, $T_{\rm m2}$, values into the Eq. (2) and replacing the values in the Eq. (3). The $n_{\rm s}$ represents the refractive index of the glass used to coat the nanoparticle solutions (Swanepoel, 1983).

2.2.5 Water vapor transmission rate analysis on textiles

The methods of measuring water vapor transmission rate (WVTR) represents the permeability of the coated textiles to water vapor (Hu et al., 2001). The highly permeable films are generally preferred in products for daily use such as in self-cleaning textiles. In order to provide human skin respiration continuity after the coating procedure, the water vapor transmission rate is measured through a modification of the wet cup method described by the ASTM E 96-95 standard (Hu et al., 2001). In this method, the textile sample is used as a cover on a cup filled with DI-water and the change in mass is recorded as a function of time. The weight change is due to the evaporation of water through the textile and Eq. (4) is used to determine the water vapor transmission rate.

$$WVTR = \frac{mass H_2 O lost}{time \times area}$$
(4)



The textiles were prepared for water transmittance tests by cutting 10 cm square samples to cover the top of the beakers after adding 100 ml DI-water in each beaker. The system was weighed to follow the change in mass in weekly periods under ambient conditions (22 °C and 20 % humidity-winter and the 35 °C and 50 % humidity-summer). The system mass change was recorded for 700 hours (~30 days).

3. Result and discussion

3.1 Characterization of nano-particle systems in DI-water and textile finishing solution

The size distribution and shape of powders change the total surface area of the particles and affect the rate of reactions, stability as well as product appearance and texture. Hence, particle size measurement is one of the indicators of quality and performance of suspensions for a successful implementation of the nanoparticles on textiles. Fine particles with high total surface area speed up chemical reactions and dissolution rates while simultaneously becoming more prone to settling due to the loss of suspension stability. Unstable suspensions lead to inhomogeneous coatings since the photocatalytic particles settle out of liquid suspension and cannot hold on to the textile surface properly. Therefore, the particle size of anatase and branched titania were measured in DI-water as well as finishing solution by using static light scattering via Coulter LS 13 320 as well as through AFM scanning.

Table 1 summarizes the mean particle size measurements obtained by Coulter LS 13 320. It can be seen that the anatase particles were similar in size both in DI-water and finishing solution with $0.087 \pm 0.005 \,\mu\text{m}$ and $0.084 \pm 0.001 \,\mu\text{m}$ mean diameter, respectively. The consistency in the measured mean size with a controlled standard deviation indicates the stability of the anatase particles in both environments. We have demonstrated in the earlier studies that the titania particles are more stable in the finishing solution which has a pH of 3.52 as compared to the DI water which has a pH of ~6 (Cerhan-Haink and Basim, 2020). This is due to the fact that the isoelectric point of anatase is at pH 5.8 (McNamee et al., 2005) and hence

Table 1 Change of material stability depending on zeta-potential size.

Photocatalytic particle	Mean Particle size (µm)	Standard Deviation (μm)
Anatase in DIW	0.087	0.005
Anatase in F.S.	0.084	0.001
Branched titania in DIW	0.541	0.003
Branched titania in F.S.	1.029	0.058

retains more positive surface charge in the finishing solution with pH 3.52 as compared to the DI water with pH of 6. Stability of the suspensions is expected to reduce when the pH is close to the iso electric point (i.e.p) of the system due to the fact that the particles retain no surface charge at the i.e.p (Ney, 1973). If the suspension is to be stabilized, one of the ways to do this is to change the pH away from the i.e.p to increase the electrical repulsion in between the particles (Salopek et al., 1992). Alternatively, mechanical vibration can be induced through effective ultrasonication. In this case, titania particles were stabilized in both suspensions through rigorous ultrasonication as can be seen from the consistent mean size measurement values.

In the case of branched titania, measurements showed a mean size of $0.55 \pm 0.003 \mu m$ with tight control on the standard deviation for the solutions prepared in the DI-water background. In the presence of the finishing solution, on the other hand, the mean size increased almost twice and measured to be $1.029 \pm 0.058 \mu m$. It is believed that in the presence of the ingredients of the finishing solution, such as the silicon particles, the branches created on the titania particles attach to these additives and measure larger in mean size as compared to the DI-water based measurements. The increase in the variance of the measurement also supports the proposed concept in the finishing solution environment.

In order to understand the stability and verify the proper size of the synthesized branched titania particles, morphological particle size analyses were conducted by AFM scanning. Particles deposited on mica substrates were characterized and summarized in Table 2. The scanning of the anatase versus the branched titania particles with the AFM technique allows the characterization of the particles in their dried form. It can be seen that the mean sizes of the anatase and the branched titania particles are much closer measured as $0.277 \pm 0.035 \ \mu\text{m}$ for anatase and $0.244 \pm 0.118 \ \mu\text{m}$ branched titania. This is an indication that the branched titania particles have similar size cores but measure larger due to the presence of polymeric branches in the solution background. Furthermore, the standard deviation of particle size measurements obtained with light scattering on branched silica particles is lower as compared to the AFM measurements, while the particle sizes measured with AFM are almost half of the mean size measured by the Coulter LS 13 320. The smaller size measurement by AFM can be attributed to the fact that the branches attached to the main

 Table 2
 AFM scanning results for mean particle size evaluations of anatase and branched titania.

Photocatalytic particle	Mean Particle size (µm)	Standard Deviation (µm)
Anatase	0.277	0.035
Branched titania	0.244	0.118



particle are collapsed by drying, whereas they are extended effectively in the solution environment for the light scattering measurements. Furthermore, the presence of the silicon and the polymeric additives in the finishing solution also results in the measurement of a larger size which is more pronounced with the branched structure of titania.

3.2 Optimization of photocatalytic activity with methylene blue solution

Optimization of photocatalytic activity initially studied by using MB^+ and the experimental setup adopting ISO 10678 standards. **Fig. 1** illustrates the stain bleaching on suspensions prepared by 0.001, 0.01 and 0.1 wt % anatase in DI water and finishing solution for optimization of photocatalytic activity as a function of titania particle addition. It can be seen that in DI-water, anatase did not show any photocatalytic activity even under the UV light. When we conducted the same tests in finishing solution, on the other hand, 0.1 wt % anatase concentration showed significant degradation of methylene blue under the UV light changing the color of the suspension to white. It can be concluded that the presence of finishing solution helps activate the anatase under the UV light, which can be attributed to the additives like silicon in the active ingredients of the finishing solution.

Further improvement in the photocatalytic activity was obtained with the addition of branched titania to the 0.1 wt % anatase solutions. **Fig. 2** illustrates the change in the color of methylene blue solutions in finishing solution as a function of the branch titania doping at 0, 0.001, 0.01, and 0.1 wt % concentrations. As it can be seen in **Fig. 2**, finishing solution by itself did not show photocatalytic activity as observed by no change in the methylene blue



Fig. 1 Methylene blue stain bleaching on suspensions prepared by 0.001, 0.01 and 0.1 wt % anatase in (a) DI water and (b) finishing solution for optimization of photocatalytic activity as a function of titania particle addition.



Fig. 2 Optimization of anatase/branched titania mix ratio in both finishing solution by methylene blue degradation analyses.



color. This is consistent with the observation of no stain bleaching on the textiles which were coated only with the



Fig. 3 Absorbance versus wavelength representing the MB⁺ degradation under the cool light as a function of time for, (**a**) 0.1 wt % anatase, (**b**) 0.1 wt % anatase doped with 0.001 wt % branched titania and (**c**) 0.1 wt % anatase doped with 0.01 wt % branched titania in finishing solution.

finishing solution in our earlier studies (Cerhan Haink and Basim, 2020). The optimal photocatalytic performance was obtained with 0.1 wt % anatase with 0.001 wt % branched titania doping as per the visual observations. Nevertheless, the determination of the photocatalytic activity according to the color change can be misleading a better quantification is needed. As an example, appearances of 0.1 wt % anatase doped with 0.001 wt % 0.01 wt % branched titania after UV exposure are similar. Therefore, the methylene blue degradation for these solutions was also evaluated by UV spectrophotometer absorbance tests as a function of time, as can be seen in Fig. 3. The decrease in the absorption is an indication of better transmittance in the solution and hence indicates the cleaning of the solution by the photocatalytic activity. Comparing the absorption peaks of the 0.1 wt % anatase (Fig. 3a), 0.1 wt % anatase doped with 0.001 wt % branched titania (Fig. 3b) and 0.1 wt % anatase doped with 0.01 wt % branched titania (Fig. 3c) show that the UV absorption peaks representing methylene blue degrades fastest for the combination of 0.001 wt % branched titania with anatase. Consequently, better photocatalytic cleaning efficiency is observed in the presence of 0.001 wt % branched titania in 0.1 wt % anatase. The speed of photocatalytic degradation can also be seen in Table 3, where the absorption delta is tabulated as a function of time for the selected three treatments. This observation highlights the fact that the ingredients in the finishing solution can enhance the kinetics of the photocatalytic activity when the polymeric branches interact with the silicon in the environment. It can be suggested that the polymeric branches on the titania particles can induce the synergistic effect of better particle attachment on the textile surfaces while simultaneously enhancing the photocatalysis.

3.3 Evaluation of photocatalytic efficiency on the textiles coated with the optimized nanoparticle systems

In order to observe the photocatalytic performance of the textiles coated with the optimized particulate systems, absorbance tests were also conducted on the textiles coated with the selected optimal nano-particle combinations and compared to the industrial standards. **Fig. 4** illustrates the

Table 3 Absorption delta for methylene blue degradation in finishing solution with 0.1 wt % anatase, 0.1 wt % anatase doped with 0.001 wt % branched titania and 0.1 wt % anatase doped with 0.01 wt % branched titania as a function of time.

Solutions	Time (minute)								
	0	2	3	4	6	8	9	10	12
0.1 wt % Anatase 0.01 wt % Branched titania	3.985			3.929		3.142			2.703
0.1 wt % Anatase 0.001 wt % Branched titania	3.863		3.801		3.100		2.497		
0.1 wt % Anatase	3.898	3.789		3.313	2.857	2.571		2.504	



absorbance tests performed for textile samples coated with 0.1 wt % anatase, 0.1 wt % anatase doped with 0.001 wt % branched titania, and 0.1 wt % P25 (used as a benchmark to compare photocatalytic activeness) in the finishing solution. It can be seen that the textile coated with the optimized solution, which is 0.1 wt % anatase doped with 0.001 wt % branched titania, degraded the methylene blue solution most effectively with a high drop in the absorbance value indicating efficient photocatalytic activity. The optimized combination of the nanoparticle system resulted in a significantly better performance relative to the standard P25 and even anatase coated by themselves.

To better observe the stain removal efficiency of the coated textiles, the stain tests were also performed, as can be seen in **Fig. 5**. The textiles coated with the specified particle combinations were stained in one half and compared to the unstained half as they are exposed to UV light and pictured daily basis. Branched titania particles were synthesized by following the procedure described in the literature (Simakov and Tsur, 2007). It was illustrated by SEM micrographs that the diethylene glycol monomethyl ether attached on the titania surface and extended out as branches. It was also reported by XPS measurements that the binding energy of the carbon atoms and the oxygen atoms was detected to be around 250 eV and 530 eV, respectively (Simakov and Tsur, 2007). In this study, the UV



Fig. 4 Absorbance values of textiles coated with 0.1 wt % Degussa P25, 0.1 wt % anatase and, 0.1 wt % anatase doped with 0.001 wt % branched titania dipped into methylene blue solutions under exposure to 665 nm wavelength light as a function of time.



Fig. 5 Discoloration scale of textiles coated with 0.1 wt % Degussa P-25, 0.1 wt % anatase, and 0.1 wt % anatase doped with 0.001 wt % branched titania in finishing solution.

light energy applied on the textile samples coated with the branched titania was around 3.4 eV and the textiles were exposed to UV source which was 15 cm away from the textile surface in the CAMAG UV Cabinet. Therefore, the polymer degradation is not expected to occur under the experimental set-up. Furthermore, no particular color change was observed on the branched titania coated textiles within the duration of the experimental evaluations. Furthermore, the stain test results also demonstrated that the textile sample coated with 0.1 wt % anatase and 0.001 wt % branched titania in the finishing solution showed the maximum level of stain discoloration based on the visual judgment of stain bleaching by the human eye. This observation is in an agreement with the absorbance measurements performed on the textiles coated with the same particle combinations.

3.4 Zeta potential of coated textiles

The textiles coated with photocatalytic particles were compared to the baseline uncoated textile to analyze any changes in the surface charge as a function of the solution pH. The zeta potential analyses were carried out for the uncoated textiles and the textile samples coated with 0.1 wt % anatase, 0.001 wt % branched titania and the optimal photocatalytic concentration of 0.1 wt % anatase doped with 0.001 wt % branched titania in the finishing solution. **Fig. 6** illustrates the measured surface potentials as a function of pH to be very similar regardless of the surface treatment. It can be seen that the i.e.p of all the textile samples was measured between pH of 2.5 and 3, indicating that the procedure of photocatalytic enhancement by coating with various particle systems maintain a consistent surface finish while improving the photocatalytic efficiency.

3.5 Bandgap energy determination for optimal particle combination

To quantify the photocatalytic efficiency of the optimized particulate system, band gap energy measurements were conducted as described in the experimental evalua-



Fig. 6 The zeta potential as function of pH of un-coated textile and textiles coated with anatase concentrations doped with 0.001 wt % branched titania in finishing solution.



tions. The transmittance and absorbance of the thin films prepared from the solutions composed of 0.1 wt % anatase and 0.1 wt % anatase doped with 0.001 wt % branched titania in finishing solution were measured to determine the thickness and bandgap energy as shown in **Fig. 7** and **Fig. 8**.

The film thicknesses (t) were attained by placing peak values of transmittance into Eq. (2) and Eq. (3), respectively. Furthermore, the thickness values were used to determine the energy bandgap for the thin films generated. The bandgap value of the 0.1 wt % anatase doped with 0.001 wt % branched titania was calculated to be 2.8 eV. This bandgap corresponds to the visible light range of 443 nm, according to the Plank-Einstein relationship (Landsberg, 1978). The band-gap energy, or in other words, the initial energy for photocatalysis being in the visible light range, means that the photocatalytic activity is plausible under the visible light exposure. Whereas the band

gap energy of the pure anatase at 0.1 wt % concentration in the finishing solution was determined to be 3.31 eV, which is close to the value reported in the literature (3.26 eV) but still corresponding to the UV light region (400 nm). Thus, the enhanced performance with the optimized anatase, branched titania combination can be attributed to the energy bandgap shift into the visible light range in the presence of the polymeric additive doping. This observation also aligns with the earlier findings in the literature suggesting the core-shell particle decorated with polymeric branches can actively control the binding event by pairing ion, metal complex recognition, and hydrogen-bond recognition (Randazzo et al., 2012). Furthermore, textiles have an inherently rough surface and they are not conductive and hence the photocatalytic reaction should be considered as independent from any change in the surface area of the textiles by the addition of particles. The surface charge evaluations also do not indicate a significant change to



Fig. 7 Thickness and transmittance graphs of thin films coated with (a) 0.1 wt % anatase and (b) 0.1 wt % anatase doped with 0.001 wt % branched titania in finishing solution.



Fig. 8 Band gap energy and absorbance graphs of thin films coated with (a) 0.1 wt % anatase and (b) 0.1 wt % anatase doped with 0.001 wt % branched titania in finishing solution.



|--|

Type of Textile	WVTR (%) (20 °C-20 %RH)	WVTR (%) (35 °C-50 %RH)
Uncoated	34.12 ± 0.37	77.26 ± 0.36
0.1 wt % Anatase in finishing solution	34.61 ± 0.48	75.61 ± 0.59
0.1 wt % Anatase and 0.001 %w Branched titania in F.S.	33.80 ± 1.43	72.52 ± 0.99

infer that an increase in the surface area would make the observed photocatalytic activity improvement.

3.6 Water vapor transmission evaluation for daily usage evaluation of the textiles

The water vapor transmission through the textiles is a vital factor affecting the thermo-physiological comfort of people wearing the textiles by allowing respiration of human skin (Arabuli et al., 2010). After coating the textiles with the selected particulate systems, the permeability could change due to the reduction of the textile porosity, which may limit the breathability of the garment.

Textiles coated with 0.1 wt % anatase and 0.1 wt % anatase doped with 0.001 wt % branched titania in the finishing solution were exposed to the WVTR analyses for detecting water vapor transmission rates. The weight change of the full experimental set-up as a function of time is summarized in Table 4 as evaluated for winter and summer conditions. It can be seen that the WVTR is around 35 % for each textile sample for winter set up under 22 °C and 20 % moisture environment. The WVTR values measured in winter were lower than the values measured in summer 35 °C and 50 % moisture, which were measured to be around 75 %. The results were statistically the same other that the trend of slightly lower values observed with the textiles coated with the 0.1 wt % anatase doped with 0.001 wt % branched titania. It can be concluded that the photocatalytically more active coating combinations are equality suitable for the daily use.

4. Summary and conclusions

Extension of photocatalytic activity into the visible light range through modification of the bandgap energy was accomplished by polymeric branches decorated on titania particles. Branched titania synthesis was performed chemically, and the particle size measurements conducted in the solution and post drying suggested the free elongation of the polymeric branches from the core particle in the solution environment. An optimal concentration was established with 0.1 wt % anatase doped with 0.001 wt % branched titania in a hydrophobic finishing solution. The composite branched titania particles, in combination with the anatase in finishing solution, achieved a 2.8 eV bandgap corresponding to the visible light range with 443 nm wavelength. The synergistic effect of the branched titania particles in the presence of anatase was further confirmed by measuring the bandgap of 0.1 wt % anatase in finishing solution, which was found to be 3.1 eV. It was further demonstrated that the implementation of the optimized particle combination to the textile finishing process enhanced the self-cleaning efficiency in addition to better attachment of the particles on the textile surface through the polymeric branches. In summary, the new polymeric branched particles have the synergy of better coating capability on textiles with an enhanced photocatalytic activity that can be extended into the visible light range.

Acknowledgements

The authors acknowledge the financial support from the Eureka PhotoCat project E!8080 and Kivanc Tekstil Company in Adana Turkey.

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Book Review

"Nanoparticle Technology Handbook (third edition)" edited by Makio Naito, Toyokazu Yokoyama, Kouhei Hosokawa and Kiyoshi Nogi

Elsevier B.V., 3rd ed. 2018, 904 p. ISBN: 978-0-444-64110-6, DOI: 10.1016/C2017-0-01011-X

A "powder", which is an assemblage of small solid particles, exhibits very unique behavior. For example, depending on the circumstances, a powder can behave like a gas, a liquid, or a solid. Furthermore, because of the larger specific surface area relative to its bulk counterpart, powders can have very distinct properties. This is especially true for "nanoparticles". The unique behavior and properties of particle and powder give them a wide range of industrial applications that makes them ubiquitous in our daily lives. Particles and powder are also building blocks to make promising materials for creating scientific and technical innovations in the future.

Mr. Masuo Hosokawa, the chief editor of the first edition of this Handbook, was a pioneer in this industry. When he was the President of Hosokawa Micron Corp., he founded Hosokawa Powder Technology Foundation in 1991 to contribute to the advancement of powder technology on a global scale, and published the first issue of "KONA Powder and Particle Journal" in 1983. Since then, KONA has been published annually, and distributed worldwide.

Mr. Hosokawa proposed the concept of "nanoparticle technology" long before the United States President Bill Clinton's National Nanotechnology Initiative in 2000. One of the activities of the Foundation was to publish the Nanoparticle Technology Handbook in Japanese in 2006, which was translated into English and published its first edition of this Handbook in 2007. Nanoparticle technology advanced considerably after 2007, prompting Mr. Hosokawa to start preparing an updated second edition of the Handbook. He unfortunately passed away on March 31, 2010 before the second edition was published in 2012.

Because nanoparticle technology has rapidly evolved since 2012, and has been applied more broadly in new areas, Mr. Yoshio Hosokawa, the second President of Hosokawa Powder Technology Foundation and President of Hosokawa Micron Corporation decided to publish a third edition of the Handbook. In this third edition, the applications section of the Handbook has been updated to include the most recent advances in nanoparticle technology. Nineteen chapters have been added. The 79 chapters in the applications section are organized into four categories as shown in Table 1. The third edition has totally 877 pages including fundamental part as shown in Table 1. Over 140 experts in nanotechology and/or powder technology contributed to this new edition.

Nanoparticle technology is a new and revolutionary technology. It handles the preparation, processing, application and characterization of nanoparticles and has become the core of nanotechnology as an extension of conventional fine

particle/powder technology. Nanoparticle technology plays an important role in the implementation of nanotechnology in many engineering and industrial fields.

I hope the third edition will give readers state-ofthe-art information and knowledge to develop their own innovative technologies and new products, further enhancing our understanding of the fundamentals of nanoparticle technology.



1st edition (2007)

3rd edition (2018)





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Author's Short Biography

Makio Naito



Makio Naito is a professor at the Joining and Welding Research Institute (JWRI), Osaka University in Japan. He received his Ph. D. degree in chemical engineering from Nagoya University in 1987. He served as the President of The Society of Powder Technology, Japan from 2015 to 2019. His publications cover a wide range of studies in the fields of advanced materials and novel powder processing and characterization. He has authored or coauthored more than 300 refereed journal papers and 120 review articles. He has contributed 80 books, edited 27 books and holds more than 60 patents. He has received several prestigious awards including the Richard M. Fulrath Award from the American Ceramic Society (ACerS) in 2002 and the KONA Award in 2019. He has been a Fellow of the ACerS since 2010, and serves on the ACerS Board of Directors from 2020. He has been a Professional Academy Member of the World Academy of Ceramics since 2012, and has served on the Academy's Advisory Board since 2018.

3rd International Hosokawa Powder Technology Symposium Held in China

As the special event aiming at the globalization in Asia of the Hosokawa Powder Technology Foundation, the 3rd International Hosokawa Powder Technology Symposium took place on Tuesday, November 19, 2019, at the Shanghai Institute of Ceramics of the Chinese Academy of Sciences (SICCAS) in China. This International Hosokawa Powder Technology Symposium was held abroad for the third time after the first one (2014, at Hosokawa Alpine AG in Augsburg, Germany) and the second (2017, at Hosokawa Micron Powder Systems Div. in New Jersey, U.S.A.) organized by the Hosokawa Powder Technology, Japan (SPTJ) and supported by the Hosokawa Micron Corporation (HMC) and Hosokawa Micron (Shanghai) Powder Machinery Co., Ltd. (HMS). At the symposium, five lectures were given on the theme of "Powder and Particle Technology for Advanced Materials" after the opening remarks of President Yoshio Hosokawa.

In the first lecture, high-purity, ultra-fine powder production and processing technologies for advanced materials such as ultra-high temperature heat-resistant rocket members, reflectors, and transparent materials were presented. Then the new nanoparticle size measuring devices, and the in-situ and real-time nanoparticle measurement using this device was introduced. The third lecture was concerning the functional materials based on the form of natural organisms to create new innovative functionalities. After the lectures by the Chinese professors, two presentations were given from the Hosokawa Group on the application of powder processing technology to various industrial product fields, and the development and commercialization of cosmetics and pharmaceuticals using PLGA nanoparticles. Finally, Mr. Uchida of HMS closed the conference with the closing remarks.

The symposium was attended by about 130 people from universities and industries in China and the neighborhood countries including Japan, Korea, and Taiwan. At the venue, a panel exhibition was also made to inform the participants of the activities of the Foundation, introducing the history and main business contents. The latest issue of the KONA Powder and Particle Journal was displayed as well. HMS also exhibited panels to introduce the company and the powder processing machines. The SICCAS was founded in 1928. The lecture hall on the fourth floor was a high-grade inclined conference room with heavy chairs in all rows. Attendees were given a copy of lecture slides in English, printed in color, along with a program brochure. After the lectures, moving to the middle-sized meeting room on the 14th-floor, a social gathering was held using the lobby in front of the room, where discussions between the lecturers and participants continued, and personal exchanges were cultivated. At the lobby, there were a few large, colorful pots and a large, beautiful ceramic screen on display that seemed to be fine arts closely related to the ceramics research and technology, and the fabulous cultural tradition of China.

This first international symposium held in Asia was very successful with interesting lectures and many participants who have been provided with good chances to increase knowledge about the leading powder and particle technology and to get in contact with the people concerned. Without the very kind and active cooperation and assistance of especially the people in Shanghai, those of SICCAS and HMS, it could not have been such a great meeting at all. Following this symposium, the International Symposium on Powder Processing Technology for Advanced Ceramics was organized by the SICCAS and the SPTJ and sponsored by the HPTF at the same venue for the next two days. There were lively talks and discussions on powder processing technology for advanced ceramic materials.



Lecture scenery

People involved in the lecture









HMS supporting team with the Foundation members



The Opening address by Mr. Y. Hosokawa at the social gathering in front of the ceramic screen (right: Mr. Y. Uchida, left: Ms. X. Yan)

The KONA Award 2019

The KONA Award 2019 was presented to Dr. Makio Naito, Professor of Joining and Welding Research Institute, Osaka University, Japan. He has conducted ground breaking and foundational studies contributing to novel powder processing technology to develop advanced materials to address energy and environmental issues. He aimed to develop smart powder processing techniques to support green and sustainable manufacturing of advanced materials. He has proposed and advanced new concept to achieve direct bonding between particles by activating their surfaces with mechanical energy, without any externally applied heat or added binders of any kind in the dry phase. By introducing controlled composite particles made by the direct bonding as precursors, new microstructure electrodes for Molten Carbonate Fuel Cells (MCFC) and Solid Oxide Fuel Cells (SOFC) have been created. Based on this concept, Professor Naito has produced electrodes for SOFC that operate at lower temperature, and developed other new materials such as fibrous nanoparticle compacts having high thermal insulation performance at the high temperatures. By making use of particle bonding, he has developed a new one-pot processing method to synthesize nanoparticles without applying extra heat. Furthermore, the one-pot processing method can combine the synthesis of nanoparticles and their bonding with other particles to make nanocomposite granules in one step. Nanostructured granules of active materials for the cathodes and anodes for lithium ion batteries have been successfully synthesized by this novel method. Now, Professor Naito is developing electrodes for all-solid-state lithium ion batteries in collaboration with industry partners to reduce the huge thermal energy consumption traditionally required to manufacture high quality powders and ceramics.

Professor Naito has also conducted research on powder processing to increase the performance and reliability of advanced ceramics, which is a very important issue in engineering ceramics. He has developed characterization tools to examine the evolution of large defects in ceramics during processing. Applying these tools in the ceramics manufacturing process, he has elucidated the failure mechanism, and demonstrated that very few large particles and/or large pores will significantly degrade the fractural strength of ceramics manufactured through traditional routes. His achievements and publications have been cited by numerous researchers, and are recognized in many review articles and journals worldwide. Several characterization tools developed by his research group have been adopted by the International Organization for Standardization (ISO) for Technical Committee, TC 206 (Fine Ceramics).

As President of The Society of Powder Technology, Japan, he has contributed significantly to the development of powder technology, and presented many lectures to various material researchers on developing innovative synergetic materials. He also has contributed to the publication of many books to establish a foundation of international infrastructure on powder technology. The "Nanoparticle Technology Handbook" published by Elsevier is one example of the books he has edited.

Due to the worldwide problems with the COVID-19, the presentation ceremony of the KONA Award 2019 did not take place at the 54th Symposium on Powder Technology, which had been originally planned to be held in September, 2020 in Tokyo, Japan but decided to be postponed.



Selected research achievements for the KONA Award 2019: One-pot processing methods developed by applying particle bonding principle.



KONA Powder and Particle Journal No. 38 (2020) 288/Doi:10.14356/kona.2021024

General Information

History of the Journal

In the history of KONA Powder and Particle Journal, two organizations have been playing an important role. The one is the Council of Powder Technology, Japan (CPT) and the other is the Hosokawa Powder Technology Foundation (Hosokawa Foundation). The CPT was established in 1969 by Hosokawa Micron Corporation as a nonprofit organization to enhance the activities of research and development on powder science and technology. The Hosokawa Foundation was established in 1991 as a public-service corporation approved by the Ministry of Education, Culture, Sport, Science and Technology of Japan. The issues from No.1 (1983) to No.12 (1994) of KONA were published by CPT and the issues from No.13 (1995) by the Hosokawa Foundation.

The aim of KONA in the early days was to introduce excellent Japanese papers to the world and thus KONA consisted of papers recommended by some Japanese academic societies and translated from Japanese to English. From the issue of No.8, the CPT changed its editorial policy to internationalize the KONA and to incorporate papers by authors throughout the world in addition to translated papers. In response to this change, three editorial blocks have been organized in the world; Asian-Oceanian, American, and European. The policy and system have not changed even after the Hosokawa Foundation has taken over from the CPT. From the issue of No.27 (2009), publication of translated papers has been terminated and only original papers have been published. The CPT is still active today and is collaborating with the Hosokawa Foundation.

Aims and Scope

KONA publishes review and original research papers in a broad field of powder & particle science and technology, ranging from fundamental principles to practical applications. The papers on critical reviews of existing knowledge in special areas are very welcome.

The submitted papers are published only when they are judged by the Editor to contribute to the progress of powder science and technology, and approved by any of the three Editorial Committees.

The paper submitted to the Editorial Secretariat should not have been previously published.

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Publication in KONA is free of charge.

Publication Schedule

KONA is published annually. The publication date is around January $10^{\rm th}. \label{eq:kond}$

Subscription

KONA is distributed free of charge to senior researchers at universities and laboratories as well as to institutions and libraries in the field throughout the world. The publisher is always glad to consider the addition of names of those, who want to obtain this journal regularly, to the mailing list.

Instructions to Authors

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