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Self-assembly Patterning of Nano/micro-particles

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About the Cover of Journal "KONA"

The Chinese character "粉" is pronounced "KONA" in Japanese, and means "Powder". The hand written "3" is after the late Mr. Eiichi Hosokawa, founder of the Hosokawa Micron Corporation.



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The Letter from the Editor





Yutaka Tsuji Editor-in-Chief

It is my pleasure to issue KONA Number 25. KONA is an annual journal and so this number 25 means that a quarter of the century has passed since its Number 1 was published. The period of 25 years might not be very long but not so short. In the early days, the KONA was issued by an organization named the Council of Powder Technology. The Council was supported by Hosokawa Micron Corporation. Taking the opportunity of establishing the Hosokawa Powder Technology Foundation in 1991, KONA has been issued by the Foundation. The Hosokawa Foundation is a public-service corporation authorized by the Ministry of Education, Culture, Sport, Science and Technology of Japan. KONA has been keeping the spirit of public service from the beginning. That is why the KONA journal is offered free of charge no matter what it is the printed version or the electric version. All the expenses for the publication of KONA are covered by the budget of the Foundation. The president of the Foundation is Mr. Masuo Hosokawa, the president of Hosokawa Micron Corporation. The Foundation is managed by the board of directors. I have been appointed to be the managing director since September, 2006. Allow me to explain the activities of the Foundation and the relation to KONA.

The Foundation has various activities such as granting funds for research and academic meetings, presenting the KONA Award and organizing symposiums besides issuing the journal. Concerning the KONA Award, a distinguished researcher of powder science and technology is presented with this award every year. The recipient of the Award is introduced in the Information Articles of the journal which appears after research and review papers. The recipient this year 2007 is Prof. Kikuo Okuyama (Hiroshima University), a prominent figure in the field of aerosol science and nanoparticle processing.

The symposium organized by the Foundation has a long history of more than 40 years. It was commenced before the establishment of the Foundation. The symposium in 2007 is the 41st one. The name of the symposium, translated from Japanese to English, is "Lecture and discussion of powder technology" . This symposium has some special subject every year. You can see the program of the symposium also in the Information Articles of the KONA journal. The subject of the 41st symposium is "nanoparticle technology: development of new markets and entry into them". The nano-particle has been the subject of the symposium these 7 years on end. You can see the trend of nano-particle related R & D in Japan from the sub-title of the symposium. Seven years ago, the topics were general aspects of nano-particles. Gradually, they developed from general ones to specific ones. The word "new market of nano-particle" appeared in 2007 at last. As most readers of KONA feel, there are still many barriers ahead of us and many problems should be overcome to reach such a point of new market in reality. However, it is notable that interest in nano-particles does not decay when we think that things are changing very fast nowadays. As described in the foregoing the Hosokawa Foundation has been playing an important role for KONA.

On the way of writing about nano-particle technology, I would like to introduce a publication news to you. In 2006, the Nano-Particle Technology Handbook was published by a Japanese publisher, Nikkan-Kogyou Shinbun under the support of Hosokawa Micron Company but the handbook was written only in Japanese. In the fall of 2007, the English version of the same handbook was published by Elsevier B.V. The Hosokawa Foundation partially supported this project.

Finally, I must inform you of a sad news. Prof. Yoshinobu Morikawa, who used to be an editorial member of the KONA journal and also the managing director of the Foundation from 1998 to 2002, passed way in July 2007. He was a professor of Osaka University for many years and after retiring from Osaka University he worked in the Osaka Industrial University. He performed a big achievement in the field of pneumatic conveying. He was my boss in Osaka University. Without his guide, I would not have entered the field of powder technology. With grateful appreciation for numerous services rendered by Prof.Morikawa during his lifetime, I offer this token of my deepest sympathy.





Comment of the Cover Photograph Self-assembly Patterning of Nano/micro-particles

Yoshitake Masuda National Institute of Advanced Industrial Science and Technology (AIST)



Fig. 1 Conceptual process and SEM micrographs of spherical particle assemblies.

"Self-assembly" has been attracted much attention as next generation nano/micro fabrication process. In this study, we developed spherical particle assemblies and micropatterns of them using self-assembly processes. SiO₂ particles were thoroughly dispersed in water and dropped on a hydrophobic OTS (octadecyltrichlorosilane)-SAM (**Fig. 1**). The OTS-SAM with droplets was then immersed in hexane and ultrasonicated for 1 min. Large water droplets containing SiO₂ particles were separated into many small emulsions that kept them spherical on hydrophobic OTS-SAM. Water in the emulsions was gradually extracted to hexane to reduce the size of emulsions forming spherical particle assemblies. After having been immersed for 12 h, spherical particle assemblies with different diameters were observed on OTS-SAM; it was also observed that the assemblies were constructed from various numbers of particles such as 3, 5, 6, 8 or many particles. Quantities of 3, 5, 6 or 8 particles were assembled into triangular, pyramidal, octahedral or decahedral particle clusters, respectively. The number of particles in spheres can be controlled by the change of emulsion size or particle concentration in water. The spherical shape of particle assemblies was caused by the high contact angle of water emulsion on hydrophobic OTS-SAM in hexane. Consequently, various sizes of spherical particle assemblies can be prepared using self-assembly process.

"Self-assembly" has been attracted much attention





Fig. 1 Micropatterns of colloidal crystals.

as next generation nano/micro fabrication process. There are a great deal of self-assembly phenomena in nature, for instance, crystallization of solids in supersaturated solution, crystals of snow having various morphologies, patterns of butterflies, zebra, giraffe, and beat of the heart. In the particle science, novel nano/micro fabrication has been developed by the use of "self-assembly". Opal is constructed of close packed particle assembly to form fcc (hcp). Periodic architecture is formed by the combination of particles and air to be photonic crystal. Photonic crystal has photonic band gap and diffracts visible light to show structural color. There are many photonic crystals in nature, for instance, opal, morpho butterfly, blue damselfish, chrysochroa fulgidissima (schonherr), peacock etc. In order to apply photonic crystal for next generation device, microfabrication and patterning process of photonic crystal are required to realize photonic devices.

In this study, we developed spherical particle assemblies and micropatterns of them using selfassembly processes. SiO₂ particles were thoroughly dispersed in water and dropped on a hydrophobic

OTS (octadecyltrichlorosilane)-SAM (Fig. 1). The OTS-SAM with droplets was then immersed in hexane and ultrasonicated for 1 min. Large water droplets containing SiO2 particles were separated into many small emulsions that kept them spherical on hydrophobic OTS-SAM. Water in the emulsions was gradually extracted to hexane to reduce the size of emulsions forming spherical particle assemblies. After having been immersed for 12 h, spherical particle assemblies with different diameters were observed on OTS-SAM; it was also observed that the assemblies were constructed from various numbers of particles such as 3, 5, 6, 8 or many particles. Quantities of 3, 5, 6 or 8 particles were assembled into triangular, pyramidal, octahedral or decahedral particle clusters, respectively. The number of particles in spheres can be controlled by the change of emulsion size or particle concentration in water. The spherical shape of particle assemblies was caused by the high contact angle of water emulsion on hydrophobic OTS-SAM in hexane. Consequently, various sizes of spherical particle assemblies can be prepared using this emulsion process.



Modelling Powder Compaction[†]

Dr. I.C. Sinka Department of Engineering, University of Leicester¹

Abstract

Die compaction of powders is a process which involves filling a die with powder, compression of the powder using rigid punches to form a dense compact, and ejection from the die. The choice of powder composition and selection of process parameters determine the microstructure and final properties of the compacts. The practical issues in the powder-forming industries (powder metallurgy, ceramics, hard metals, pharmaceuticals, detergents, etc.) are related to mechanical strength, control of microstructure, avoidance of cracks and defects, content uniformity, etc.

We review the modelling strategies used for powder compaction. The main focus is on the constitutive model development for finite element analysis. Knowledge of the following input factors is required:

- 1. constitutive equations which describe the deformation of a volume of powder under the loads applied during compaction
- 2. friction interaction between powder and tooling
- 3. geometry of die and punches
- 4. pressing schedule, e.g. sequence of punch motions
- 5. initial conditions that relate to the state of the powder in the die after die fill

The constitutive model and friction relate to fundamental properties of the material and are reviewed in more detail. The methodologies used for model calibration are also described. The remaining factors (geometry, pressing schedule and initial conditions) are specific to particular problems. Their relative effect is discussed by presenting examples for a range of powder materials. We show how compact microstructure can be manipulated by changing the factors discussed above and illustrate the effect of microstructure on final properties. The model predictions are validated using experimental data. The use of numerical analysis in powder formulation design and optimisation of the process parameters is discussed.

Keywords: Compaction, Constitutive model, Friction, Modelling

1. Introduction

A wide range of engineering components is manufactured using the powder route. Die compaction of powders followed by sintering is used in powder metallurgy, industrial ceramics and the hard metal sectors. Pharmaceutical tablets and detergents are also made from powders using compaction. Thus die compaction is a common operation across a range of industries. The process involves filling a powder formulation into a die, compression using rigid punches, and ejection from the die. Post-compaction operations such as sizing, sintering, coating, etc. are usually also applied depending on the application.

In this review we focus on modelling die compaction. In Section 2, we introduce the manufacturing operation and describe characteristics of the process that are common across materials and industries. Product requirements and process-specific issues are discussed for various applications. The modelling approaches are reviewed in Section 3 with focus on

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continuum methods. Section 4 expands on the constitutive models used for powder compaction. The models are presented with reference to the experimental procedures used for calibration. The presentation focuses on the structure of the constitutive models rather than on computational aspects. The friction behaviour between powder and die wall during compaction is reviewed in Section 5.

A series of examples is presented in Section 6, highlighting how modelling could help in tackling the practical problems incurred in powder compaction. Experimental results are presented for model validation purposes. The concluding section discusses the current uses of compaction models and future challenges in this field.

2. Practical Aspects and Issues in Powder Compaction

In broad terms, compaction machinery can be divided into two categories: single-station and rotary presses. Single-station presses are typically used in powder metallurgy for manufacturing components that are relatively large, have a complex geometry and require high compression forces. Essentially, the process consists of 4 steps: die fill, transfer, compaction and ejection. The transfer stage is introduced so that after die fill, the powder is transferred at a constant volume into a shape that is proportional with the compressed part. The transfer stage is necessary to avoid crack formation. The sequence of punch motion is carefully selected as cracking can occur during each of the 4 stages.

The compressed parts (also referred to as green parts) require a high density in order to achieve the required specifications in terms of strength and dimensional tolerances after sintering. The density distribution in green parts must be kept at a minimum in order to avoid distortions during sintering. Structural ceramics and hard metal components are also subject to similar requirements. Ceramic parts in the green state usually have low strength and can present handling difficulties. The control of tolerances is particularly important for hard metals which are expensive to machine after sintering.

Rotary presses are used for smaller parts with a relatively simple geometry. Rotary presses are used for high-volume production that can exceed 1 million units/hour for pharmaceutical tablets. Powder transfer does not exist as a distinct stage on rotary presses. However, more modern presses allow some degree of powder transfer between die fill and compaction. Rotary presses require powder handling processes to prevent segregation and robust die fill to ensure weight uniformity.

The practical issues related to density distribution, cracking, dimensional tolerances, and consistency are common across the applications. The compaction process can be analysed in terms of 2 main contributing factors: powder formulation and process parameters. Numerical modelling can be used to optimise the composition of the powder blend (i.e. selection of powder constituents that offer the required constitutive response during compaction) and the selection of process parameters, so that the product, the process and the tooling are designed on a rational basis instead of trial and error which is still widely (and often exclusively) used in powder forming industries at this point in time.

3. Modelling Approaches for Powder Compaction

Powder compaction can be described as a large irrecoverable deformation during which the material is transformed from a powder state into a dense compact. This process can be modelled using two main approaches:

- 1. discrete method, where the behaviour and interaction of individual particles are considered
- 2. continuum method, where the powder is regarded as a mechanical continuum

The two approaches are reviewed below.

3.1 Discrete element models

The discrete element method (DEM) was proposed by Cundall (Cundall and Strack, 1979) for rock and soil mechanics problems. The DEM solves the equations of motion of particles taking into account the interactions between particles in contact. The method has been used to analyse granular flow (Oda and Iwashita, 1999; Landry et al., 2003; Bagi, 1993; Tsuji et al., 1993; Tzaferopoulos, 1996; Tuzun and Heyes, 1997; Thornton and Antony, 2000; Oda and Iwashita, 2000; Thornton and Zhang, 2003). Most DEM studies treat regular particles for which wellestablished interaction laws exist. Irregular particles were also considered (Mirghasemi et al., 2002). The application of DEM has been extended to model die fill (Wu and Cocks, 2006) and powder transfer (Wu et al., 2003).

More recently, the method was also used to model the early stages of powder compaction (Kong and Lannutti, 2000; Heyliger and McMeeking, 2001; Re-



danz and Fleck 2001). Martin et al. (2003) showed that DEM results were consistent with micromechanical models (described in Section 4.2) for isostatic loading (which assume affine motion of the particles), but with differences occurring as the shear strain is increased. More material-specific applications included metallic powders (DeLo et al., 1999), detergents (Samimi et al., 2005), magnetic materials (Kitahara et al., 2000) and pharmaceutical powders (Hassanpour and Ghadiri, 2004).

DEM, however, normally uses a simplified contact interaction. For detailed contact laws and incorporation of arbitrary material properties for the particles, the response of individual particles was modelled using the finite element method (Ransing et al., 2000, Lewis et al., 2005). This treatment was termed "multiparticle finite element model" (MPFEM) by Procopio at Zavaliangos (2005), and could be used near full density. Similar to the DEM simulations of Redanz and Fleck (2001), the MPFEM was used to investigate the effect of friction between particles on the macroscopic yield response of the aggregates. Common features with the micromechanical models and continuum models were identified.

3.2 Continuum models

The powder material can also be regarded as a mechanical continuum. This assumption is considered valid if the size of the powder particles is several orders of magnitude smaller than the size of the die or final compact. Thus representative volumes of sufficiently large numbers of particles can be defined which adequately represent the macroscopic behaviour of the material. Using this approach, the details of the motion, deformation and interaction of a particle with its environment are all included in macroscopic constitutive laws. Within the continuum mechanics framework, powder compaction can be modelled similarly as a large deformation plasticity problem. Such a problem lends itself to specific methods such as finite element analysis, which is used to solve the balance laws (conservation of mass, momentum and energy) and constitutive laws (stressstrain and friction laws). For powder compaction, knowledge of the following factors is necessary:

- constitutive law, which describes the deformation of a volume of powder under the loads applied during compaction
- 2. friction interaction between powder and tooling
- 3. geometry of die and punches
- 4. pressing schedule, i.e. sequence of punch motions

5. initial conditions that relate to the state of the powder in the die after die fill

The constitutive model and friction are fundamental ingredients that require detailed characterisation and formulation, and are discussed in Sections 4 and 5, respectively. The geometry and pressing schedule are process-specific parameters which depend on the application. The initial condition of the powder in the die is the final outcome of the die fill process that precedes compaction. The details of the die fill process have been studied extensively by Cocks and coworkers (e.g. Wu and Cocks, 2006) and are outside the scope of the current review.

Once the problem is formulated in terms of the 5 factors above, the finite element method can be used to predict the compact microstructure and calculate the tool loading and deformation. Sensitivity studies of all intervening factors and material parameters can be carried out. Finite element modelling results can be used to optimise the formulation of the powder and the selection of process parameters for a given performance criterion. This approach is general for all classes of powders and can be used in formulation design and process development across the powderforming industries.

4. Constitutive Models for Powder Compaction

4.1 Phenomenological models

The fundamental aspects of the mechanics of powder compaction from a constitutive modelling point of view have been discussed by Cooks (2007).

Review papers on constitutive models for metallic, ceramic and pharmaceutical powders have been presented in the literature (Trasorras et al., 1998; Aydin et al., 1997; Cunningham et al. 2004; Kremer and Hancock, 2006). Early empirical models assume quadratic yield surfaces (Shima and Oyane, 1976; Kuhn and Downey, 1973) where the state of the material is described using density. These models were developed using data for sintered materials and assume the same strength in tension and compression for the compact. Experiments (Brown and Weber, 1998) have shown, however, that the properties of green compacts are considerably different.

At the two ends of the density spectrum (or low and high porosity), the behaviour of powders can be described as similar to that of soils and mildly voided metals, respectively. The models developed for these applications are discussed below.

The model introduced by Gurson (1977) on the micromechanical principles for void nucleation



and growth during plastic failure was modified by Tvergaard (1981) and became known as the porous plasticity model. This model is also symmetric with respect to the origin, and therefore predicts the same strength in tension and compression. To overcome these difficulties, constitutive models developed in the field of rock and soil mechanics such as the Cam Clay (Schoefield and Wroth, 1968), Drucker-Prager cap (Drucker and Prager, 1952) or the model proposed by Di-Maggio and Sandler (1971) have also been adapted to model powder compaction.

The experimental methods for model calibration are also derived from the soil mechanics literature. The methods are discussed alongside the Drucker-Prager cap model as this is a phenomenological model which makes use of well-known material parameters such as cohesion and the internal friction angle. The yield surface is described by a shear failure line and a compaction surface, as illustrated in Fig. 1 in the effective stress (σ_e) and hydrostatic stress (σ_m) space. The shear failure line is defined by cohesion (c) and the internal friction angle (β) , which are determined using simple tests such as uniaxial tension and compression, simple shear and diametrical compression. Triaxial tests, where a cylindrical sample is subject to a confining pressure and superimposed axial load, can be used to characterise the failure line for hydrostatic stress states that are greater than during uniaxial compression. Triaxial testing also originated from rock and soil mechanics and has been used to determine the flow (Eelkman Rooda and Haaker, 1977) and compaction properties (Doremus et al., 1995; Shima et al., 1997; Akisanya et al., 1997; Kamath and Puri, 1997; Sinka et al., 2000; Zeuch et al., 2001; Schneider and Cocks, 2002; Lee and Kim, 2007) of a wide range of powder materials.

The compaction (cap) surface is described using an ellipse which is determined by 2 parameters and therefore requires 2 points in stress space, which can be obtained using various types of triaxial tests as illustrated in **Fig. 1**. A more pragmatic approach (exemplified in Section 6.1) is represented by the use of a die with radial stress measurement capability. However, in this case the response of the powder also includes the effect of friction between powder and die wall.

The Cam-Clay and Drucker-Prager cap models became widely adopted. Comparative studies from 5 research centres (PM Modnet Computer Modelling Group, 2002; Cocks et al. 2007) on modelling the compaction of the same multilevel part were benchmarked against experimental data from a press (Kergadallan et al., 1997). These efforts highlighted the sensitivity of the output with respect to friction, fill density and constitutive models. The predictions in terms of density distributions were broadly consistent across the case studies. This is not surprising: Fig. 1b illustrates yield surfaces for 3 models (porous plasticity, Cam-Clay and Drucker-Prager cap) calibrated using the same set of closed-die compaction data. In the vicinity of the closed-die compaction point, the models are almost identical, therefore the



Fig. 1 Constitutive models for powder compaction, a) experimental procedures for determining Drucker-Prager cap model parameters. Failure line: (1) uniaxial tension, (2) simple shear, (3) diametrical compression, (4) uniaxial compression. Compaction surface: (5) triaxial testing: 5A consolidated triaxial test, 5B simulated closed-die compaction, 5C radial loading in stress space, 5D isostatic test; (6) instrumented die compaction. b) Yield surfaces for microcrystalline cellulose using various models calibrated on a closed-die compaction experiment: C-C Cam-Clay, D-P Drucker-Prager cap, P-P porous plasticity. The closed-die compaction trajectory is indicated with a dotted line.



predictions would be similar. Differences however, would be obtained for high shear stress states, i.e. around the transition corners in multilevel parts.

The models developed for soil behaviour have been modified over the years in terms of the shape of the shear failure line, the shape of the cap surface and the flow rule. 3D simulations of the compaction of complex parts (Coube and Riedel, 2000; Khoei et al., 2007) are becoming common.

In the models above, density is used almost exclusively as the state variable. The main reason is that metal powder component manufacturers are interested in high density (to maximise mechanical performance) and low density variations in the green parts. However, triaxial test results on metallic powders, hard metals and ceramics (Sinka et al., 2001) suggest that density may not be the most appropriate state variable to describe the compaction response of powders. It is therefore instructive to critically examine the structure of the constitutive models in order to identify a simple, single state variable model that is able to describe the material response when subject to loading paths similar to those encountered in industrial practice. An appropriate basis for evaluating the structure of constitutive models for compaction is represented by micromechanical models which are reviewed below.

4.2 Micromechanical models

The micromechanical model developed by Fleck et al. (1992) uses the upper bound plasticity theorem to determine the macroscopic response (i.e. yield surface) of a random array of particles. The particles are assumed to be rigid-plastic spheres. The contact between particles is frictionless and the contact strength in tension and compression is considered equal. Although the assumptions used in the micromechanical model greatly simplify the geometry and material properties of real powders, it is shown in Section 4.3 that the resulting models produce similar features to the compaction and failure surfaces of the Drucker-Prager cap model.

Early micromechanical models predict similar yield strength in tension and compression. By relaxing the underlying assumptions (Fleck, 1995), Fleck demonstrated that yield surfaces depend on the loading history, which cannot be captured by a single state variable such as density. The models were further developed to include other contact laws and different particle sizes and properties (Fleck et al., 1997). Yield surfaces predicted for isostatic, closeddie and pure shear deformation are presented in **Fig.**



Fig. 2 Normalised surface of constant complementary work predicted by micromechanical models and yield surfaces for (i) isostatic compaction, (ii) frictionless closed-die compaction and (iii) pure shear deformation. This figure was published in Mechanics of Materials, Vol. 39, Cocks A.C.F. and Sinka I.C., Constitutive Modelling of Powder Compaction – I. Theoretical Concepts, 392-403, Copyright Elsevier (2007).

2. The micromechanical model predictions were in broad agreement with the yield surfaces obtained by triaxial tests on monosized spherical copper particles (Akisanya et al., 1997; Schneider and Cocks, 2002). As illustrated in **Fig. 2**, micromechanical models suggest that for monotonically increasing loading paths, the yield surfaces present a vertex at the loading point. This is an important feature of the micromechanical models which have been used to develop alternative approaches for powder compaction as described in the following section.

4.3 Deformation theory for powder compaction

All models described above are developed using the incremental plasticity framework, which is based on the existence of a yield surface and a flow rule. The empirical models described in Section 4.1 assume prescribed yield surfaces (i.e. the Drucker-Prager cap model) which are not critically assessed and the experiments used to determine the material properties are not normally representative of the stress histories that occur in practice. The micromechanical models described in Section 4.2 are based on limiting assumptions. Indeed, for irregularly shaped powders, the yield surfaces determined experimentally can have completely different shapes (Schneider and Cocks, 2002). Also, yield surfaces presenting vertices present numerical difficulties.

Cocks and co-workers (Cocks, 2001; Cocks and

Sinka, 2007) examined whether it was possible to develop a simple, single state variable model that captured the material behaviour for loading histories experienced in practical die compaction operations. The micromechanical models were re-examined to consider an observation of Budiansky (1959) that for situations where the yield surfaces present vertices, the material response is not too sensitive to the loading path followed to achieve the terminal state. For such loading histories, it is appropriate to consider a deformation plasticity model. Using the extremum theorems of Ponter and Martin (Ponter and Martin, 1972), the material behaviour was described using a potential function expressed in terms of Kirchhoff stress. The strains can then be determined by differentiating the potential with respect to stress.

A normalised surface of constant complementary work predicted by the micromechanical models is presented in **Fig. 2**. This surface forms an envelope of the actual yield surfaces obtained along radial loading paths to the same terminal state. The theoretical framework for the deformation is presented elsewhere (Cocks and Sinka, 2007).

Triaxial tests were conducted to validate the model for commercial metal powders (Sinka and Cocks, 2007a). **Fig. 3** illustrates that it was possible to construct a consistent set of contours of constant complementary work done along radial loading paths in stress space. The underlying assumptions of the



Fig. 3 Contours of constant complementary work done (MJm³) per unit initial volume in Kirchhoff stress space. The data points represent stress states along radial loading paths in stress space and closed-die compaction, labelled CD. This figure was published in Mechanics of Materials, Vol. 39, Sinka I.C. and Cocks A.C.F., Constitutive Modelling of Powder Compaction – II. Evaluation of Material Data, 404-416, Copyright Elsevier (2007).



deformation plasticity model (path independence, normality) have also been verified experimentally. The detailed form of the constitutive model was developed (Sinka and Cocks, 2007a) to satisfy appropriate limit conditions when the material approaches full density. Triaxial tests for hard metals and ceramic powders (Sinka et al., 2001) suggested that the approach can be used for a wider range of materials. It is interesting to note that the shape of the potential surfaces in **Fig. 3** is very similar to the Drucker-Prager yield surfaces made of a shear failure line and a cap.

The simplicity of the deformation plasticity model allows practical die compaction processes to be analysed efficiently. However, the model does not capture the material response during unloading, ejection and post-compaction operations, which require detailed knowledge of the actual yield surfaces. To model unloading and ejection, it is necessary to change to an incremental plasticity framework in which the form of the yield surface at the end of compaction is determined from the plastic state determined from the deformation plasticity model (Sinka and Cocks, 2007b).

5. Friction Between Powder and Tooling

The friction interaction between powder and die wall plays an essential role in powder compaction because it leads to density variations, increased compression and ejection forces and die wear. In industrial practice, friction is reduced by admixing a lubricant to the powder blend or by pre-lubricating the die wall (i.e. by depositing a lubricant onto the die wall before die fill).

Friction is described by Coulomb's law, and a wide range of devices have been developed to characterise friction for various engineering applications. For powder pressing, two types of apparatus have gained acceptance: sliding piece-type devices and instrumented dies. Pavier and Doremus (1997) found that the coefficient of friction was 1.5 times higher when measured using an instrumented die than when determined using the sliding piece test. It was therefore accepted that the friction coefficient should be measured under conditions similar to those encountered during the process under investigation, i.e. die compaction.

For die compaction, dies instrumented with radial stress measuring devices have been developed (Ernst and Barnekow 1994; Pavier and Doremus, 1997; Mosbah et al., 1997). In this configuration, a cylindrical powder specimen is pressed such that one



of the punches is stationary. As friction opposes the sliding of the powder with respect to the die wall, the stress applied by the moving punch is larger than the stress applied by the stationary punch. The friction coefficient can be calculated from the axial stresses and the radial stress transmitted to the die wall (or contact pressure) using the method of differential slices attributed to Janssen in 1895 (Nedderman, 1992), which was developed for hopper and bunker design.

Constitutive models for friction can also be developed from first principles such as plasticity theory (Gearing et al., 2001), contact mechanics approaches or empirical studies (Adams et al., 1987). These models may be complex and/or restricted for certain densification or powder flow regimes.

Experimental studies indicate that friction depends on several factors including: contact pressure, local powder density, sliding velocity, sliding distance, temperature, and wall roughness. (Pavier and Doremus, 1997; Mallender et al., 1974; Ernst and Barnekow 1994; Mosbah et al., 1997; Wikman et al., 1997; Roure et al., 1999). In Section 6.2, we adopt the instrumented die method and present a number of case studies below where the friction coefficient is dependent on contact pressure and die wall condition.

6. Applications

In the preceding sections, we have reviewed a number of approaches that can be used for modelling powder compaction. The methodologies are general, i.e. are applicable to a wide range of powder materials such as metallic powders, ceramics, hard metals, magnets, detergents, pharmaceuticals, etc. For example, the discrete element approach captures particle rearrangement, inter-particle friction and allows complex contact laws to be implemented. Similarly, the continuum models are not dependent on the details of the compaction mechanisms of the particles (e.g. plastic flow at the contacts, particle rearrangement and particle breakage are not relevant when calibrating empirical models).

The micromechanical approach is based on the contact law between rigid-plastic spheres, where densification occurs by plastic deformation at the contacts between particles. This behaviour is characteristic to metallic powders; nevertheless, the methodology can be extended to brittle materials. More importantly, however, micromechanical models can present a framework for developing new constitutive theories (i.e. deformation plasticity) which can be generalised to suit any powder system.

In Sections 6.3-6.6, we present examples to illustrate the use of numerical models for powder compaction. A pragmatic calibration procedure for the constitutive law and friction is described in Sections 6.1-6.2 for a pharmaceutical powder. Examples 1 and 2 focus on the density distribution in simple and complex pharmaceutical tablets and illustrate generic issues that are relevant across other powder pressing industries. It is important that model predictions are validated; supporting experimental data are therefore presented when discussing modelling results.

Example 3 illustrates the use of the deformation plasticity model for two ceramic materials, while Example 4 discusses issues related to crack development in pharmaceutical tablets and multilevel metal powder components.

6.1 Experimental data for constitutive model calibration

The powder material used in Examples 1 and 2 is microcrystalline cellulose (Avicel PH102 manufactured by FMC Biopolymer), which is commonly used in pharmaceutical tablet formulation. The powder is made of irregular porous particles. The bulk density of the powders is around 300kgm⁻³, while the full density is 1520kgm⁻³. The average particle size is 100μ m.

We adopt a modified Drucker-Prager cap model where the elastic and plastic model parameters are expressed as functions of relative density. The general methodologies for determining the parameters of the model are well established (see Section 4.1). Below, we use a pragmatic method based on data generated using a die instrumented with radial stress sensors. A detailed description of the experimental procedures is given elsewhere (Sinka et al., 2003). The instrumented die approach has been adopted in industrial practice as a simple and efficient way to characterise both constitutive response and friction.

The elastic and plastic model parameters are presented in **Fig. 4**. Assuming isotropic linear elasticity, Young's modulus and Poisson's ratio can be determined from the unloading curve after the material is compressed to a given density. In order to minimise the effect of friction on the constitutive response, the die was pre-lubricated before each compaction experiment. The evolution of Young's modulus and Poisson's ratio as a function of relative density are given in **Fig.s 4a** and **4b**.

The Drucker-Prager cap model is composed of a shear failure line and a cap surface as described in Section 4.1. The shear failure line is characterised





Fig. 4 Constitutive model data for microcrystalline cellulose using relative density as a state variable; a) Young's modulus, b) Poisson's ratio, c) families of Drucker-Prager yield surfaces. The labels indicate relative density. This figure was published in Powder Technology, Vol. 133, Sinka I.C., Cunningham J.C. and Zavaliangos A., The effect of wall friction in the compaction of pharmaceutical tablets with curved faces: A validation study of the Drucker-Prager Cap model, 33-43, Copyright Elsevier (2003).

by cohesion and the internal friction angle, and can be determined using a number of simple tests, as illustrated in **Fig. 1a**. We use diametrical compression and uniaxial compression of cylindrical compacts.

The cap surface is described by an ellipse which is also characterised by two parameters, the size and shape. During compaction in an instrumented die, the stress state (axial and radial stresses) and the strain increment direction (zero radial strain) at the loading point are known. The parameters of the cap surface are determined using the normality rule. Families of Drucker-Prager cap surfaces with increasing relative density are presented in **Fig. 4c**, which illustrates the evolution of the size and shape of yield surfaces during densification. The stress path corresponding to closed-die compaction is also indicated in **Fig. 4c**.

6.2 Experimental data for friction between powder and die wall

The friction coefficient between powder and die wall is also measured using a die instrumented with radial stress sensors. The friction coefficient was calculated using the method of differential slices (see Section 5). For microcrystalline cellulose, it was found that the friction coefficient was dependent on contact pressure. Starting from high values at the early stages of compaction, the friction coefficient asymptotes to a lower value as the contact pressure (and density) is increased. **Fig. 5** illustrates the variation of friction coefficient for two cases:



Fig. 5 Coefficient of friction between powder and die wall. This figure was published in Powder Technology, Vol. 133, Sinka I.C., Cunningham J.C. and Zavaliangos A., The effect of wall friction in the compaction of pharmaceutical tablets with curved faces: A validation study of the Drucker-Prager Cap model, 33-43, Copyright Elsevier (2003).



- 1. clean die wall condition, where the die wall is degreased prior to compaction,
- 2. lubricated die wall condition, where a tablet of pure lubricant powder (magnesium stearate) is compressed prior to the experiment.

The relevance of high and low friction between powder and die wall (and powder and punches) is illustrated in Example 1.

6.3 Example 1: density distribution in curvedface pharmaceutical tablets

The importance of density variations in powder compacts has been highlighted since the early 1900s, e.g. Train (1957). Experimental results by Macleod and Marshall (1977) have highlighted the importance of the friction between powder and die wall. The effect of friction on density variations in pharmaceutical tablets is discussed below.

For pharmaceutical tablets, the internal density distribution is important because it affects the local material properties, which in turn can influence the bioavailability of the drug and the mechanical properties of the tablets. The importance of numerical modelling was recognised by Khattat and Hassani (1987). The other contributing factors (material behaviour, geometry, loading sequence and initial conditions of the powder after die fill) have also been identified.

Before discussing the effect of density distribution on tablet strength and breakage, it is instructive to review the methods developed for measuring density distributions as these methods form the experimental basis for model validation. Earlier methods were based on differential machining, hardness tests or X-ray images of lead particles embedded in the powder and surface topography (Train and Hersey 1960; Kandeil and De Malherbe 1977; Sixsmith and McCluskey 1981; Charlton and Newton 1985; Ozkan and Briscoe 1996; Sinka et al., 2003; Eiliazadeh et al., 2004). More modern non-destructive techniques (Lannutti 1997) including X-ray CT and NMRI were also applied to characterise density distributions (Sinka et al., 2004a; Djemai and Sinka, 2006) and defects (Wu et al., 2005) in pharmaceutical tablets.

In the first example, we examine the density distributions in curved-face tablets (diameter 25 mm, curvature radius 19.82 mm) compressed using clean and pre-lubricated tooling, which give high and low friction coefficients between powder and tooling, respectively.

Fig. 6 illustrates the density variations in two tablets compressed to the same average relative density. The experimental density contours (**Fig. 6a,b**) were determined using indentation hardness mapping (Sinka et al., 2005). The numerical modelling was carried out by implementing the density-dependent Drucker-Prager model presented in Section 6.1 in the finite element package Abaqus Standard (Hibbit, Karlsson and Sorensen, 1988).



Fig. 6 Relative density distribution in 25-mm diameter curved-face tablets. Experimental data for tablet compressed using a) clean and b) lubricated tooling. Numerical results for c) high and d) low friction. This figure was published in Powder Technology, Vol. 133, Sinka I.C., Cunningham J.C. and Zavaliangos A., The effect of wall friction in the compaction of pharmaceutical tablets with curved faces: A validation study of the Drucker-Prager Cap model, 33-43, Copyright Elsevier (2003).



The low-friction (pre-lubricated die) case was modelled using variable friction data as presented in **Fig. 5**. For the high-friction case, the friction coefficient was taken as 0.5 (constant). The bottom punch was maintained stationary during the compression. The die was filled by hand with attention paid to obtaining a uniform initial packing in the powder bed.

The relative density distributions predicted by the model for the high- and low-friction cases are presented in **Fig. 6c** and **d**, which are in good agreement with the experimental density maps.

Fig. 6 illustrates that it is possible to make two identical tablets in terms of shape, weight and material which have different microstructures depending on the friction conditions employed. The numerical modelling provides insight into the powder movement during compaction, which depends on friction and punch geometry. High friction hinders the relative sliding of the powder into the top punch cavity as the top punch makes progressive contact with the initially flat top surface of the powder. Although the powder movement is relatively complex, the high-friction case can be described as pressing columns of powders to different heights. Higher density regions therefore develop around the outer edge of the tablet due to the curvature of the punch.

If the friction coefficient is reduced (i.e. by prelubricating the die and punches before compaction), then the relative sliding of the powder with respect to the punch face is facilitated. This results in a density distribution that is the inverse image of that for high friction, i.e. the density is highest in the middle of the tablet.

A practical question is: what is the effect of density distributions on tablet strength, friability, disintegration and failure behaviour (if any)? **Fig. 7a** presents diametrical compression experiments for tablets compacted to different densities using clean and prelubricated tooling, and illustrates that the strength is not unique. **Fig. 7b** presents the failure modes of the tablet during diametrical compression experiments, illustrating that the failure mode is dependent on the internal tablet structure (Sinka et al. 2004b).

Somewhat similar density patterns have been induced in tablets of a more representative size (8.7 mm diameter, punch curvature radius 8.03 mm). A compaction force of 3 kN was applied for compressing two microcrystalline cellulose tablets using clean and pre-lubricated tooling. The relative densities were 0.724 and 0.751, respectively. It can be observed that the same compaction force produces higher average density if the friction is low. **Fig. 8** illustrates the density distributions obtained experimentally using the NMRI technique (Djemai and Sinka, 2006) for these two tablets and the corresponding numerical modelling studies. The density patterns are consis-



Fig. 7 Effect of microstructure on tablet behaviour; a) break force in diametrical compression experiments, b) failure mode for tablet compacted in clean and pre-lubricated dies. This figure was published in Journal of Pharmaceutical Sciences, Vol. 93, Sinka I.C., Cunningham J.C. and Zavaliangos A., Analysis of tablet compaction. Part 2 – Finite element analysis of density distribution in convex tablets, 2040-2052, Copyright Wiley-Liss, Inc. (2004).





Fig. 8 Relative density distribution in 8.7-mm-diameter curved-face tablets. NMRI data for tablet compressed using a) clean and b) lubricated tooling. Numerical results for c) high and d) low friction.

tent with the observations for the 25-mm-diameter tablets discussed above. High friction results in highdensity regions around the outer circumference, whereas low friction facilitates more complex radial movement of the powder, resulting in a high-density region which has an X-shaped vertical cross-section. It can be speculated that this pattern could promote a cone-shaped crack formation; this is discussed in Example 4.

The density distribution in the 8.7-mm-diameter tablets presents features that are distinct from **Fig. 6**. For the high-friction case, the density around the upper circumference is higher than around the lower circumference. This pattern comes about from the punch motion: the lower punch is stationary. The effect is less pronounced for the 25-mm-diameter tablets where the initial height to diameter aspect ratio is lower. Further effects of density distribution on the strength, friability, abrasion and disintegration behaviour of tablets are discussed elsewhere (Sinka et al., 2007).

It is important to note that the density distribution and its effects on tablet properties depends on all 5 factors discussed in Section 3.2. The examples above highlight that generalisations are not always appropriate and that each situation should be considered individually.

6.4 Example 2: bilayer tablets and compression coating

In this section we discuss modelling issues for more complex tablet systems: bilayer tablets and compression coating. These dosage forms were developed for a number of reasons such as to co-administer two different drugs in the same dosage form, release the same drug at different rates or to modify the release property of a formulation.

The manufacturing process of bi-layer tablets requires special rotary presses (Pitt and Sinka, 2007) where the first layer is fed into the die and partially pressed, but not ejected from the die. Then the second layer is fed followed by compaction and ejection. This example focuses on the density distributions in the powder at various stages of the compaction process.

Numerical analysis has been carried out for a 20-mm-diameter bilayer tablet with flat faces. For both layers, microcrystalline cellulose was used, starting from an initial relative density of 0.3. The first layer was compressed to 10 kN and the second layer to 40 kN as indicated in **Fig. 9**. The bottom punch was maintained stationary during the entire compression schedule.

Fig. 10 presents snapshots of the density variations at various stages during the process:

• Fig. 10a corresponds to the end of compression of the first layer. At this stage, we obtain a density





Fig. 9 Compression schedule for the bilayer tablet. This figure was published in Chapter 14: Modelling die compaction in the pharmaceutical industry, Sinka I.C. and Cocks A.C.F. (pp. 225-244) in: Modelling of Powder Die Compaction. Series: Engineering Materials and Processes Eds. P.R. Brewin, O. Coube, P. Doremus and J.H. Tweed. Copyright Springer (2007). With kind permission of Springer Science and Business Media.

distribution that is specific to a flat-faced tablet compressed such that the lower punch is stationary. In the present example, in order to accentuate frictional effects, the friction coefficient was set to 0.5 (constant), which is a relatively high value, specific to clean (unlubricated) die wall conditions.

- After compression of the first layer, the powder for the second layer is delivered into the die, Fig. 10b. The initial density of the second layer is uniform (this assumption is used in all examples discussed).
- **Fig. 10c** is a snapshot of the density distribution during bilayer compaction. At this stage, densification occurs in the second (top) layer only and the density distribution in the first layer has not yet changed. Concurrent densification of both layers occurs only after the second layer reaches a similar state as the first layer, which occurs approximately when the compaction force reaches the value used to compress the first layer (10 kN in this case).
- Density distribution at the end of compression of the bilayer tablet (40 kN force). The mismatch at the die wall gradually disappears towards the end of the bilayer compaction. In the final stage it is also interesting to note that the interface between the two layers becomes distorted. The top surface of the first layer becomes concave and the model predicts a variation in height of 0.5 mm for the input data used in the simulation. The prediction of face curvature can be verified experimentally by performing a tensile test, which results in separation at the interface.

The interface properties are important as they affect the strength and properties of the bilayer tablet.



Fig. 10 Density distribution in bilayer tablets during compaction, a) end of first layer compaction, b) after the second layer was filled, c) snapshot during bilayer compression, d) end of bilayer compression.





Fig. 11 Density distribution in a compression-coated tablet system, a) initial relative density 0.6955 and 0.3536 in core and coating, respectively, b) density distribution in the coating after compression, c) density distribution in core after compression. This figure was published in Chapter 14: Modelling die compaction in the pharmaceutical industry, Sinka I.C. and Cocks A.C.F. (pp. 225-244) in: Modelling of Powder Die Compaction. Series: Engineering Materials and Processes Eds. P.R. Brewin, O. Coube, P. Doremus and J.H. Tweed. Copyright Springer (2007). With kind permission of Springer Science and Business Media.

In the above analysis, the interaction between the two layers was described as frictional sliding using a high friction coefficient (0.5). In practice, an adhesive normal interaction also develops between the layers. A comprehensive analysis of the stress states during compression, unloading and ejection requires more detailed experimental characterisation of the interlayer strength as well as numerical implementation. The problem of layered compacts has relevance to other industries and products as well, e.g. detergents.

A particular case of bilayer compression is represented by the so-called compression coating process, which involves enclosing a smaller tablet (core) into a larger one (coating). In this case, a partially compressed tablet (formulation 1) is enclosed into a powder bed (formulation 2) as illustrated in **Fig. 11a**. After compression, tablet 1 is completely enclosed in tablet 2. Complex tablet systems can be designed using variations of layered and compression-coated systems. Tri-layer tablets and three nesting tablet systems have been developed.

The compression of a microcrystalline cellulose core (initial relative density 0.6955) in a bed of the same material (initial relative density 0.3536) is illustrated in **Fig. 11**. At the end of compression the material in the core reaches near full density. The material in the core is compressed to near full density. However, the regions around the vertical edges of the coating only reach a relative density of the order of 0.75-0.8. This illustrates that the chosen geometry is not optimal. Lower-density areas implies lower strength, which makes fractures possible. Commercial core-coated tablets have curved faces that facilitate powder movement around the core. Detailed analysis of all stages of the problem can identify the conditions which are favourable for defect formation during compression, unloading, ejection, or subsequent handling. Thus numerical modelling can be used to optimise the geometry and initial pre-compression of the core as well as material properties and process parameters. A more detailed discussion on modelling bilayer tablets and compression coating is given elsewhere (Sinka and Cocks, 2007c).

6.5 Example 3: deformation plasticity model

The deformation plasticity framework is summarised in Section 4.3. **Fig. 3** illustrates that contours of constant complementary work done per unit initial volume could be constructed based on triaxial test data. A detailed form of a suitable potential function was proposed (Sinka and Cocks, 2007a) for steel powders. However, this form is complex given that





Fig. 12 Radial and axial stress during die compaction of calcium phosphate.

the contours in **Fig. 3** are not self-similar. Ceramic and hard metal powders exhibit a simpler behaviour. For this class of powders the contours of constant complementary work are self-similar (Sinka and Cocks, 2007b), which could be described using a simple potential function that can be implemented in the Abaqus finite element package.

Fig. 12 illustrates the radial and axial stress evolution during die compaction of calcium phosphate. This material is a ceramic-like powder and is used as an excipient in pharmaceutical tablet compaction.

The experimental data were used to calibrate the deformation plasticity model (Sinka and Cocks, 2007b). Using the same set of data, a Drucker-Prager cap model was also calibrated. **Fig. 12** presents the radial and axial stress traces for the experimental data, the prediction of the deformation plasticity model and the prediction of the Drucker-Prager cap model for die compaction. The traces overlap, which is not surprising as both models were calibrated using the same data. **Fig. 12** nevertheless suggests that the implementation of both deformation and incremental plasticity models is correct.

The deformation plasticity model was calibrated also for alumina powder. **Fig. 13** illustrates the application of the deformation plasticity model to the compaction of a ring with an outside diameter of 30 mm and an inside diameter of 10 mm. The tooling is composed of a die, a central rod, and upper and lower punches, which are modelled as rigid surfaces. For this geometry, any density variations come about from the friction interaction between powder and tooling (we used a friction coefficient of 0.1 for all contact surfaces), and the pressing sequence (here the lower punch was prescribed stationary) as the initial relative density (0.35) was assumed constant.

Snapshots of the evolution of internal density distribution during compaction are presented in **Fig. 13** in a vertical cross-section of the compact. Density variations in ceramic compacts are important as they influence the shrinkage behaviour during sintering.

6.6 Example 4: crack development

In the final set of examples, we discuss the important issue of crack formation, which is common across the powder pressing industries. Wu et al. (2005) employed X-ray CT to identify crack formation in round tablets with flat faces made using lactose powder, which is used as an excipient in pharmaceutical tablet formulation.

Capping (or crack formation) is a common defect in pharmaceutical formulations of low mechanical strength and consists of a cone-shaped failure as illustrated in **Fig. 14**. Numerical modelling studies conducted by Wu et al. (2005) using the Drucker-Prager



Fig. 13 Density distribution during die compaction of an alumina ring.





Fig. 14 Crack development in pharmaceutical tablets, vertical cross-section shown. This figure was published in Powder Technology (In Press, Corrected Proof), Wu C.-Y, Hancock B.C., Mills A., Bentham A.C., Best S.M. and Elliott J.A., Numerical and experimental investigation of capping mechanisms during pharmaceutical tablet compaction, Copyright Elsevier (2006).

cap model demonstrated that capping occurs due to the development of intensive shear bands during unloading. **Fig. 14** illustrates the shear stresses during unloading alongside the crack identified by X-ray CT.

Further finite element studies by Wu et al. (2006) examined the effect of powder die-wall friction and pressing sequence, and concluded that capping could not be eliminated by operating upon these factors.

Coube and Riedel (2000) examined the causes of crack formation in multilevel parts compressed from metal powders. They employed a modified Drucker-Prager model where the constitutive parameters were expressed as functions of density. The density distribution in the compact in **Fig. 15** was in good agreement with experimental results (Kergadallan et al., 1997). This compact was also used in the benchmark study summarised in Section 4.1.



Fig. 15 Crack development in multilevel parts made of metallic powder. This figure was published in Powder Metallurgy, Vol. 43, Coube O. and Riedel H., Numerical simulation of metal powder die compaction with special consideration to cracking, 123-131, Copyright Maney Publishing (2000).

Coube and Riedel (2000) noted that the models employed are capable of accurately predicting the density distributions in green parts. While such simulations can be indicative of the risk of crack formation, it cannot definitively predict whether or not a crack would indeed develop.

7. Final Remarks

Powder compaction is a complex engineering process. The material undergoes a transformation from a loose powder state to a dense compact, thus physics-based constitutive models are inherently complicated. Similarly, the friction between powder and die wall requires appropriate description. Complex multilevel parts that are typical to powder metallurgy require expensive tooling and an appropriate selection of punch motions to avoid crack formation during powder transfer, compaction, unloading and ejection from the die. Early developments in powder compaction modelling were motivated by replacing empiricism and trial and error in tool design and pressing sequence set-up.

The development, calibration, implementation and validation of constitutive models has matured over the last decade. Models today are capable of predicting density distributions and tool loading with sufficient accuracy for practical use. A number of outstanding issues, however, remain. As described in Section 6.6, current models can give only an indication of crack formation. Also, the failure patterns in **Fig. 7** cannot be predicted using isotropic models.

Crack formation in pharmaceutical tablets is further complicated by the high compression rate used in industrial tableting. Pharmaceutical powders are light, having a true density in the region of 1.5-2.5 kgm⁻³. In addition, their initial relative density



(0.3-0.4) is also significantly lower than that of metallic or ceramic powders. The compression operation can take as little as a few milliseconds. Therefore, airpowder interaction can become important and the air pressure build-up within the pore space can be of a magnitude that is comparable with the local strength of the material. At a more fundamental level, a better understanding of the processes requires insight into complex phenomena occurring at various length scales from particle contacts to product. Multi-scale modelling approaches are therefore currently the subject of intense research.

At this moment in time, compaction models cannot predict each and every product property or performance measure that has practical relevance. Nevertheless, the models offer unique insights into the relationships between material properties and process parameters. Significant progress has also been made in establishing relationships between material and process parameters. The examples above illustrate that numerical models are able to offer a rational basis for and a practical tool to guiding the optimisation effort in product, process and tool design in powder compaction.

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Author's short biography



Dr. Csaba Sinka

Dr. Csaba Sinka was appointed in 2006 to a Lectureship in Mechanics of Materials in the Department of Engineering at the University of Leicester. Previously he was a Research Fellow at Merck Sharp and Dohme where he worked in formulation design and process development of pharmaceutical tablets.

He has as a background in mechanical, mineral and process engineering and has worked in academic and industrial research in the UK and the US. His main research interest is in powder technology and particulate engineering and has developed experimental and numerical modelling techniques to address practical problems involving powder flow and compaction with applications to powder metallurgy, ceramics, hard metals and the pharmaceutical industry.

His current research is in the following 3 areas: the flow of powders in constrained cavities (where air pressure build-up plays an important role) with application to industrial die fill; multi-scale modelling of particle-particle interactions; and modelling the biodegradation of polymeric materials with application to orthopaedic fixation devices and controlled release tablets.



Heat Transfer Intensification Using Nanofluids[†]

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Abstract

This paper summarises some of our recent work on the heat transfer of nanofluids (dilute liquid suspensions of nanoparticles). It covers heat conduction, convective heat transfer under both natural and forced flow conditions, and boiling heat transfer in the nucleate regime. The results show that, despite considerable data scattering, the presence of nanoparticles enhances thermal conduction under macroscopically static conditions mainly due to nanoparticle structuring / networking. The natural convective heat transfer coefficient is observed to decrease systematically with increasing nanoparticle concentration, and the deterioration is partially attributed to the high viscosity of nanofluids. However, either enhancement or deterioration of convective heat transfer is observed under the forced flow conditions and particle migration is suggested to be an important mechanism. The results also show that the boiling heat transfer is enhanced in the nucleate regime for both alumina and titania nanofluids, and the enhancement is more sensitive to the concentration change for TiO₂ nanofluids. It is concluded that there is still some way to go before we can tailor-make nanofluids for any targeted applications.

Keywords: Nanofluids, Thermal conduction, Natural convective heat transfer, Forced convective heat transfer, Boiling heat transfer, Mechanisms

1. Introduction

Nanofluids are dilute liquid suspensions of nanoparticles with at least one critical dimension smaller than ~100nm. Much attention has been paid in the past decade to this new type of composite material because of its enhanced properties and behaviour associated with heat transfer (Masuda et al. 1993; Choi 1995), mass transfer (Krishnamurthy et al. 2006, Olle et al. 2006), wetting and spreading (Wasan and Nikolov 2003) and antimicrobial activities (Zhang L et a. 2007), and the number of publications related

* Corresponding author TEL: +44 113 343 2747; E-mail: y.ding@leeds.ac.uk http://www.engineering.leeds.ac.uk/ipse/ to nanofluids increases in an exponential manner. The enhanced thermal behaviour of nanofluids could provide a basis for an enormous innovation for heat transfer intensification, which is of major importance to a number of industrial sectors including transportation, power generation, micro-manufacturing, thermal therapy for cancer treatment, chemical and metallurgical sectors, as well as heating, cooling, ventilation and air-conditioning. Nanofluids are also important for the production of nanostructured materials (Kinloch et al. 2002), for the engineering of complex fluids (Tohver et al. 2001), as well as for cleaning oil from surfaces due to their excellent wetting and spreading behaviour (Wasan & Nikolov 2003).

Despite considerable research effort and significant progress in the past decade, our fundamental understanding of nanofluids is limited. This is indeed reflected in the significant scattering / disagreement of published data and less convincing arguments in interpreting the data (see Sections 2-4). It is fair to

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say that there is a long way to go before we can actually tailor-make nanofluids for targeted applications. This paper aims to provide a brief overview of the thermal properties and behaviour of nanofluids. The focus will be on our own work on conduction, convection and phase change heat transfer of nanofluids, though a brief review of the literature is also carried out where appropriate. Discussions will be made on possible mechanisms of heat transfer enhancement. Formulation of nanofluids and the flow behaviour of nanofluids will not be included. Interested parties are referred to recent publications by, for example, Kwak and Kim (2005), Prasher et al. (2006a) and Ding et al. (2007).

The paper is organised in the following manner. Section 2 presents the work on the thermal conduction of nanofluids under macroscopically static conditions. Section 3 is devoted to the heat transfer of nanofluids under forced and natural convection conditions. Section 4 will discuss boiling (phase change) heat transfer. Finally, concluding remarks are made in Section 5.

2. Thermal Conductivity of Nanofluids

The thermal conductivity of nanofluids has dominated the literature in the past decade, though this pattern has changed slightly over the last few years; see Keblinski et al. (2005), Das et al. (2006) and Wang and Mujumdar (2007) for recent reviews. Note that the term 'thermal conductivity' refers to the 'effective thermal conductivity', as nanofluids are twophase mixtures. For simplicity, we shall not differentiate the two terms in the paper.

2.1 Experimental data

The published data of the thermal conductivity of nanofluids are mostly obtained at room temperature with two methods, namely the hot-wire method and the conventional heat conduction cell method (Choi 1996; Lee et al. 1999; Eastman et al. 2001; Choi et al. 2001; Wen and Ding 2004a). There are also a few recent reports on the measurements using the $3-\omega$ method (Yang and Han 2006). The hot-wire method is well known and will not be described here. The $3-\omega$ method is relatively new and accurate, and uses a metal wire suspended in nanofluids. The wire acts as both a heater and a thermometer. A sinusoidal current at frequency ω is passed through the metal wire and generates a heat wave at frequency 2ω . The temperature rise at frequency 2ω in the metal wire can be deduced by the voltage component at frequency

 3ω . The thermal conductivity of the fluid is determined by the slope of the 2ω temperature rise of the metal wire.

Fig. 1 summarises the room temperature data from our own work (Wen and Ding 2004a, 2004b, 2005a, 2005b, 2006; Ding et al. 2006; He et al. 2007) and those reported in the literature (Lee et al. 1999; Eastman et al. 2001; Choi et al. 2001; Xie et al. 2002a & 2002b; Biercuk et al. 2002; Das et al. 2003a; Patel et al. 2003; Kumar et al. 2004; Assael et al. 2004; Zhang X. et al. 2007). The data shown in Fig. 1 include aqueous, ethylene glycol, minerals oil and polymerbased composite materials and are classified according to the material type of nanoparticles. One can see a significant degree of data scattering. In spite of the scatter, the presence of nanoparticles in fluids can substantially enhance the thermal conductivity and the extent of enhancement depends on the nanoparticle material type and volume fraction.

Note that the particle size is not included in Fig. 1. The main reason is that almost all publications only give the primary size of nanoparticles obtained by electron microscopes. It is well known that nanoparticles are prone to agglomerating and/or aggregating, and, as will be discussed later, it is the nanoparticle structuring that gives rise to the thermal conduction enhancement. Nanoparticles used in our own work include multi-walled carbon nanotubes supplied by Prof W. Fei of Tsinghua University, China (20-60nm in diameter, a few micrometres long), alumina purchased from Nanophase Technologies, USA (primary particle diameter 27-56 nm, but they are in the aggregate form with a diameter of ~150nm), and titania purchased from Degussa, Germany (primary particles ~25nm in diameter, they are in aggregate form with a size ranging from 95 - 210nm depending on the processing method). Except where otherwise mentioned, titania aggregates with an average size of 120nm are used in this work.

An inspection of **Fig. 1** suggests that the data points can be approximately divided into two groups separated by a demarcation band. The data points on the left-hand side of the band are for nanofluids made of metal nanoparticles and carbon nanotubes, whereas those on the right-hand side of the band are for nanofluids made of metal oxide and carbide nanoparticles. The width of the band represents overlapping between the two groups. Broadly speaking, the demarcation band seems to indicate that nanofluids made with high thermally conductive materials give a higher effective thermal conductivity. There are, however, deviations within each of the two re-





Fig. 1 Thermal conductivity of nanofluids: data taken from Lee et al. (1999), Eastman et al. (2001), Choi et al. (2001), Xie et al. (2002a & 2002b), Biercuk et al. (2002), Das et al. (2003a), Patel et al. (2003), Kumar et al. (2004), Wen and Ding (2004a, 2004b, 2005a, 2005b, 2006), Assael et al. (2004), Ding et al. (2006), He et al. (2007) and Zhang X et al. (2007).

gions separated by the band. For example, at room temperature, the thermal conductivities of gold and copper are 317 and 401 W/K.m, respectively, whereas the thermal conductivity of carbon nanotubes is observed to be between 3000 and 6000 W/K.m (Kim et al. 2001; Berber et al. 2000). The sequence of the three materials as shown in the left-hand side of band in **Fig. 1** is gold, carbon nanotubes and copper. On the other hand, the thermal conductivities of CuO, alumina and SiC at room temperature are 20, 40 and 120 W/K.m, respectively. **Fig. 1** shows that copper oxide nanofluids give the highest enhancement and little difference is seen between SiC and alumina nanofluids.

The experimental data shown in Fig. 1 are compared with various macroscopic models proposed for suspensions and composite materials as listed in Table 1. These models were developed based on the socalled effective medium theory, which has been detailed by Choy (1999). The models have been shown to be applicable under various conditions as indicated in the last column of Table 1. It has been shown that, for spherical particles, all the models give a predicted line that is slightly lower than the lower bound of the demarcation band, and there is a very small difference between these models within the range of particle concentration as shown in Fig. 1. This indicates that the conventional way of using macroscopic models gives an underprediction for most nanofluids, particularly for Au, Cu and CuO nanofluids. For carbon nanotube nanofluids, the models provide an overprediction, mainly because the interfacial resistance in not considered in the model; see Section 2.2 for more details.

2.2 Mechanisms of the thermal conduction enhancement

A number of mechanisms have been proposed for interpreting the experimentally observed thermal conduction enhancement including Brownian motion of nanoparticles, the interfacial ordering of liquid molecules on the surface of nanoparticles, the ballistic transport of energy carriers within individual nanoparticles and between nanoparticles that are in contact, as well as the nanoparticle structuring / networking (Keblinski et al. 2002; Wang et al. 2003; Nan et al. 2003; Yu and Choi 2003; Patel et al. 2003; Kumar et al. 2004; Shenogin et al. 2004a & 2004b; Prasher et al. 2006b). There has been much debate on these mechanisms over the past few years and the focus of debate has been on the role of Brownian motion (Kumar et al. 2004; Koo and Kleinstreuer 2005; Keblinski and Cahill 2005; Evans et al. 2006) and interfacial ordering (Yu and Choi 2003; Shenogin et al. 2004a & 2004b; Prasher et al. 2005). A brief discussion will be made in the following text on the two much-debated mechanisms.

The role of Brownian motion The Brownian motion of nanoparticles could contribute to the thermal conduction enhancement through two ways, a direct contribution due to motion of nanoparticles that transport heat, and an indirect contribution due to micro-convection of fluid surrounding individual nanoparticles. The direct contribution of Brownian motion has been



Model	Expressions	Remarks	
Maxwell (1873)		Spherical particles	
	$\frac{K_{eff}}{K} = \frac{K_s + 2K_L + 2(K_s - K_L)\phi_s}{K + 2K - (K - K_L)\phi_s}$	ϕ_s – solids volume	
	$\mathbf{K}_{L} \qquad \mathbf{K}_{s} + 2\mathbf{K}_{L} - (\mathbf{K}_{s} - \mathbf{K}_{L})\boldsymbol{\varphi}_{s}$	fraction	
	$\frac{K_{eff}}{K_{L}} = \frac{K_{s} + (n-1)K_{L} - (n-1)\phi_{s}(K_{L} - K_{s})}{K_{s} + (n-1)K_{f} + \phi_{s}(K_{L} - K_{s})}$	n depends on particle	
Hamilton &		shape and Ks/KL,	
Crosser		$n=3/\psi$ for	
(1962)		Ks/KL>~100, n=3 for	
		other cases, ψ -	
		sphericity	
Jeffrey (1973)		High order terms	
	$\frac{K_{eff}}{K} = 1 + \frac{3\phi_s(K_s / K_L - 1)}{K / K + 2} + 3\phi_s^2(\frac{K_s / K_L - 1}{K / K + 2})^2 \cdot [1 + 1]$	represent pair	
	$\frac{1}{4} \left(\frac{K_s / K_L - 1}{K_s / K_L + 2} \right) + \frac{3}{16} \left(\frac{K_s / K_L - 1}{K_s / K_L + 2} \right) \left(\frac{K_s / K_L + 2}{2K_s / K_L + 3} \right) + \dots \right]$	interactions of	
		randomly dispersed	
		particles	
	$K = 2(K \mid K = 1) \left[\phi + f \phi^2 + O(\phi^3) \right]$	High order terms due	
		to pair interactions of	
Davis	$\frac{K_{eff}}{K} = 1 + \frac{J(K_s + K_L - 1) - [\psi_s + J + \psi_s + O(\psi_s)]}{(K + K_L - 1) - (K + K_L - 1)\phi}$	randomly dispersed	
(1986)	\mathbf{A}_L $(\mathbf{A}_s, \mathbf{A}_L + 2)$ $(\mathbf{A}_s, \mathbf{A}_L - 1)\varphi_s$	spheres, f=2.5 & 0.5	
		for $K_s/K_L=10$ and ∞ ,	
		respectively	
Bruggeman (1935)	V v	Spherical particles,	
	$\frac{K_{eff}}{V} = [(3\phi_s - 1)\frac{K_s}{V} + (2 - 3\phi_s) + \sqrt{\Delta}]/4$	interactions between	
	$\Delta_{L} = (3\phi - 1)^{2} (K / K)^{2} + (2 - 3\phi)^{2} +$	particles considered,	
	$\frac{\Delta - (3\phi_s - 1)}{2(2+9\phi_s - 9\phi_s^2)(K_s / K_L)} + (2 - 3\phi_s) + 2(2+9\phi_s - 9\phi_s^2)(K_s / K_L)$	applicable to high	
		concentrations	

Table 1	A list of the most f	requently used	models for	effective thermal	conductivity
Table 1	A list of the most f	requently used	models for	effective thermal	conductivi

shown theoretically to be negligible as the time scale of the Brownian motion is about 2 orders of magnitude larger than that for the thermal diffusion of the base liquid (Keblinski et al. 2002). The indirect contribution has also been shown to play a minute role by theoretical analysis (Evans et al. 2006). Furthermore, nanoparticles are often in the form of agglomerates and/or aggregates. The Brownian motion should therefore play an even less significant role. In the following text, further experimental evidence of the minor role of the Brownian motion is presented.

Fig. 2 shows the thermal conductivity enhance-

ment as a function of temperature for nanofluids made of three types of metal-oxide nanoparticles. One can see that, except for the data of Das et al. (2003a) for CuO/H₂O nanofluids, the thermal conductivity enhancement is a very weak function of temperature. The weak temperature dependence suggests that the Brownian motion of nanoparticles is not a dominant mechanism of the enhanced thermal conductivity of nanofluids under the conditions of this work and other recent studies such as Kabelac and Kuhnke (2006) and Zhang X. et al. (2007). **Fig. 3** shows the results of alumina nanofluids made from





Fig. 2 Effect of temperature on the thermal conductivity enhancement: data source see the legend.

three base liquids with very different viscosities. No clear trend in the dependence of the thermal conductivity enhancement on the base liquid viscosity again suggests the minor role of the Brownian motion.

The role of liquid molecular layering At the solid-liquid interface, liquid molecules could be significantly more ordered than those in the bulk liquid. By analogy to the thermal behaviour of crystalline solids, the ordered structure could be a mechanism of thermal conductivity enhancement (Keblinski et al. 2002). On such a basis, a number of macroscopic models have been proposed to interpret the experimental data; see for example, Yu and Choi (2003) and Wang et al. (2003). It is now clear that the liquid-nanoparticle interface is one of the main factors that decrease (rather than increase) the effective thermal conductivity due to the so-called Kapita interfacial resistance (Shenogin et al. 2004a & 2004b, Nan et al. 2003; Gao et al. 2007). The experimental data for carbon nanotube nanofluids as presented in Section 2.1 agrees with this argument.

It should be noted that the effect of interfacial resistance on the overall effective thermal conductivity depends on the particle size (Keblinski et al. 2005; Prasher et al. 2005; Putnam et al. 2006; Gao et al. 2007). When particle size is relatively small in comparison with the characteristic length scale due to the interfacial resistance, nanoparticles act as insulators. This leads to deterioration of the thermal conduction of nanofluids.

The last standing mechanism The above discussion indicates that neither Brownian motion nor interfacial liquid layering can be a dominant mechanism. As the ballistic transport of energy carriers in nanofluids has been excluded as a dominant mechanism, the last



Fig. 3 Effect of base liquid property on thermal conductivity enhancement for alumina nanofluids: data taken from Lee et al. (1999), Eastman et al. (2001), Xie et al. (2002a), Das et al. (2003b) and Wen and Ding (2004b).

mechanism standing is the nanoparticle structuring / networking (Prasher et al. 2006b, Keblinski 2007). This has actually been validated by our experimental results and theoretical analyses of ethylene-glycolbased titania nanofluids. We found that the size of the aggregates is approximately 3.5 times that of the primary nanoparticles (**Fig. 4**). By using the Maxwell model for aggregate suspensions and the Bruggeman model for aggregates (**Table 1**), a nanoparticle structuring model is formulated which gives a fairly good agreement with the experimental data (**Fig. 5**, Chen et al. 2007a).

3. Convective Heat Transfer of Nanofluids

Convective heat transfer refers to heat transfer between a fluid and a surface due to the macroscopic motion of the fluid relative to the surface. The sur-



Fig. 4 SEM image of based TiO_2 nanofluids: Degussa P25 TiO_2 with primary particle diameter ~ 25nm.





Fig. 5 Comparison of measured thermal conductivity enhancement with the model based on nanoparticle structuring: based TiO₂ nanofluids.

face can be a solid wall or an interface with another liquid. We are interested in the solid surface due to its great industrial significance. Convective heat transfer can be divided into two types, natural convective heat transfer where fluid motion is induced by buoyancy, and forced convective heat transfer where fluid is forced to flow through a confined region or across a confining wall.

3.1 Natural convective heat transfer

Very few studies have been found in the literature on nanofluids heat transfer under natural convection conditions. By using the numerical technique, Khanafer et al. 2003) predicted that nanofluids enhanced natural convective heat transfer. The enhancement was also observed experimentally by Nnanna et al. (2005) for Cu / ethylene glycol nanofluids and by Nnanna and Routhu (2005) for alumina / water nanofluids. In contrast, Putra et al. (2003) found experimentally that the presence of nanoparticles in water systematically decreased the natural convective heat transfer coefficient. Interestingly, the decrease in the natural convective coefficient was also reported by Nnanna et al. (2005) for alumina / water nanofluids, which is in contradiction to the observation of Nnanna and Routhu (2005). Our work was therefore aimed to investigate the controversy (Wen & Ding 2005b & 2006) and the details are presented in the following text.

Materials and experimental techniques Aqueous-based TiO₂ nanofluids were formulated for the work by dispersing dry titania nanoparticles in distilled water without the use of any dispersant/surfactant. The size of the titania nanoparticles was given in Section 2. A high-shear mixer was used to break agglomer-



Fig. 6 Effect of nanoparticle concentration on the convective heat transfer under natural convection conditions.

ates of nanoparticles, and electrostatic stabilisation was used to stabilise the suspensions. The experimental system used in the work consisted of two horizontally positioned aluminium discs of diameter 240mm and thickness 10mm, separated by a 10mm gap through a short insulating PTFE cylinder. A silicon rubber flexible heater was attached to the lower surface of the bottom disc. Six type J thermocouples and two surface heat flux sensors were mounted on the aluminium surfaces to measure temperatures and heat fluxes, which allowed calculation of the natural convective heat transfer coefficient.

Experimental data Fig. 6 shows the convective heat transfer coefficient (h) in the form of a Nusselt number (Nu) as a function of the product of the Grashof number (Gr) and Prandtle number (Pr) defined as $Nu = hd_q/K_f$, $\Pr = \nu_f/\alpha$, $Gr = g\beta\Delta T d_q^3/\nu_f^2$, respectively, with d_g representing the separation between the two discs, K_f the thermal conductivity of the fluid, v_f the kinematic viscosity of the fluid, α the thermal diffusivity of the fluid, g the gravitational acceleration, β the volume expansion coefficient of the fluid and ΔT the temperature difference between the two disc surfaces. The product of the Gr and Pr numbers is also termed as the Rayleigh number defined as $Ra = g\beta\Delta T d_g^3/(\nu_f \alpha)$. One can see clearly that the Nusselt number decreases with increasing nanoparticle concentration. Possible reasons are discussed in the following text.

Why the observed deterioration? It is known that the natural convective heat transfer coefficient depends not only on the properties of the fluid and geometry under consideration, but also on other factors such as method of heating, configuration and orientation of the heater, as well as the properties of the heating



and cooling surfaces. Given the experimental system and nanofluids used in this work, the Nusselt number takes the following form (Wen and Ding 2006):

$$Nu = c' \left[\frac{\rho_f C_{Pf} \beta \Delta T}{\nu_f K_f}\right]^n \tag{1}$$

where *c*' and *n* are constants, ρ_f is the fluid density and C_{Pf} is heat capacity of the fluid. The constant nlies between 1/4 and 1/3. Equation (1) indicates that the physical properties of nanofluids that affect their heat transfer behaviour include heat capacity, thermal conductivity, density and viscosity. The effects of density and heat capacity are expected to be small due to small concentrations of nanoparticles. The maximum enhancement of thermal conductivity and increment of the viscosity are ~5% and 20% under the conditions of this work, respectively. This brings to a maximum Nusselt number a decrease of ~8%, which is much smaller than the experimentally observed 30% decrease. Thus, there must be other factors that play roles. More work is needed in identifying these factors.

3.2 Forced convective heat transfer

There are a limited number of published studies on the forced convective heat transfer. Most of the reported studies show the enhancement of convective heat transfer by using nanofluids (Lee and Choi 1996; Xuan and Roetzel 2000; Li and Xuan 2002; Xuan and Li 2003; Jang and Choi 2006; Heris 2007). A few studies show inconsistencies, i.e. enhancement under certain conditions but little enhancement under other conditions (Pak and Cho 1998; Chein and Chuang 2007; Lee and Mudawar 2007). There are also studies that show little enhancement or even a decrease in the convective heat transfer coefficient when nanoparticles are added to the base liquids (Yang et al. 2005). Our work has aimed to understand and interpret the controversies through both experimental work and simple analyses using various nanofluids (Wen and Ding 2004b; Ding et al. 2006; He et al. 2007; Chen et al. 2007b; Ding et al. 2007).

Materials and techniques Five types of nanomaterials, alumina, titania, titanate nanotubes, carbon nanotubes and nano-diamond particles were used in our work. Titania and alumina nanofluids were formulated by using dry nanoparticles manufactured by Degussa (Germany) and Nanophase Technologies (USA), respectively. The carbon nanotubes were supplied by Prof F. Wei of Tsinghua University (China). The nano-diamond and titanate nanotubes were synthesised by our collaborators in Newcastle and Bath Uni-

versities, respectively. Details of these materials and preparation methods can be found in Wen and Ding (2004b), Ding et al. (2006), He et al. (2007), Chen et al. (2007b) and Ding et al. (2007). Distilled water was used as the base liquid for formulating most of the nanofluids, whereas a few titania nanofluids were made with ethylene glycol. Two experimental systems were used for the forced convective heat transfer studies, one for a horizontal arrangement and the other one for a vertically oriented pipe. Fig. 7 shows the schematic diagrams of the two experimental systems and the details can be found elsewhere (Wen and Ding 2004b; Ding et al. 2006; He et al. 2007). Experimental data Experiments on the forced convective heat transfer were carried out on all the nanofluids formulated under various flow conditions. Pure

base liquids were tested first for use as a basis for comparison. The results are summarised as follows:
In general, the convective heat transfer coefficient of nanofluids has the highest value at the entrance but decreases with axial distance and reaches a constant value in the fully developed region. The entrance length depends on the properties and behaviour of nanofluids. For a given nanofluid, the

entrance length at low flow rates, e.g. laminar flow for Newtonian fluids, is longer than that at high flow rates, e.g. turbulent flow for Newtonian fluids.







Fig. 7 Experimental systems for forced convective heat transfer studies.





Fig. 8 Enhancement of forced convective heat transfer coefficient as a function of axial position from the inlet of the test section: carbon nanotube (CNT) and alumina nanofluids tested in the rig as shown in Fig 7(a); titanate and titania nanofluids measured with the system shown in Fig 7(b).

- At given particle concentrations and flow conditions, aqueous-based carbon nanotube nanofluids give the highest enhancement of convective heat transfer coefficient, followed by (in descending order) aqueous-based titanate nanotube nanofluids, aqueous-based titania nanofluids, aqueous-based alumina nanofluids, ethylene-glycol-based titania nanofluids and aqueous-based nano-diamond nanofluids. Fig. 8 shows some experimental data in the form of enhancement as a function of the axial position (x) normalised by the tube diameter (D). As the ethylene-glycol-based titania nanofluids and aqueous-based titania nanofluids and aqueous-based titania nanofluids.
- For aqueous-based alumina, titania, and titanate and carbon nanotube nanofluids, the convective heat transfer coefficient generally increases with increasing flow rate or increasing particle concentration, and the enhancement exceeds by a large margin the extent of the thermal conduction enhancement, indicating that thermal conduction enhancement is not the dominant mechanism for the

convective heat transfer enhancement. However, if one takes into account the enhancement of the thermal conductivity, deterioration of the convective heat transfer is found for ethylene-glycol-based titania and aqueous-based nano-diamond nanofluids. The exact reason for this has been a subject of our recent investigation. Some of the findings are discussed later in this section.

- For titania nanofluids, we found no clear trend in the effect of particle size on the convective heat transfer coefficient for particles between 95 and 210nm (He et al. (2007).
- The data for the aqueous-based titania and titanate nanofluids seem to indicate that particle shape plays an important role in the convective heat transfer enhancement given other conditions, i.e. larger aspect ratios (length/diameter) give a higher enhancement. This is also supported by comparing the results of this work on carbon nanotube nanofluids with those by Yang et al. who found no enhancement of convective heat transfer using water-based disc-like graphite nanofluids (Yang et al. 2005).
- For nanofluids made of particles with large aspect ratios, e.g. carbon nanotubes, there seems to be a relationship between the rheological behaviour and the convective heat transfer behaviour. For example, for aqueous-based carbon nanotube nanofluids, a drastic increase in the convective heat transfer coefficient occurs at a flow rate corresponding to a shear rate where the shear viscosity is close to the minimum (Ding et al. 2006).

Why enhancement in some cases but deterioration in other cases? The experimental observations can be examined from both macroscopic and microscopic aspects. Considering a flow with uniform velocity and temperature distributions through a pipe, the flow has a different temperature from the wall temperature (**Fig. 9**). Due to friction between the fluid and the pipe wall, a hydrodynamic boundary layer will





Fig. 9 Boundary layer development in a pipe flow in the laminar flow regime; for turbulent flow, the entrance region is much shorter and the boundary layer thickness is thinner.

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form at the wall region in which the flow velocity increases from zero at the wall to maximum in a radial position depending on the axial position from the entrance. At a certain axial position from the entrance, the thickness of the boundary layer approaches constant, and the flow is regarded as fully developed. Similarly, due to the different temperatures of the fluid and the pipe wall, a thermal boundary layer is developed, though its thickness and the entrance length can be different. Macroscopically, the forced convective heat transfer coefficient, h, is given by $h = K_f / \delta_t$, with δ_t representing the local thickness of thermal boundary layer and K_f the local effective thermal conductivity of nanofluids adjacent to the wall surface. This simple expression indicates that either an increase in K_f and a decrease in δ_t , or both, can result in an increase of the convective heat transfer coefficient. This explains why the entrance region gives a higher convective heat transfer coefficient. As nanofluids have a higher thermal conductivity in comparison with the base liquid, the simple expression also partially explains the enhanced convective heat transfer coefficient. The expression, however, cannot provide an adequate explanation of the experimental observations that, in some cases, the convective heat transfer coefficient enhancement is much higher than the thermal conduction enhancement, while in other cases, there is no convective heat transfer enhancement despite considerable thermal conduction enhancement, e.g. aqueous-based nano-diamond and ethylene-glycol-based titania nanofluids (Ding et al. 2007). This may be explained from the microscopic point of view; see below.

Microscopically, nanofluids are inhomogeneous. There are at least two possible reasons for the inhomogeneity (Ding et al. 2006, Ding et al. 2007). One is the presence of agglomerates in nanofluids, which can be associated with either sintering during nanoparticle manufacturing or solution chemistry during nanofluids formulation. The former is often seen in processes involving elevated temperatures, e.g. aerosol reactors. The resulting agglomerates are very strong and are difficult to break down to primary nanoparticles even with prolonged high-shear processing and ultrasonication. The latter is due to the attraction between nanoparticles, e.g. van der Waals' attractive force and depletion phenomena. The agglomerates (aggregates) can be controlled by adjusting the solution chemistry and applying shear. The second reason is particle migration due to viscosity and velocity gradients. Experimental evidence of particle migration is the longer entrance length of

nanofluids as discussed above and in a recent experimental study by Merhi et al. (2005). There are also plenty of theoretical studies on particle migration; see, for example Phillips et al. (1992), Frank et al. (2003) and Ding and Wen (2005). If particles are very small, Brownian motion is strong and the effect of the above-mentioned particle migration is negligible. If particles are large, e.g. aggregates of hundreds of nanometres, the contribution of the Brownian motion is small, and a particle depletion region may exist at the wall region, which gives non-uniform distributions of particle concentration, viscosity and thermal conductivity. The direct results of particle migration are lower particle concentration at the wall region and a thinner boundary thickness due to disturbance by the moving particles. This, according to $h = K_f / \delta_t$, can lead to three possible scenarios: (i) h is enhanced if the decrease in δ_t exceeds the decrease in K_{f} (ii) h does not change if the decrease in δ_t is equal to the decrease in K_f , and (iii) h is reduced if the decrease in δ_t is lower than the decrease in K_f . This qualitatively explains the experimental results. However, quantitative explanation requires understanding of how nanoparticles behave under shear and how they interact with each other and with fluid in the boundary layer.

4. Phase Change (boiling) Heat Transfer of Nanofluids

There are a limited number of studies on the phase change heat transfer (Das et al. 2003b & 2003c; Tsai et al. 2003; You et al. 2003; Tu et al 2004; Vassallo et al. 2004; Bang and Chang 2005; Kim H et al. 2006; Kim S. et al. 2006). The results of these studies show that the presence of nanoparticles in liquid enhances Critical Heat Flux (CHF). The mechanism of the CHF enhancement is attributed to the deposition and sintering of nanoparticles on the boiling surfaces so that the surface area is increased. Experimental results also show that the properties of nanofluids affect the extent of the enhancement (Kim H et al. 2006; Kim S. et al. 2006). However, there is a disagreement in boiling heat transfer of nanofluids in the nucleate regime. Our work was therefore aimed at understanding and interpreting boiling heat transfer in the nucleate regime (Wen and Ding 2005a; Wen et al. 2006).

Materials and experimental techniques Aqueous-based alumina and titania nanofluids were used in the work. No dispersant / surfactant was used in the formulation. The experimental system consisted of a boiling vessel with 160mm inner diameter and 300mm





Fig. 10 Heat flux as a function of the wall superheat.

height, a heating and measuring unit and a data acquisition unit. The boiling surface was situated at the bottom of the vessel, which was the upper side of a polished stainless steel disc with 150mm diameter. A ring heater with a maximum power of 2.4 kW was attached to the back surface of the stainless steel disc, and heat flux was controlled through varying the voltage. By measuring the temperatures of the boiling surface and the bulk liquid, and the voltage and heater resistance, one can calculate the heat transfer coefficient.

Experimental results and discussion Fig. 10 shows the heat flux as a function of the wall superheat (temperature difference between the bulk fluid and the boiling surface), together with the prediction by the classical correlation of Rehsenow (1952) for pool boiling. One can see that the experimental data for water agree well with the Rehsenow correlation. The data of nanofluids deviate from the Rehsenow equation and the deviation increases with nanoparticle concentration.

The data shown in Fig. 10 are processed to give the heat transfer coefficient. Fig. 11 shows the results in the form of the ratio of heat transfer coefficient of nanofluids to that of pure water given other conditions. Enhancement of the boiling heat transfer is significant for both alumina and titania nanofluids in the nucleate regime, and the enhancement cannot be entirely attributed to the thermal conduction enhancement (data shown in Figs. 1-3). Fig. 11 also shows that the heat transfer enhancement increases with nanoparticle concentration and the enhancement for titania nanofluids is more sensitive to the change of particle concentration in comparison with that for alumina nanofluids. The different heat transfer behaviour of alumina and titania nanofluids indicates that the nanofluid properties have an influence



Fig. 11 Heat transfer coefficient ratio as a function of heat flux.

on the boiling heat transfer in the nucleate regime.

The experimental results of this work as presented above agree with that of You et al. (2003) and Tu et al. (2004). Our results, however, disagree with those of Das et al. (2003b & 2003c), Bang and Chang (2005) and Kim S et al. (2006), who observed deterioration of boiling heat transfer in the nucleate regime. The exact reason for the discrepancy is unclear. Possible reasons are discussed in the following text:

- Thermal conductivity and viscosity affect the heat transfer behaviour of nanofluids in opposite ways. As a result, a combination of thermal conductivity enhancement and increment of the viscosity can give either enhancement or deterioration of the heat transfer coefficient. However, there is too little information in the published studies to permit making a conclusive assessment.
- Stability of nanofluids and the presence of a dispersant / surfactant affect the behaviour of nanofluids, which are often not provided in the published studies. For example, settling of nanoparticles in nanofluids with poor stability can change the properties of the boiling surface, and surfactants / dispersants may fail at elevated temperatures.
- Boiling heat transfer consists of a number of subprocesses in parallel and/or series, including unsteady-state heat conduction, growth and departure of bubbles, and convection due to bubble motion and liquid re-filling. These sub-processes are affected by parameters such as heater geometry, properties of the boiling surface, orientation of the heater, liquid sub-cooling, system pressure, and the mode in which the system is operated. Among these, the boiling surface properties are among the key factors that influence


the boiling heat transfer. The surface properties include surface finish (roughness), surface wettability, and surface contamination, as they all influence the number and distribution of active nucleation sites for bubbles and their subsequent growth. In the published studies, however, surface roughness is the most often-used parameter, and interpretation of the effect of surface roughness on the boiling heat transfer has been based on the size of the suspended particles relative to the surface roughness. For example, Bang and Chang (2005) used a boiling surface of nanometre-scale roughness, hence sedimentation of the particles was regarded to effectively increase the roughness of the surface, whereas a commercial cartridge heater with a micron-scale surface roughness was employed by Das et al. (2003b, 2003c) onto which sedimentation of the nanoparticles was thought to decrease the effective surface roughness.

 Different temperature measurement methods may lead to the different experimental results obtained by different investigators. For example, all thermocouples were welded on the outer surface of the cartridge heater by Das et al. (2003b & 2003c). This would inevitably influence the surface characteristics of the boiling surface, as bubbles have a tendency to nucleate on the welded positions and the measured temperature may not be representative of the boiling surface. Vassalao et al. (2004) used fine resistance wires for temperature measurements. Large uncertainties are expected for this sort of method as temperature is converted from the measured resistance of the heating wire against the standard temperature-resistance curve. Indeed, for boiling with pure water, more than 10° deviance of superheat was observed under a fixed heat flux condition in different runs; see Fig. 1 of Vassallo et al. (2004). It may be sensible for a qualitative comparison of the critical heat flux (CHF), but it may not be adequate for a quantitative comparison of nucleate boiling heat transfer.

Obviously, the above discussion is crude and on a qualitative basis. Nevertheless, these points provide possible ways towards interpreting the controversies in the literature.

5. Concluding Remarks

This paper summarises some of our work on nanofluids over the past few years. It covers conduction, convection under both natural and forced convective heat transfer conditions, and boiling heat transfer in the nucleate regime. A brief review of the state-of-theart developments in these aspects is also given. The following conclusions are obtained:

- Despite considerable scattering, the presence of nanoparticles enhances thermal conduction under macroscopically static conditions, and direct application of the conventional thermal conductivity models for suspensions and composite materials does not provide an adequate prediction of the experimental observations. The enhancement is a function of particle concentration, particle material type and particle shape. The effect of temperature is weak, whereas the effects of the base liquid properties and particle size are unclear. Over the many possible mechanisms proposed for the thermal conductivity enhancement, nanoparticle structuring / networking seems to be the last mechanism standing.
- The natural convective heat transfer coefficient systematically decreases with increasing nanoparticle concentration. Although the exact reason is still unclear, the deterioration can be partially attributed to the high viscosity of nanofluids.
- Either enhancement or deterioration can occur in the forced convective heat transfer of nanofluids. The exact reason is unclear but particle migration is shown to be an important mechanism.
- Enhancement of the boiling heat transfer is observed in the nucleate regime for both alumina and titania nanofluids, and the enhancement is more sensitive to the concentration change for TiO₂ nanofluids.

Nanofluids research has been carried out for over 10 years. Significant progress has been made over the years, particularly in the past few years. However, there is still some way to go before we can tailor-make nanofluids.

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List of symbols

- *c*' constant in Eq.(1)
- *C*_{Pf} heat capacity
- d_g separation between the two discs
- D pipe diameter
- f interaction coefficient
- g gravitational acceleration
- Gr Grashof number
- *h* heat transfer coefficient
- *K*_{eff} effective thermal conductivity
- *K*^{*f*} fluid thermal conductivity
- *K*^{*L*} liquid thermal conductivity
- *K*_s solid thermal conductivity
- *n* shape factor
- n' constant in Eq.(1)
- Nu Nusselt number
- Pr Prandtl number
- *R*_a Rayleigh number
- Re Reynolds number
- ΔT temperature difference
- *x* axial distance

Greek

- a thermal diffusivity
- β thermal expansion coefficient
- ρ_f fluid density
- ϕ_s solid volume fraction
- δ_t thermal boundary layer thickness
- ψ shape factor of particles

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Author's short biography



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Plasma Synthesis of Nanoparticles[†]

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Abstract

This paper gives a review on the plasma synthesis of nanoparticulate powders. The concept of plasma synthesis is used quite comprehensively, it covers all processes where charged particles are observed. Therefore, the topic of this paper ranges from high-temperature processes and microwave processes to the laser and flame synthesis of nanopowders. For each of the processes discussed in this paper, the product characteristics are explained. This may be used as guidance for the selection of a process. The presentation of the paper is quite basic; this is to give people working in industry on daily problems a chance to see what is going on in this field. There is a vast amount of literature in the field of plasma synthesis. The literature was therefore selected in a way to demonstrate basic phenomena and not to give a comprehensive review of the literature.

Keywords: Nanoparticles, Plasma, RF processing, Micro wave Synthesis

1. Introduction

Gas-phase processes are environmentally benign as they are not connected to liquid effluents. The cleaning of liquid effluents is difficult and costly. In addition, because the synthesis of nanopowders is in most cases connected with low concentrations, the amount of solvents needed in the process is huge. Powder synthesis based on reactions in the gas phase is based on purely random processes for particle formation. In general, this leads to a broad distribution of particle sizes and, in some variants of these processes, to the formation of particle clusters. There are applications where broad particle size distributions and clustered particles are disadvantageous. To solve this problem, many process variants and nuances in processing were developed.

A broad group of gas-phase processes is connected to plasma. Generally, plasma is considered as being a distinct state of matter. It consists of positively and negatively charged elements (electrons, ions, or nanoparticles) in such a way that the sum of all electric charges is zero. These electrically charged elements are intermixed with neutral gas atoms or molecules. The degree of ionization, which is the ratio of charged particles over the uncharged ones, may be quite small. Due to the mobile electric charges, a plasma is electrically conductive. A plasma containing particle is called dusty plasma. Particle synthesis is always connected to dusty plasma. In addition, one has to ask for the thermal equilibrium in the plasma, which is a further important point for the classification of plasma processes. One distinguishes between equilibrium plasma und non-equilibrium plasma. In the first case, the thermal energy (may be represented as temperature) of all constituents is equal. This is also called thermal plasma. In the non-equilibrium case, the different constituents of the plasma have different thermal energy levels. In this case, the electrons have the highest, the ions a significantly lesser, and neutral gas species the least energy. It is important to note that any flame is partially ionized; therefore, it is often called low-temperature partial plasma. This is an interesting point waiting for final exploitation.

Within the large group of plasma processes for

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Fig. 1 Two basic types of plasma burners applicable for nanopowder production, differing in the supply for the precursor. Both designs may use liquid or powder precursors.

nanoparticle synthesis, a very special class of methods is connected to plasma produced by electrical systems. The other processes where plasma is involved apply laser or just high temperatures for excitation. One additional characteristic to differentiate plasma processes is the gas pressure. Some of the processes work at ambient pressure, however, most of them at reduced gas pressure. A third means to differentiate plasma processes is based on the precursors. They may be gaseous, solid, liquid, or solutions.

2. High-Temperature Plasma Processes

2.1 AC and DC systems

High-temperature plasma processes are the oldest and most common ones. They work at atmospheric pressure and use electric power originating from DC, AC, or RF sources. In high-temperature plasma processes, the energy distribution is usually close to thermal equilibrium. Fig. 1 shows two distinct types of arrangements applied for powder synthesis using AC or DC electrical power. In both cases, the plasma burns between two co-axial electrodes. It is blown out of the system by a powerful gas stream. This gas stream fulfills two major tasks: It is the gas supply for the plasma and it prevents the electrodes from overheating. An additional water-cooling system may be necessary in the case of high-power systems. Reactive components such as oxygen or ammonia necessary to obtain the intended product from the selected



precursor may be admixed. The two arrangements for plasma synthesis depicted in **Fig. 1** differ in the supply of the precursor. Systems such as those may use solid precursors supplied as powder or liquid precursors supplied in most cases as an aqueous or organic solution. In the latter cases, the energy content of the plasma flame is influenced dramatically.

In the case of axial feed of the precursor, the precursor is sucked into the system by the co-axial gas stream. Generally, the designs provide a sheath gas circumferentially to the nozzle system to avoid unplanned deposition of the product on the structures of the system. In most cases, an additional pump for the precursor is not necessary. Feeding the precursor from the side directly into the plasma flame is, at most, applied for powders only. The temperature in the plasma is extremely high. One may expect temperatures significantly above 4000 K. At this temperature, all of the metals and most of the oxides are already evaporated, or at least melted. Therefore, as the precursor largely evaporates, one has almost no problems with respect to particle or droplet size. In this instant and in the case of applying an RF plasma, the design of the nozzle is the crucial point with respect to the processing parameter. Nozzle design ranges from very simple ones to highly sophisticated ones with hypersonic gas velocities^{1,2)}.

Within the plasma, the particles move in the direction of the gas stream, and in addition, they move randomly. Just as in any other aerosol process, there is therefore a high chance for particle collision and the formation of clusters. The probability of cluster formation is reduced significantly by the rapid cooling of the gas immediately after the reaction zone. The design of this quenching zone is crucial for the product quality. The quenching gas is introduced into the system either radially or axially against the flow direction. Quenching improves the quality of the product. In the context of nanopowders, improving means narrowing of the particle size distribution and avoiding large particles or agglomerates. For many applications, a reduction of the average particle size is seen as an improvement of the quality.

Fig. 2 shows the typical flow diagram of a production system for powders using a plasma torch system at ambient pressure. After synthesis, a quenching step follows. Furthermore, it may be important to recirculate the process gas. Examples where this is necessary are, e.g. the synthesis of nitrides, where pure nitrogen or nitrogen/ammonia mixtures are used for nitriding and in the case of metal carbide synthesis, argon is used as the carrier gas in most





Fig. 2 Flow diagram for a production plant based on plasma burners. The recirculation system is of special importance in the case of expensive reaction or carrier gases.

cases.

Even when it is not always a disadvantage, processes using AC or DC plasma torches suffer from the prejudice of producing only highly agglomerated powders. A typical example for such a product is depicted in Fig. 3. This figure depicts aluminum nitride, AlN. Aluminum nitride is a highly hygroscopic ceramic with excellent electric insulating properties. It is extremely difficult to synthesize nanoparticulate AlN. In this instance, AlN was synthesized from aluminum vapor in a 50/50 vol% nitrogen/ammonia atmosphere. An ablating aluminum electrode was used as the source for the metal vapor²⁾. To obtain sufficiently high plasma temperatures, the plasma was supplied with electrical energy using a pulsed DC source. The nozzle was designed in a way to obtain hypersonic gas velocities.

Two characteristic features characterize the product shown in **Fig. 3**: There is quite a broad particle size distribution. It is interesting to see that the smaller particles are arranged in chains. The diameter ratio between the largest to smallest particles seems to be in the range of ten. The particles, in particular the largest ones, are not spherical. By careful selection of the processing conditions and the precursor, it is also possible to obtain a product with spherical particles and a relatively narrow particle size distribution. As an example, **Fig. 4** shows an electron micrograph of zirconia powder³.

Karthikeyan et al. used a 2.4-wt.% zirconia solution made of zirconium butoxide dissolved in *n*-butanol³⁾. This liquid was injected radially into the plasma

torch. The transmission electron micrograph shown in **Fig. 4** is characterized by almost spherical particles with an average particle size of around 12 nm. Besides the majority of particles of nearly equal size, a few huge particles with a diameter of around 45 nm are visible. The electron diffraction pattern inserted into **Fig. 4** represents these visual findings perfectly. It shows the diffraction rings stemming from the tetragonal small particle fraction and, additionally, a few separated spots originated from the few large particles. These larger particles were crystallized in the monoclinic structure. In general, one can say that



Fig. 3 TEM micrographs of nanocrystalline AlN synthesized with a hypersonic pulsed DC plasma torch. Nitriding of the evaporated aluminum vapor was performed with a mixture of nitrogen and ammonia in equal parts.²⁰ Reproduced by permission of Elsevier.





Fig. 4 Zirconia powder made from an organic 2.4-wt% zirconium butoxide solution in n-butanol in a plasma torch. The liquid precursor was injected radially.³ Reproduced by permission of Elsevier.



Fig. 5 Set-up of a device for powder synthesis applying an inductively coupled plasma. The precursor may be supplied axially, as shown in this figure, or radially as shown in Fig. 1.

the product shown in **Fig. 4** is almost perfect.

Plasma synthesis using AC or DC power sources is a mature and widely used process that led to a vast amount of literature where, however, the most important technical details are kept secret because of their huge technological relevance. Some interesting recent results may be found in⁴⁻⁹⁾.

2.2 RF systems

Fig. 5 shows the typical layout for an RF plasma device for nanopowder synthesis. It consists of a system to introduce process gas and precursor. This part of the system is set up similarly to the one for plasma processes using DC or AC power. The frequencies applied in such systems range from 50 kHz up to 10 MHz.

The only and important difference is the fact that these RF systems work without electrodes. There is therefore no risk of contamination from the electrodes, and in addition, these systems do not have any wear parts with a limited service life. On the other hand, consumable electrodes cannot be used as precursors. Besides the design shown in **Fig. 5**, a design where the flow of the precursors is opposite to the streaming direction of the plasma flame is also described. It is said that such a design has the advantage of a longer time period where the product is in direct contact with the hot plasma flame^{10,11)}. This may be of advantage in the case of products where the reaction rate of particle formation is extremely low.

Moreover in inductively coupled RF systems, quenching improves the quality of the product, narrows the particle size distribution and avoids large particles. As an example, the comparison of silica powders produced with identical production parameters except for quenching is shown in **Fig. 6a** and **6b**¹². The powder shown in the electron micrographs



Fig. 6 Silica nanopowder made of silica powder synthesized in an RF plasma torch. After the plasma torch, the product shown in Fig. 6a was not quenched, in contrast to the one in Fig. 6b. Please note the different particle sizes and size distributions. The magnification in Fig. 6b is more than double that of Fig. 6a.¹² Reproduced by permission of Berkeley Electronic Press.

in **Fig. 6a** was produced without quenching. At the first glance, the most characteristic features of the unquenched product are a few huge spherical particles surrounded by many smaller ones, visibly a broad particle size distribution. This is different in **Fig. 6b**, where the product obtained after quenching is shown. (The magnification in **Fig. 6b** is more than double that of **Fig. 6a**) In this product, the huge spherical particles are missing. Certainly, the particle size distribution remains broad, however, the tail on the large particle side of the size distribution is not that significant.

Complete systems in accordance with those shown in **Fig. 1** and **5** for industrial powder production are commercially available. A typical plant is shown in **Fig. 7**¹³⁾. The production capacity of synthesis plants like this is in the range of kilograms per hour.

Optimized industrial production systems deliver nanopowders of sufficiently good quality with particle sizes of less than 100 nm. The range of possible products is broad; it ranges from metals and oxides to carbides and nitrides. Except for the oxides and the powders of precious metals, all of these products may indeed be highly pyrophoric. It is therefore advisable to handle these products in an inert gas atmosphere, if possible within glove boxes. A typical example of such a nanopowder is shown in **Fig. 8**. This figure shows copper powder produced with equipment such as that shown in **Fig. 7**.

The product shown in **Fig. 8** has a particle size distribution that is not too broad. With respect to the fact that this is a product of commercial and not laboratory equipment, the size distribution is remarkably good.

A few further more recent applications of powder synthesis applying RF plasma torches outside of in-



Fig. 7 Industrially manufactured production plant for nanopowders delivered by Tekna Plasma Systems Inc, Canada.¹³⁾

dustrial use are found in¹⁴⁻¹⁸⁾. It may be interesting to realize that high-temperature plasma applications are perhaps driven with microwave power sources, too¹⁹⁾.

3. Low-Temperature Plasma Processes

3.1 General considerations

Low-temperature plasma processes are always connected to systems with reduced pressure. In this context, low-temperature systems may be defined as ones that apply temperatures below 1000 K. In these systems, the power is introduced either by RF or microwave power supplies. Even if that appears almost identical, the physics of using RF or microwaves is to some extent different. To understand the influence of the frequency, one has to study the energy transfer to charged particles in an oscillating electrical field. The energy U transferred to a particle with the electric charge Q in an electrical field with the frequency f is inversely proportional to the mass of the particle m and the squared frequency.

$$U \propto \frac{Q}{mf^2}$$
 (1)

As the mass of the electrons is a few thousand times smaller than the mass of the ions, a few thousand-fold



Fig. 8 Nanopowder of metallic copper produced with an industrial RF plasma system similar to the one shown in Fig. 7¹³. With respect to an industrial mass product, this powder shows a remarkably narrow particle size distribution.

larger amount of energy is transferred to the electrons, as compared to the energy transferred to the ions. In addition, an RF system works with frequencies up to the megahertz range; microwave systems are in the gigahertz range. Therefore, in a microwave system, there is six orders of magnitude less energy transferred to the charged particles as compared to an RF system. This favors low-temperature systems. In both cases, the plasma is not in thermal equilibrium; the "temperature" of the electrons is significantly higher than that of the ions or neutral particles. The "reaction temperature" is therefore an average value determined at the exit of the plasma zone.

Equation (1) is valid for one isolated charged particle in an oscillating electrical field only. The situation is different in a plasma, there, one finds free electrons, ions, dissociated gas and precursor molecules in addition to neutral gas species. Therefore, collisions between charged and uncharged particles limit the mean free path of the charged particles accelerated in the electric field. This influences the energy transfer to the particles. The collision frequency *z* of the gas species must therefore be considered²⁰⁾. This changes equation (1) to:

$$U \propto \frac{Q}{m} \frac{z}{f^2 + z^2} \tag{2}$$

Equation (2) shows the reduction of the energy transfer to the charged particles by collision with



other neutral species. The collision frequency z in the plasma depends on the gas pressure. As a rule of thumb, one can say: In a RF system, z is significantly larger than f; whereas in microwave systems, z and fare almost equal, usually, the gas pressure is adjusted such that the microwave frequency is larger than the collision frequency. This makes a significant difference. In RF systems, because of the short free path length of the electrons, the energy of the electrons is in the range of a few eV, whereas the energy of electrons in a microwave plasma is in the range of keV. Electrons with energies of just a few eV can attach to the surface of particles; this is different in the case of energy rich electrons, as they ionize the particles. Therefore, in RF systems, one expects negatively charged particles, whereas the electric charge of particles in microwave systems is positive. In both cases, in good approximation, the electric charge of the particles increases linearly with the particle diameter²⁰. Fig. 9 shows the charge of nanoparticles in an RF electrical field as a function of the diameter²¹.

The increasing charging of the particles with increasing diameter has severe consequences on the processes of particle coagulation and agglomeration. Particles with electric charges of equal sign repel each other. As the charge of the particles increases with increasing particle diameter, particles with larger diameters repel each other more than ones with smaller diameters. This suppresses the formation of larger particles and the formation of agglomerates.



Fig. 9 Average number of electric charges carried by a single nanoparticle. The particle charge increases linearly with the diameter over many orders of magnitude.²¹⁾ Reproduced by permission of Springer.



In other words: In a well-designed low-temperature plasma system for the synthesis of nanoparticles, one obtains particles with a narrow particle size spectrum.

3.2 RF Systems

As the energy transfer to the electrons is quite good, it is necessary to operate at relatively low gas pressures to avoid too high temperatures. Usually, the gas pressure is selected to be in the range between 0.1 and 1 mbar. Such a low gas pressure limits the production rates significantly. These processes are therefore only used to synthesize small quantities of highly specialized materials. A typical system using a capacitive-coupled plasma according to Anderson et al.²³ is shown in **Fig. 10**.

The designers of the equipment shown in **Fig. 10** claim that besides simple oxides, such a device allows the synthesis of complex oxides such as high-temperature superconductors and nitrides²⁵⁾. Generally, the synthesis of metal powders should be possible, too, provided that one finds a possibility to avoid condensation of the product on the walls of the reaction tube.

Well-suited for the synthesis of metal powders is the RF system shown in **Fig. 11**. By abandoning the advantage of an electrodeless system, the designers of the device shown in **Fig. 11** achieved a series of additional advantages. However, in this case also, the design is for small production quantities.

The design of Matsui²⁴⁾ works with a pulsed RF plasma. The pulse length is in the range up to 30s. As an example, the authors show the synthesis of FePt, a hard magnetic intermetallic compound. For both constituents, organic compounds were used as precursors. There was a steady flow of gas through the reaction zone, which is the space between two permeable electrodes. As long as RF power was on, the particles stayed in the reaction zone and grew. After switching off RF power, the particles moved out of the reaction zone and were collected. Therefore, with increasing pulse duration, the particle size increased. This behavior is shown in **Fig. 12**.

As the charge of the particles increased with increasing pulse time, coagulation and agglomeration of the particles was almost impossible. Therefore, for each pulse duration, a certain equilibrium particle size may be expected. Indeed, electron micrographs show that the particles are in a very narrow range of sizes. A typical electron micrograph of such a product is shown in **Fig. 13**.

This electron micrograph shows that all particles are of equal size. This batch was produced with a plasma-on time duration of 5s. The particles with a diameter in the range between 30 and 35 nm are almost spherical. The average size was about 33 nm and the





General layout of a capacitive-coupled RF system for nanoparticle synthesis working at reduced pressure. Fig. 11 Design of a system to synthesize nanopowders with a pulsed RF source. During synthesis and growing, the particles are kept in between the permeable electrodes²⁴. Reproduced by permission of Springer.





Fig. 12 Average particle size, obtained in a device according to Fig.
 11, as a function of the plasma duration, which is the dwell time of the particles in the plasma.²⁴ Reproduced by permission of Springer.

size variation was within \pm 12%.

3.3 Microwave systems

3.3.1 Microwave processes working under reduced pressure

A low-pressure microwave system promises the lowest reaction temperatures. One may therefore expect the least agglomerated product. And in fact, by an appropriate design of such a system, these promises can be fulfilled. Vollath succeeded as the first one to design such a system. It is shown in **Fig. 14**.

A long reaction tube that passes through a tuned microwave cavity characterizes this design. At the intersection between reaction tube and cavity, the plasma is ignited^{22,25)}. The evaporated precursors are transported with a carrier gas into the reaction zone. For the synthesis of oxides, oxygen is added to the carrier gas, and for nitrides it is ammonia. A typical oxide, ZrO₂, produced with such a system is shown in Fig. 15a. The product shown in Fig. 15a excels in a small variability of the grain size, an observation which is typical for this microwave plasma process. As mentioned in 3.1, in a low-pressure plasma process, the particles carry positive electric charges. One can prove this statement simply by adding water to the carrier gas. In this case, some of the water molecules dissociate and react with the particles: The positively charged particles are neutralized by collision with OH^{-} ions by the following process:

 $H_2 O \Rightarrow H^+ + (OH)^$ particleⁿ⁺ + n(OH)^- \Rightarrow (particleⁿ⁺ + n(OH)^-)^{neutral}

The neutralized particles carry a hydroxide layer



Fig. 13 Typical product obtained with an RF system according to Fig. 11.²⁰ Reproduced by permission of Springer.

at the surface. Besides this, as the particles are no longer repelling each other, one may expect larger particles with broad size distributions. In fact, exactly this behavior was observed experimentally. Fig. 15b demonstrates the outcome of this process. Fig. 15a shows the product with a narrow particle size distribution synthesized without water addition, whereas the product obtained after water addition is shown in Fig. 15b. What a difference! The product synthesized without the additions of water shows a grain size of around 8 nm. Most of the grains are of equal size, whereas the material produced with water additions is characterized by a broad distribution of particle sizes in the range from 10 to 50 nm. This dramatic difference between these two batches of the same material clearly demonstrated the validity of this simple model. It moreover proves that the particles are, in contrast to low-pressure RF processes, positively charged.



Fig. 14 Design of a microwave plasma system working at reduced pressure^{22,25}. The cut-off tube, an important part of the microwave design, prevents microwaves leaking outside of the cavity.





- Fig. 15 Electron micrographs of zirconia powders synthesized by the microwave plasma process from $ZrCl_4$ under different conditions²². Reproduced by permission of Springer.
 - **a** Typical product of the microwave plasma process obtained under water-free conditions. Please note the narrow particle size distribution, a consequence of the size-limiting effect of particle charging during synthesis.
 - **b** This product was obtained with water additions; the other parameters of synthesis were kept constant. As the positively charged particles are neutralized by (*OH*)⁻ groups stemming from the dissociated water, the size-limiting effect of particle charging is lost.

Zirconia is an example of a product with good crystallization properties . Many other products such as alumina, silica, etc. crystallize only poorly. In some cases, they form loose "cloudy" aggregates and not well-defined particles. Well-defined particles of alumina or silica are obtained only with high-temperature processes. On the other hand, such cloudy aggregates exhibit huge surfaces giving sometimes entirely new or significantly improved properties to the material. **Fig. 16** shows such a product.

Further products in the range of the possibilities of the low-pressure plasma process are nitrides, sulfides, selenides, etc. As an example, **Fig. 17** shows nanoparticulate zirconium nitride.

Fig. 17 highlights that the size-limiting phenomenon also works in the case of nitrides. In this example, the nitride was prepared from a reaction of the chloride with ammonia. Shimada et al.²⁷⁾ synthesized GaN successfully in a system using a resonant microwave cavity of different design with similar good success.

3.3.2 Synthesis of coated nanoparticles

There are additional possibilities to exploit the repelling phenomenon between the particles. The most attractive one is coating with a second phase. This second phase may be a ceramic or a polymer one. Coated nanoparticles are of special interest with respect to their physical properties. On the one hand, a coating acts as a spacer to reduce interaction of the particles, a property which is important, e.g. for magnetic particles, and on the other hand, coated particles allow the combination of different properties in



Fig. 16 Alumina, Al₂O₃ ex AlCl₃, as an example for a product that does not form particles under the low-temperature conditions of the microwave plasma process²⁰.



Fig. 17 Zirconium nitride synthesized with the microwave plasma process using the chloride and ammonia as precursors and nitrogen as the carrier gas²⁰.





Fig. 18 Cascaded arrangement of microwave plasma reactors to synthesize ceramic nanoparticles coated with a second ceramic phase ²⁷.



Fig. 19 Device to produce ceramic nanoparticles with a second stage to apply a polymer coating²⁸⁾.

one particle. A typical example is the combination of ferromagnetism and luminescence.

Fig. 18 shows the set-up to synthesize coated nanoparticles in a one-pass through process. The layout shown in the figure is for one coating; however, there is no serious problem in making two or even more coatings.

The device shown in Fig. 18 consists of two independent reaction zones connected by the reaction tube. The particles synthesized in the first reaction step act as a condensation seed in the second reaction zone. To avoid loss of the particle charges, it is important that the two reaction zones are as close as possible. Otherwise the particles will start to agglomerate before they are coated. However, for reasons of safety, it is not possible to bring the two reaction zones directly together, because at the end of each microwave cavity, a cut-off tube is needed to avoid microwave leakage. It is quite difficult to find a good compromise between microwave leakage and loss of particle charges. Replacing the second microwave cavity by a tubular furnace permits coating the particles with a polymer instead of a second ceramic phase. Fig. 19 shows such a system.

Typical examples of coated nanoparticles are

shown in **Fig. 20a** and **20b**. In **Fig. 20a**, a zirconia particle coated with alumina is shown. Please note the continuous coating of equal thickness around the particle. The same is visible in **Fig. 20b** which shows iron oxide particles coated with PMMA.

3.3.3 Microwave plasma processes working under ambient pressure

It was often tried to perform the process explained above at atmospheric pressure or with other simplifications. Typical designs are close to the one depicted in **Fig. 21**.

This kind of systems generates a plasma torch. The precursors are introduced after the plasma torch; therefore, the reaction zone is at a reduced temperature. However, as these systems work at atmospheric pressure, the mean free path length of the electrons is that small that within the reaction zone, number and energy of the remaining electrons is small. Therefore, particle charging and repulsion are poor. However, this design gives the chance to add downstream a second precursor to coat the particles synthesized in the first step. Additionally, the reaction temperature may be adjusted by varying the distance between plasma torch and precursor input.





Fig. 20 Examples of coated nanoparticles produced by the microwave plasma process operating under reduced pressure.

- a Zirconia particles coated with alumina.
- **b** Iron oxide particles coated with PMMA.

Comparing these products with those obtained by the low-pressure microwave process, the qualities of the products were not really satisfying. However, this may be wrong comparison. The competing products are those produced by RF processes. This comparison shows a competitive product.

Like in many other cases working at ambient pressure, the products of this plasma process are agglomerated with broad particle size distribution. **Fig. 22** shows silver particles produced by such an equipment.³²⁾

The powder shown in **Fig. 22** shows a broad spectrum of particle sizes. They range from fine fuzz to large facetted particles with diameter up to nearly 40 nm. As mentioned above, by using two consecutive supplies for the precursor, it is possible to produce coated particles, too. **Fig. 23a** shows pure cobalt powder and in **Fig. 23b** the same product, however coated with SiC.³²

Again, as it is characteristic for this type of processes, the particles show a broad size distribution. Additionally, these electron micrographs make clear that the particles are agglomerated; they are sintered together. Certainly, after coating these problems are not eliminated, in contrast, they got to be more severe. The differences in contrast visible in **Fig. 23b** show clearly the Co cores and the SiC coating.

4. Further Plasma Processes

4.1 Laser processes

In general, plasma processes driven by lasers may be subdivided into two groups:

• Laser ablation processes working with solid targets and



Fig. 21 Microwave plasma system working under ambient pressure. This design with two consecutive inputs for precursors allows the production of something like coated nanoparticles.^{30:34)}



Fig. 22 Silver particles produced in a system according to Fig. 21.³¹⁾ Reproduced by permission of Elsevier.





- Fig. 23 Cobalt and cobalt/silicon carbide particles produced in a microwave device at ambient pressure according to Fig. 21
 - a Cobalt particles forming chain-like agglomerates.
 - b~ Cobalt particles coated with SiC. The dark particles represent cobalt particles, the lighter material consists of SiC. $^{\rm 320}$

• laser processes working with gaseous targets. These processes have in common that the beam of a laser is focused to a spot. The intensity in the focus is so high that the gas phase is ionized; plasma is formed and responsible for the further progress of the reaction leading to particle synthesis. Also for these processes a wealth of literature exists, however, it is possible to extract a few characteristic design features.

Fig. 24 shows the general layout of a synthesis device according to the laser ablation process.

In the laser ablation process, a high intensity laser beam is focused onto the surface of a target. The target may be a pure metal or oxide, or even a mixed system. Because of the high-energy input coming from the pulsed laser, the material of the target is vaporized instantaneously. This process preserves even the stoichiometry of a complex mixed target in the vapor phase. The intense electrical field of the laser beam ionizes the vapor; a supersonic jet of evaporated material, a plume, is ejected perpendicular to the surface of the target. The temperature in the plume reaches values of 3800 K and more.³⁵⁾ During the adiabatic expansion of the plume, the temperature decreases and, as the vapor gets supersaturated, particles are nucleated. Within the short time interval of supersaturation, the particles are formed. The lower the gas pressure in the system, the faster expands the plume; the shorter is the time for particle formation. This limits particle growth. However, with



Fig. 24 Design of an experimental device for powder synthesis according to the laser ablation process. The high intensity laser beam focused at the surface evaporates the target, metal or oxide. This leads too a plume, a supersonic jet of evaporated material, ejected perpendicular to the target surface. A carrier gas containing reactive gas components; to such as oxygen to obtain oxides, methane for carbides, and ammonia for nitrides, transports these particles to the powder collector.





Fig. 25 Average diameter of $C_{0_3}O_4$ particles produced by the laser ablation process. It is important to realize smallest sizes of the particles at the lowest and highest gas pressure.³⁶⁾

increasing supersaturation, the number of nuclei increases, a process that leads to small particles, too. In reality, one observes a complicated interaction between these two mechanisms. Experimental results on the dependency of the particle size as function of the gas pressure are shown in **Fig. 25**.

It is remarkable to see that one obtains the smallest crystallites at low and at high pressure; in the intermediate range one finds the largest particles. However, this is just half of story. Due to the high particle density in the expanding plume, there is a high probability that the particles form agglomerates. The probability of cluster formation is highest at high gas pressure, a finding that is well understood by the high particle density in the plume. By proper selection of the process parameters, agglomeration can be controlled to some extent. **Fig. 26** shows as a typical example Fe₂O₃ synthesized by this process.³⁷

In this figure, one additional problem of the laser ablation process, which is typical for all gas phase processes working with high particle densities, is visible: The particle size distribution is very broad.

The second plasma process, driven by a laser, works with a gas target. A typical design is shown in **Fig. 27**.

It is typical for successful designs of laser gas phase synthesis that the focus of the laser is directly above the orifice, where the gaseous precursor and the reaction gas enter, already premixed, the reaction vessel. At this point plasma is formed. In the laser focus, similar as in the laser ablation process, the concentration of reactants is extremely high. Therefore, also this process suffers from the tendency to form agglomerates. **Fig. 26** shows as a typical example Fe_2O_3 synthesized from iron carbonyl, $Fe(CO)_5$.³⁸⁾

The product depicted in Fig. 28 shows the typical



Fig. 26 Fe₂O₃ particles produced by the laser ablation process. The particles are well-separated particles with relatively broad size distribution.³⁷ Reproduced by permission of Elasevier.



Fig. 27 Set-up of a system for nanoparticle synthesis using a laserdriven plasma with a gas target.

chain-shaped agglomerates which are characteristic for these processes. This micrograph shows clearly that the particles are sintered together.

Often, the absorption of optical energy by the precursor or the carrier gas is not sufficient. In these cases, the addition of sensitizer gases that have a high degree of absorption in the wavelength range of the laser, is helpful. Because of its wide availability,





Fig. 28 Iron oxide, Fe₂O₃ ex Fe(CO)₅, synthesized in a system according to Fig. 27. In this electron micrograph, it is clearly visible that the particles are sintered together in chains.³⁸⁾ Reproduced by permission of Elsevier.

the application of CO₂ lasers emitting in the infrared field is very common. However, the absorption of the 10.6- μ m emission is, in general, very poor. Therefore, the addition of SF₆, which is a perfect absorber especially for this type of radiation, is widely used³⁸⁴⁰. Additions of ethylene, C₂H₂, are also described. This measure, naturally, does not have only advantages. A typical example of an adverse by-effect was reported by He et al.³⁹. For the synthesis of nickel nanopowders from the carbonyl, these authors added SF₆ to improve optical absorption. In the reaction product, besides the intended nickel particles, NiF₂ was detected. However, these unavoidable side reactions may be used to obtain very special products. In an experiment using Fe(CO)₅ as a precursor, C_2H_2 as a carrier gas and SF₆ as a sensitizer, David et al.⁴⁰⁾ synthesized *a* -Fe particles embedded in graphite. The carbon used for the embedding graphite stemmed from the C₂H₂, dissociated in the laser plasma. Although the reaction rate and particle density in the plasma are high, the resulting product did not lead to coated particles as they are obtained in the microwave plasma process.

4.2 Flame processes

As mentioned in the introduction, flames may be considered as "partial plasmas", however, until now, there is only one attempt to exploit this property. The plasma properties of flames are utilized in the combination with electrical fields. This may be a microwave field to introduce more energy or a DC field to separate electrical charges according to their sign. Pratsinis and co-workers studied the latter possibility^{41,42)}. One of the possible configurations is shown in Fig. 29a. It shows a flame emerging from a system of orifices, which can be similar to the ones depicted in Fig. 1, located between two plate electrodes. Fig. 29b shows this arrangement in operation. The electrical field strength was below 2 kVcm⁻¹. With increasing strength of the electric field, this arrangement leads to a significant reduction of the particle size. It was found that the width of particle size distribution reduces with increasing electrical field strength. The important point, visible in Fig. 29b, is that powder is collected at the surface of both electrodes.

Analyzing the experiments as shown in Fig. 29,



Fig. 29 Set-up to synthesize nanoparticulate powders in flames connected to transversal electric fields between plate electrodes.

- a Experimental set-up.
- **b** Appearance of a flame producing TiO_2 ex TiCI_4 in a methane-oxygen flame with transversal electrical field. The electric field broadens and splits the flame. Particles charged electrically with different sign are attracted by the plate electrodes and deposited⁴¹.





- a Reference material produced without an electric field.
- **b** Product obtained by applying a transversal electrical field of 1.6 kVcm¹ between plate electrodes. Compared to **Fig. 30b**, this material shows a reduced particle size and a reduced degree of agglomeration.





the most important observation is that the field strength of less than 2 kVcm⁻¹ is by far not sufficient to ionize the gas molecules or the particles. However, the temperatures of around 2500 K in the flame lead to thermal ionization of gas molecules or particles; even ionization of the particles with free electrons accelerated in the electric field is conceivable. Therefore there is a high probability that the particles carry electric charges. Because of the atmospheric pressure of the system, the energy of most of the free electrons is small. Therefore, the attachment of free electrons to the surface of uncharged particles is also possible. These processes lead to particles carrying electric charges of both signs that are separated in the electric field and which move in the direction of the different electrodes. As a result, the probability for agglomeration is reduced. Experimental results confirm these predictions perfectly. As Fig. 29b shows, the electrically charged particles are pulled out of the flame and are deposited at the surface of the electrodes. The almost equal thickness of the particles at the electrode plates indicates an equilibrium of the electrically charged particles in the flame $^{41,42)}$.

Fig. 30a and **30b** compare the products synthesized under identical conditions except for an electrical field between plate electrodes. The result is striking. Without an electrical field, the particles are found to be in a size range between 10 and 40 nm; the application of an electrical field of 1.6 kVcm⁻¹ reduces the particle size to a range between 5 and 10 nm. A remarkable result!

5. Conclusions

It has been shown that there is a wide variety of plasma processes that are well-suited for the synthesis of nanoparticulate powders. One may subdivide these processes into two groups:

- To produce larger quantities of powders where uniformity of the particle size distribution is not that important, plasma processes at atmospheric pressure are well suited. The plasma may be energized either with RF or microwave generators. Nowadays, both types of systems are fully developed and engineered. The development in electronic systems at least in the power range up to a few kilowatt made microwave systems cheaper as compared to RF systems. Furthermore, the design of microwave systems is significantly simpler than that of RF systems.
- To obtain highly specialized products, lowpressure microwave processes are unrivalled. Over and above this, this process also allows the synthesis of coated particles. However, it may be problematic to produce particles with good electric conductivity.

The analysis of the literature revealed that products stemming from laser processes were not accorded any importance, neither in science nor in technology.

Plasma processes combining flames with electric fields may have a high potential for further development, especially since they may be well-suited to the production of larger quantities of good quality.



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Author's short biography



Dieter Vollath

Dieter Vollath, head of NanoConsulting, is since more than 15 years engaged in the field of nanomaterials. After working twelve years in the field of nanomaterials at Forschungszentrum Karlsruhe, Germany, in 2003, he founded NanoConsulting (www.nanoconsulting.de). At Forschungszentrum Karlsruhe, his activities were primarily in the field of synthesis, properties, and application of ceramic nanoparticles. With respect to synthesis, he developed the microwave plasma process, the only gas phase route for synthesis that applicable for synthesis of coated nanoparticles. In the field of properties, optical and magnetic properties were in the foreground.

NanoConsulting is devoted to help small and medium sized companies, to step into this new technology or to apply nanomaterials in their products. NanoConsulting is also engaged in education in the field of nanomaterials. Within this business area, NanoConsulting organizes courses that are specific for different companies or which are for open for any attendees. In parallel, Dieter Vollath is professor at the University of Technology in Graz, Austria. Within these obligations, he gives courses on "Ceramic Materials" and "Nanomaterials". Dieter Vollath wrote a textbook on nanomaterials that appeared in January 2008 at WILEY-VCH.



Characterization of the Wetting and Dewetting Behavior of Powders[†]

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Abstract

Experimental procedures for characterizing the wetting behavior of powders are reviewed. The fundamental processes involved in wetting – passage from one state of two-phase equilibrium (solid/gas and liquid/gas) through a three-phase condition (solid/liquid/gas) to a second two-phase condition (solid/liquid and liquid/gas) – are evaluated. A brief discussion of the use of chemical agents such as surfactants to control wetting/dewetting behavior is also included. Characterization procedures, ranging from direct measurement of three-phase contact angles to indirect measures based on observation of the behavior of particles at liquid/gas interfaces are described. For large pieces of solid, contact angles can be determined by direct observation of liquid drops or gas bubbles in contact with polished surfaces. The problems associated with applications of this approach to packed beds of powder are discussed. A procedure for estimating apparent contact angles from the relative partitioning of small particles across an interface is presented. Estimation procedures based on static and dynamic measurements of liquid penetration into powder beds are evaluated. While indirect methods do not generally provide values of well-defined quantities such as contact angles, when appropriately selected they can yield quantitative information directly relevant to practical applications. Various indirect methods including film flotation, the Hallimond tube, bubble pick-up, induction time, immersion/sink time, imbibition time and wetting rate are described. Investigation of wetting phenomena at the molecular scale using techniques such as atomic force microscopy is discussed.

Keywords: Wetting phenomena, Powder wetting, Contact angle determination, Wetting eriteria, Indirect measurs of Wettability

1. Introduction

Wetting phenomena are of critical importance in practical applications involving mixtures of powders and liquids. Wetting can be defined as the process of displacement at a solid surface of one fluid by another. In general, the fluids may be a liquid and a gas or two immiscible liquids, though the term is most commonly applied to the displacement of a gas by a liquid. In the case of powders, most applications are directed at the preparation of a suspension of the particles in a liquid or coating the particles with liquid in a paste. The use of liquids for dust control is another important application. The reverse process – displacement of liquid by gas – is important in applications such as filtration where gas displacement is used to reduce the liquid content of filter cakes and froth flotation where solid-solid separations are achieved following selective attachment of particles to gas bubbles.

Wetting behavior is essentially determined by interaction forces at the different solid-fluid and fluid-fluid interfaces. However, the approach to an equilibrium configuration of the phases can be strongly affected by the viscosity of the fluids. In fact, such viscous effects can make the final approach to equilibrium exceedingly slow leading to hysteresis phenomena. Surface modifications of the solid – for preparing socalled "wettable powders" – or the addition of surface active agents to the liquid are widely used to enhance

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wettability. Characterization of wetting behavior is an important component of these applications. In principle, wetting behavior could be predicted from a knowledge of the interfacial tensions involved. Unfortunately, however, solid-fluid interfacial tensions are not amenable to simple measurement. Theoretical treatments¹⁻⁴⁾ based on the intermolecular forces involved in wetting phenomena have provided some predictive capability, especially when the interactions are dominated by London-dispersion types of forces. Essentially, this approach involves breaking down the interfacial tensions according to the contribution of each type of force acting - polar (e.g., acidbase), non-polar, etc. Prediction of wetting behavior requires knowledge of these contributions for each of the phases involved. The lack of such information seriously limits the general application of this approach at this time. Consequently, it is usually necessary to apply less direct methods – including pure empiricism-to characterize wetting behavior. Our objective in this article is to present a critical review of the various techniques available for evaluating the wetting behavior of powders.

Background

Three distinct stages in the wetting of a solid surface can be defined⁵⁾. The first stage, *adhesional wetting*, refers to the establishment of a three-phase contact at the solid surface. *Spreading wetting* involves displacement of one fluid by the other at the solid surface. Finally, *immersional wetting* represents the complete transfer of a solid particle from one fluid phase to the other. Obviously, the three stages must proceed sequentially and, depending on the various interaction forces, may be interrupted after any stage. In the case of porous media such as a bed of powder, capillary forces, due to curvature of the interface between the fluid phases, also play a role, either enhancing or impeding the spreading phenomenon. This type can be defined as *capillary wetting*.

The process of complete wetting represents passage from a condition of two-phase equilibrium (solid-gas and liquid-gas) through a state of threephase contact (solid-liquid-gas) to a final stage of twophase equilibrium (solid-liquid and liquid-gas). If conditions favor spreading, wetting proceeds spontaneously to the fully immersed state. Otherwise a final state of partial wetting – three-phase equilibrium – is reached.

Thermodynamically, the free energy changes involved in the different stages can be expressed as follows:

$$\Delta G_A = \gamma_{SL} - \gamma_{SV} - \gamma_{LV} \tag{1}$$

$$\Delta G_s = \gamma_{sL} - \gamma_{sV} + \gamma_{LV} \tag{2}$$

$$\Delta G_I = \gamma_{SL} - \gamma_{SV} \tag{3}$$

where ΔG_A , ΔG_S and ΔG_I are the free energy changes (per unit area) corresponding to adhesion, spreading and immersion respectively. γ_{SL} , γ_{SV} and γ_{LV} are the respective solid-liquid, solid-vapor and liquid-vapor interfacial tensions. Capillary wetting involves changes in the solid-liquid and solid-gas interfaces only and is, therefore, a special case of immersional wetting and the same thermodynamic relationship applies at equilibrium. It should be noted, however that capillary forces can significantly affect the approach to equilibrium, i.e., the kinetics of wetting.

The thermodynamic relationships can also be expressed in terms of the *work of adhesion* W_A and the *spreading coefficient* S_{LS}. The work of adhesion is defined as the work required (per unit area) to separate the solid from the liquid so that, W_A = - Δ G_A. Similarly, the spreading coefficient is defined such that S_{LS} = - Δ Gs. The conditions corresponding to three-phase equilibrium (partial wetting) can be conveniently characterized by means of the *contact angle* θ defined, through the liquid phase, as shown in **Fig. 1**. Thermodynamically, the three-phase equilibrium can be expressed by Young's equation:



Fig. 1 Contact angle at a solid surface as measured through the liquid phase.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{4}$$

By substitution from Equation 4, the free energies given by Equations 1-3 can also be expressed in terms of the contact angle. Thus,

$$\Delta G_A = -\gamma_{LV} (1 + \cos \theta) \tag{5}$$



$$\Delta G_S = \gamma_{LV} (1 - \cos \theta) \tag{6}$$

$$\Delta G_I = -\gamma_{LV} \cos\theta \tag{7}$$

The variation of these free energy changes with contact angle is illustrated in **Fig. 2.** It should be emphasized that Equations 4-7 are valid only when the three-phase contact is stable, i.e., when



Fig. 2 Relative free energy changes involved in different stages of wetting.

$$-1 \leqslant \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}\right) \leqslant 1$$

Otherwise, there is no contact angle, spreading is spontaneous and the equilibrium condition corresponds to two-phase contact. A zero contact angle describes a limiting condition such that

$$\gamma_{\scriptscriptstyle SV} - \gamma_{\scriptscriptstyle SL} \geqslant \gamma_{\scriptscriptstyle LV}$$

Similar arguments apply to contact angles of 180° . While 180° angles do not occur in solid-liquid-gas systems, the full range is possible for solid-liquid-liquid contact. When the contact angle is finite ($0 \leq \theta \leq 180^{\circ}$), the two phase contact is unstable in the presence of the third phase – liquid droplets or gas bubbles adhere to the solid surface.

Spreading is a prerequisite for immersional wetting, and Δ Gs can be regarded as an activation energy for wetting by immersion. For contact angles less than 90°, transfer of a solid particle from the gas to a liquid phase (immersion) leads to a lowering of the free energy and is, therefore, favored. However, in order to reach the immersed state, additional energy must be supplied to overcome the increase in free energy associated with spreading. The three-phase equilibrium resulting from adhesion represents the most stable configuration (minimum free energy) in all cases. As a result, spreading is the critical stage in the overall wetting process.

Zisman⁶⁾ showed, empirically, that plots of the cosine of the contact angle for a series of liquids on a given solid surface against the liquid surface tension typically showed a linear relationship. Extrapolation of the plots to zero contact angle ($\cos \theta = 1$) yields the value of the *critical surface tension* γ_c which is characteristic of the solid. The contact angle becomes zero when $\gamma_{LG} = \gamma_c$. Liquids whose surface tension is less than y_c wet the solid completely and the threephase contact is no longer stable. It follows that $\gamma_{\rm c}$ represents the limit of applicability of Young's equation and relationships such as Equations 5 - 7 derived from it. An example of a Zisman-type plot for a set of liquids on a bituminous coal surface is given in Fig. **3.** Extrapolation of the quantity $(\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ to values greater than unity is, of course, arbitrary.



Fig. 3 Zisman plot showing the wetting behavior of a bituminous coal (based on experimental data of Parekh and Aplan [7]).

Substantial control over wetting behavior can be obtained through the addition of surface-active agents to the liquid phase. So-called wetting agents enhance spreading by reducing the liquid-gas or solid-liquid interfacial tensions (or both). On the other hand, the *collectors* used in mineral separations by froth flotation promote bubble attachment to the solid surface by reducing the solid-liquid interfacial tension through adsorption. Wetting behavior can also be controlled by appropriate chemical or physical modification of the solid surface either to enhance or impede spreading by the liquid. Mineral flotation is a process whereby one mineral is separated from another by an organic reagent that adsorbs on the selected mineral to make it hydrophobic. The attachment of an air bubble to a solid immersed in water is governed by relations similar to Equations 2-4 and 5-7. The free energy change, ΔG_{flot} , for the attachment of an air bubble to a solid is simply

$$\Delta G_{flot} = \gamma_{LV} \left(\cos \theta - 1 \right) \tag{8}$$

which means that any time the contact angle is greater than zero, the bubble should attach.

The development of suitable reagents or surface treatments for practical applications to the control of wetting or dewetting behavior requires reliable, quantitative procedures for evaluating wetting characteristics.

Characterization of Wetting/Dewetting Behavior

Techniques for evaluating wetting characteristics range from direct measurement of contact angles to indirect measures based on observation of the behavior of particles at liquid-gas interfaces.

Contact angle Measurement

Direct observation

The classical technique for determining contact angles is direct observation of a sessile drop of liquid on a highly polished, clean surface of the solid. Problems of simultaneously focussing on the solid surface and that of the liquid drop can be avoided by measuring the (double) angle between the surface of the actual drop and that of its reflection in the polished surface. Hysteresis effects, whereby the measured angle varies according to whether the liquid is advancing or receding at the surface, are commonly encountered. The causes of these effects are not fully understood but probably include pinning of the threephase boundary at surface inhomogeneities, natural imperfections or induced patterns, or contamination. Viscous effects due structuring in the liquid adjacent to the interface may also contribute.

An alternative approach (restricted to transparent liquids) is to immerse the solid in the liquid and observe the angle in a captive bubble brought into contact with the solid. The use of sessile drops is generally preferred for measuring liquid-advancing angles while the captive bubble approach offers advantages for liquid-receding angles. If the liquid surface tension is known accurately, uncertainties in direct contact angle measurements can be reduced by comparing observed drop (or bubble) shapes to theoretical profiles calculated using the tables of Bashforth and Adams⁸ and Blaisdell^{9,10}.

Obviously, the direct methods are impractical for measurements on fine powders. Measurements on large pieces of the same material may be inappropriate due to surface modifications that might have occurred during preparation of the powder. In some cases, it is possible to press the powder into a sufficiently coherent pellet for measurements to be made. However, since the use of binders during pellet preparation must be avoided, it is rarely possible to obtain a high polish on the surface and problems arise due to surface roughness and penetration of the liquid into pores. Hysteresis of the measured contact angle is particularly common when powder compacts are used. Nevertheless, this approach is useful for evaluating changes in wetting behavior where absolute values of the contact angle are not required – in studies of the effect of reagent concentration, for example.

Kossen and Heertjes¹¹⁾ described a procedure based on the contact angle of a liquid drop resting on the composite (solid + liquid) surface of a powder bed saturated with the liquid. Interpretation of the results involves some questionable assumptions regarding the structure of the porous surface and the general applicability of the method appears not to have been demonstrated.

Interface partitioning

When a small particle resides at the interface between two fluids, its relative immersion in each depends on the contact angle. If gravity can be neglected relative to the surface tension forces, the equilibrium location of a spherical particle at the interface will be as shown in **Fig. 4.** The interface between the two fluids meets the particle surface at the contact angle, which can be calculated from the fraction of the cross-sectional area that projects into the upper phase.



Fig. 4 Location of a solid particle at the interface between two fluids

From the geometry of Fig. 4, the area A_1 is given by:

$$A_1 = R^2 \left(\theta - \sin \theta \cos \theta\right) \tag{9}$$

where R is the particle radius and θ is the contact angle in radians. The total cross-sectional area A is equal to πR^2 so the relative area is given by



$$\frac{A_1}{A} = \frac{(\theta - \sin\theta\cos\theta)}{\pi} \tag{10}$$

Using Equation 10, the contact angle can be calculated from a measured value of the relative area A₁/A. The use of simple image-analysis techniques permits measurements to be made very rapidly. This method is especially useful for determining distributions of wettability in collections of particles¹². The need to minimize the effects of gravity restricts the use of this technique to particles smaller than about 1 mm, depending on relative density. Lower size limits are related to optical considerations. Measurements have been reported on particles as small as about 100 μ m¹². Placing a dry particle at the interface provides a measure of the liquid-advancing angle while prewetted particles give the liquid-receding angle.

Examples of contact angle distributions for spherical polymethylmethacrylate beads and irregular polyethylene and bituminous coal particles are shown in **Fig. 5.** It can be seen that the homogeneous spheres have a very narrow distribution, probably reflecting minor variations together with experimental error. The homogeneous but irregularly shaped polyethylene particles show a somewhat broader distribution while that for the coal is much broader, presumably due to heterogeneity of the material.



Fig. 5 Contact angle distributions for spherical polymethylmethacrylate beads (PMM) and irregular polyethylene (PE) and coal particles (data from Wei et al., [12]).

Liquid penetration

While direct measurements of contact angles on fine, micron-size particles are generally impractical, quantitative estimates can be obtained from studies of the penetration of fluid into (or expulsion from) a powder bed. If the pores in a packed bed are regarded as a system of fine capillaries, the capillary pressure in the bed can be described by a form of the Laplace equation:

$$\Delta p = \frac{2\gamma_{LV}\cos\theta}{r_p} \tag{11}$$

where r_p is the effective pore radius. The capillary pressure can be determined from measurements of the equilibrium capillary rise in the bed, or of the applied pressure needed either to prevent ($\theta < 90^\circ$) or to cause penetration ($\theta > 90^\circ$) into the bed¹³. The effective mean pore radius can be estimated from¹⁴

$$r_p \cong \frac{2\varepsilon}{S_v \left(1 - \varepsilon\right)} \tag{12}$$

where ε is the porosity of the bed and S_v is the volume specific surface area of the powder. Alternatively, the pore radius can be eliminated by measuring the capillary pressure for a wetting liquid ($\theta = 0$), so that:

$$\cos\theta = \frac{\gamma_w \Delta p}{\gamma_{LV} \Delta p_w} \tag{13}$$

where γ_{w} and Δp_{w} refer to the wetting liquid.

Common to each of these methods is the problem of preparing a uniform bed of particles. This is especially difficult in the case of capillary rise measurement where very thick beds-up to several meters for fine powders-may be required. The use of Equation 13 requires a high degree of reproducibility as well as uniformity in bed preparation, since measurement with the wetting liquid must be on a separate bed. Direct estimation of the pore radius from Equation 12 is subject to additional errors due to the approximations involved and the sensitivity of the equation to the bed porosity.

The rate of capillary rise can be used as an alternative to the equilibrium height, thereby substantially reducing the required bed depth. In this case, the capillary pressure is substituted into standard expressions for the rate of flow through a porous bed leading to the Washburn equation¹⁵.

$$h^2 = \frac{R_f \gamma_{LV} \cos \theta}{\mu} t \tag{14}$$

where h is the height of liquid in the bed after time t, μ is the viscosity of the liquid and R_i is a geometric factor related to the effective mean pore radius in the bed. The slope of a plot of h² against time is a measure of the quantity R_i cos θ .

Again, it is common to use measurements with a wetting liquid ($\cos \theta = 1$) to estimate R_f. It should be noted, however, that the capillary pressure given by Equation 11 is valid at equilibrium or for cases where the contact angle is finite. For wetting liquids, the γ_{LV} $\cos \theta$ term should be replaced by ($\gamma_{SV} - \gamma_{SL}$), which



is only equal to $\gamma_{\rm LV}$ at the critical surface tension $\gamma_{\rm c}$. It follows that estimates of $r_{\rm p}$ based on different wetting liquids may vary. Wolfrom et al.,¹⁶ have suggested a procedure for avoiding this uncertainty through the use of two or more wetting liquids. Obviously, the problem of preparing uniform beds reproducibly is especially critical in these applications. A standardized procedure for bed preparation has been suggested¹⁶. It should also be noted that this technique is not suitable for liquids of high viscosity for which bubble entrapment can lead to significant errors and poor reproducibility.

Procedures based on the use of thin layers of particles deposited on a substrate have also been described¹⁷⁾. Uniformity of the pore structure may be particularly difficult to achieve using this approach. Again, standardization of the specimen preparation procedure and thorough evaluation of reproducibility are necessary if meaningful results are to be obtained.

The use of short columns of powder is advantageous with respect to bed uniformity and minimization of gravity effects for vertical orientations. However, accurate measurement of penetration depth is more difficult. The latter can also present problems with opaque particles where direct observation of the liquid interface becomes difficult. The use of gravimetric methods with continuous weighing of a particle bed in contact with a fluid reservoir can substantially improve the accuracy of depth measurement. At the same time, however, the results are more sensitive to bed porosity and uniformity. The mass of liquid in the bed is given by

$$m = \rho \varepsilon A_b h \tag{15}$$

where ρ is the liquid density and A_b is the crosssectional area of the bed. Thus, the equivalent to Equation 14 is:

$$m^2 = \frac{c\rho^2 \gamma_{LV} \cos\theta}{\mu} t \tag{16}$$

where the geometric factor c is given by:

$$c = \varepsilon^2 A_b^2 R \tag{17}$$

which is significantly more sensitive to variations in porosity than R_i.

Examples of capillary rise measurements on beds of glass beads are presented in **Fig. 6**. The quantity $\mu \text{ m}^2 / \gamma_{\text{LV}} \rho^2$ is plotted to permit direct comparison of the results, allowing for differences in liquid density



Fig. 6 Replicate tests of capillary rise rates for hexane, decane and formamide in packed beds of hydrophobic glass beads (200 × 600 US mesh) (data from Wolfrom et al., [16]).

and viscosity. It can be seen from the replicate test results that quite good reproducibility can be obtained. Statistically, the results for hexane and decane ($\gamma_{LG} =$ 18.4 and 23.8 dynes/cm respectively) fall on a single line, from which the constant c can be obtained. However, if the constant is estimated from just one of the set of hydrocarbon tests, contact angle estimates for the other tests can range from zero to as much as 28°, indicating the very high sensitivity of this technique to small errors, particularly for determining low contact angles. On the other hand, the use of a value of the constant obtained from any of the hydrocarbon results gives a much narrower range (66.5–69.3°) for the contact angle for formamide ($\gamma_{LV} = 58$ dynes/ cm).

In general, the penetration methods can provide a reasonably quantitative comparison of the wetting of a solid by different liquids, but actual estimates of contact angles should probably be regarded as approximate at best. These methods normally provide an estimate of the liquid-advancing contact angle. However, the capillary pressure approach can also be used, by studying expulsion of liquid from a bed, to investigate liquid-receding angles.

Indirect Measures of Wetting Behavior

Information on wetting characteristics can also be acquired from observations of the behavior of particles at liquid-gas interfaces. While these tend to be somewhat qualitative and do not yield values of, for example, contact angles, they can provide useful measures of relative wettability and can be used to estimate quantities such as the Zisman critical surface tension γ_c .



Film Flotation

In order to devise a method for characterizing the wetting behavior of heterogeneous coal particles, Fuerstenau and Williams¹⁸⁾ developed a novel technique that they called film flotation, wherein a given sample of particles is portioned into hydrophobic and hydrophilic particles using aqueous methanol solutions of different surface tensions, with which the surface tension of the liquid can be varied from 72.8 to 22.5 mN/m.

The film flotation technique simply involves placing the test solution in a small vessel 75 mm in diameter and 20 or 30 mm in depth. Having the lower part of the vessel conically shaped, separation of particles that sink is readily achieved by draining some of the liquid. Generally enough particles are added so that a monolayer remains on the surface. In the case of coal, this may range from 0.06 to 0.3 gram, depending on the particle size being tested.

Their initial work was with coal particles, which are by nature heterogeneous. As the surface tension is varied, particles sink under conditions when the contact angle just approaches zero, that is the process is controlled by spreading wetting. This yields surface tension-vs-percent hydrophobic fraction distribution diagrams, from which the distribution and the mean critical wetting tension of the particles can be determined. Careful experimentation showed that virtually identical results are obtained with aqueous solutions of methanol, ethanol, propanol, tertiary butanol, and acetone^{18, 19)}. Since interfacial forces are so dominant, particle size does not have an appreciable effect, as found for 425 × 300- µ m, 300 × 212, 212 × 150, 150 × 106, 106 × 75 and minus 75 × 53- µ m Cambria #78 coal particles¹⁹.

Because of the heterogeneity of coal, the wetting behavior of particles in the sample may change continuously from that of hydrophobic organic materials to those of hydrophilic inorganic matter. To illustrate this, Fig. 7 presents the cumulative distribution of hydrophobic Cambria #78 coal particles as a function of their wetting surface tension, as obtained by film flotation with aqueous methanol solutions. From the results given in Fig. 7, the frequency distribution of the critical wetting surface tension of Cambria #78 coal particles can be determined since every point along the curve in Fig. 7 must represent particles for which the contact angle is zero. The frequency distribution plot is presented in Fig. 8. These two figures clearly show the heterogeneous nature of the surface of coal particles. In contrast, ideal homogeneous particles will have the same critical wetting surface ten-



Fig. 7 Partitition curve obtained from the film flotation response of Cambria #78 coal as a function of the surface tension of aqueous methanol solutions (data from Jia [29]).



Fig. 8 Frequency histogram for the distribution of the wetting surface tension of 100×150-mesh Cambria #78 coal particles (data from Jia [29]).

sion, that is, the cumulative plot is a vertical line that gives the sharp demarcation between sink and float surface tension¹⁹⁾.

From such a distribution, four wetting parameters have been defined. The critical wetting surface tension of the most hydrophobic particles in the assembly, γ_c^{\min} , is the surface tension of the liquid at which none of the particles remain (float) at the liquid surface. The critical wetting surface tension of the most hydrophilic particles in the powder, γ_c^{\max} , is the surface tension of the liquid at which all particles remain at the liquid surface. The mean critical wetting surface tension of all particles, $\overline{\gamma}_c$, can be calculated from the film flotation frequency distribution using the equation:

$$\bar{\gamma}_{c} = \int \gamma_{c} f(\gamma_{c}) d\gamma_{c}$$
(18)

where γ_c is the critical wetting surface tension of the

particles and f (γ_c) is the frequency distribution function. The standard deviation of the frequency distribution function, $\sigma_{\gamma c}$, reflects the heterogeneity of the surface and is given by

$$\sigma_{\gamma_c} = \left[\int \left(\gamma_c - \bar{\gamma}_c \right)^2 f\left(\gamma_c \right) \, d\gamma_c \right]^{1/2} \tag{19}$$

High values of $\sigma \gamma_c$ correspond to more heterogeneous materials. **Fig. 7 and 8** show the three wetting surface tensions that can be determined from film flotation experiments.

The critical wetting surface tension is an important parameter that can be used as an index of the wettability of a solid. As defined by Zisman⁶, it is the surface tension of a liquid that just forms a zero contact angle on the solid. Both theoretically and experimentally for film flotation the critical wetting surface tension of hydrophobic particles can be taken to be the surface tension of the liquid at which the particle just sinks into the liquid. The contact angle of those particles that sink at the given surface tension is essentially zero since the effect of particle size and density are sensibly negligible in the practical size range.

Since the contact angle of a small particle cannot unambiguously be determined directly, it is useful to find a way to assess its value from other kinds of experiments. In the approach developed here, it is necessary to know the value of γ_c for the individual particles²⁰. Since any point along a film flotation plot (a plot of the fraction of particles floating versus the liquid surface tension) represents conditions for zero contact angle at a specific surface tension, the distribution of wetting surface tensions obtained from film flotation results is the starting experimental information needed to evaluate contact angles.

The theoretical basis for this begins with the Neumann-Good Equation of State²¹⁾:

$$\gamma_{SL} = \frac{\left(\sqrt{\gamma_{SV}} - \sqrt{\gamma_{LV}}\right)^2}{1 - 0.15\sqrt{\gamma_{SV}\gamma_{LV}}}$$
(20)

where γ_{SV} , γ_{SV} and γ_{SV} are the interfacial energies (in erg/cm²) at the solid/vapor, solid/liquid and liquid/vapor interfaces, respectively. Substituting this into the Young Equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \tag{21}$$

yields

$$\cos \theta = \frac{(0.015 \gamma_{SV} - 2.00) \sqrt{\gamma_{SV} \gamma_{LV}} + \gamma_{LV}}{\gamma_{LV} (0.015 \sqrt{\gamma_{SV} \gamma_{LV}} - 1)} (22)$$

The contact angle θ of a particle for a liquid of a given surface tension can be calculated with Equation 22 using the values of γ_c measured by film flotation. The basis for this is taking γ_c as being equivalent to γ_{sv} , an assumption discussed by Neumann et al²¹⁾.

Many materials are nonhomogeneous, probably the most significant being coal. Because coal is a complex mixture of carbonaceous substances and inorganic minerals. the surface of coal will be a patchwork assembly of hydrophobic and hydrophilic areas. To simplify calculations, only two types of sites will be considered: hydrophobic (paraffin-like) sites with a water contact angle of 105° and hydrophilic sites with a water contact angle of 0° ²⁰⁾. Using the Cassie equation²²⁾, it is possible to evaluate the fraction of hydrophobic sites (areas of low surface energy) on the surface of coal particles α HB and the fraction of hydrophilic sites (areas of high surface energy) α HL. Under these conditions,

$$\alpha_{HB} + \alpha_{HL} = 1 \tag{23}$$

and the contact angle of the composite surface can be written as

$$\cos\theta = \alpha_{HB} \cos\theta_{HB} + \alpha_{HL} \cos\theta_{HL} \qquad (24)$$

With these assumptions, the surface composition of heterogeneous coal particles can be calculated using Equations 23 and 24 from their water contact angles calculated from film flotation results using Equation 22.

This can be illustrated by conducting film flotation tests with Cambria #78 coal: as-received, wax coated, and oxidized. If the coal is coated with vaporized paraffin wax, the hydrophilic sites on the coal are covered with paraffin, the mean critical wetting surface tension should decrease and the contact angle should approach that of pure paraffin. On the other hand, if the coal is oxidized by heating in air, hydrocarbon sites are converted to hydrophilic oxygen functional groups and the mean critical wetting surface tension increases.

Although the film flotation curves are not presented here, **Table 1** gives a summary of the wetting parameters determined in this manner, which are as would be expected by the treatments discussed above.

To further verify the approach of using film flotation experiments to determine contact angles of particles, the mean contact angles of particle assemblies were compared with the values reported for direct



measurements on flat surfaces of bulk material²⁰. **Table 2** gives a summary of contact angles of a variety of materials calculated from film flotation data with those measured by captive-bubble and/or sessile-drop methods on flat surfaces of the same material.

From the results given in **Table 2**, it can be seen that the two sets of values are in quite good agreement with each other, especially for the more homogeneous materials. Film flotation indeed through this approach allows for estimating the distribution of hydrophobic and hydrophilic sites on heterogeneous particles, such as coal, and provides a way of determining the contact angle on particles.

Modified Hallimond Tube

The modified Hallimond tube is a microflotation device designed so that gas bubbles (air or nitrogen) can be introduced at a constant rate into a bed of particles (about one gram of particles in 100 ml of water). Fig. 9 schematically shows the design and construction of this simple device, which allows determining the amount of material floated during a fixed time period under closely controlled operating conditions with high-purity materials²³⁾. In addition, an important attribute of this device is that there is no change in the solution composition by froth removal as occurs in normal flotation testing. Initially, particles are at rest or are being slowly stirred on the frit. When the gas flow is started, the hydrophobic particles attach to bubbles, rise to the top of the liquid level, and fall back down into the collection tube when the bubbles break at the surface.



Fig. 9 Schematic drawing of the modified Hallimond tube which can be used for controlled testing of flotation behavior and study of dewetting phenomena(after Fuerstenau et al., [23]).

For a given series of experiments, the flotation time is fixed at some constant value. This technique permits ready determination of conditions that can lead to the dewetting or hydrophobization of normally hydrophilic solids. The technique can similarly be used to delineate how changing pH or adding a wetting agent can affect naturally hydrophobic particles, such as graphite, talc and molybdenite. Typically, a fairly narrow particle size is used in Hallimond tube experiments, such as 65×100 mesh ($150 \times 208 \ \mu$ m) particles.

The flotation of quartz will be taken as an example of the use of the modified Hallimond tube to determine factors that control wettability by the addition

 Table 1
 Wetting parameters of as-received, wax-coated, and oxidized Cambria #78 bituminous coal obtained from film flotation results (after Fuerstenau et al.,²⁰⁾)

Treatment	γ̄c, mN/m	heta , deg	lpha HB	σ yc, mN/m
Wax-coated	25.3	101	0.92	2.60
As-received	43.0	68	0.49	4.53
Oxidized at 200C for 19 h	67.0	24	0.07	

Table 2 Contact angles of various materials calculated from film flotation results with $100 \times 150 \ \mu$ m particlesand measured by captive bubble (CB) or sessile-drop (SD) methods on flat surfaces (after Fuerstenauet al., 20)

Material	Contact Angle, degrees Film Flot., Calc'd	Contact Angle, degrees Flat Surf., Meas'd
Sulfur	86	83(SD)
Graphite	71	77(CB)
Paraffin	101	105(CB)
Methylated Silica	99	84(CB)
Cambria #78 Coal	68	65(SD)
Illinois #6 Coal	52	60(SD)
Pittsburgh #8 Coal	63	62(SD)



of a surfactant. Clean quartz is hydrophilic but can be made hydrophobic by the addition of a cationic surfactant that has a sufficiently long hydrocarbon chain on its molecule. Detailed studies have been carried out on the adsorption of the cationic surfactant dodecylammonium acetate (DDAA) and its effect on zeta potentials, contact angles and Hallimond tube flotation response²⁴. Fig. 10 shows how Hallimond tube flotation response of 208×295 - μ m guartz particles is related to the concentration of DDAA in solution. With increasing additions of DDAA in solution, the positively charged dodecylammonium ions adsorb at the negative surface of quartz. Because of the tendency for hydrocarbon chains to escape from water by associating together, long-chained surfactants form micelles in solution at higher concentrations, called the critical micelle concentration (the CMC). A micelle may be spherical or rod shaped, with the chains inside the micelle and the charged head groups oriented towards the aqueous solution.



Fig. 10 Correlation among contact angle, adsorption density, flotation response and zeta potential for quartz as a function of the concentration of dodecylammonium acetate at pH 6-7 (after Fuerstenau et al., [24]).

Similar association of adsorbed surfactant ions takes place at the solid-water surface at higher adsorption densities, but because the charged head groups are oriented towards the solid surface, the aggregated adsorbed surfactant ions essentially are similar to only half of a micelle, and hence are called hemimicelles²⁴⁾. As can be seen in **Fig. 10**, the adsorption of DDA ions increases sharply at about 10⁴ M because the chains of the aminium ions begin to associate into hemimicelles at the surface, making the solid more hydrophobic. This is reflected not only in an increase in the flotation of the quartz particles but also in the abrupt changes in the other interfacial phenomena given in Fig. 10.

Flotation is a dewetting process governed by inter-



Fig. 11 The effect of pH on the oil flotation of fine naturally hydrophobic molybdenite without the addition of a surfactant. Also plotted is the effect of pH on the oil/water contact angle of molybdenite, expressed in terms of the flotation dewetting relation, (1 - cos θ), (adapted from Wie and Fuerstenau [25]).

facial tensions (Equation 8). In Fig. 10, the results of measurement of contact angles on a polished quartz crystal in DDAA solution were not in terms of the contact angle in degrees but its cosine. In the original paper²⁴⁾, the results were plotted with contact angle in degrees. Actually, in accordance with Equation 8, flotation response should be related to the contact angle through the quantity ($\cos \theta - 1$). For correlation purposes, we want a parameter that increases with increasing flotation recovery, which means simply plotting the results in terms of the quantity $(1 - \cos \theta)$. Although not shown here, there is quite good correlation between the behavior of these two complex three-phase systems, namely that Hallimond tube flotation can be used to assess the effect of surfactants on the wettability of particles and to estimate the magnitude of the contact angle for any flotation recovery if it is known for one flotation experiment.

Oil Flotation

Oil flotation, in which an oil phase is substituted for the gaseous phase, has been extensively investigated as a means for recovering fine particles. An example is the oil flotation of fine, naturally hydrophobic molybdenite powder without the addition of a surfactant. Before flotation can take place, either with oil droplets or air bubbles, the intervening film between a particle and an oil droplet or an air bubble must thin and rupture. Any electrical double layer repulsion would clearly hinder this process by introducing a kinetically inefficient step. With most materials, pH has a marked effect on the magnitude of the surface charge and surface potentials. To illustrate the effect of pH on the oil flotation of a naturally hydrophobic material, molybdenite powder of 8.0 m²/g was dispersed in the aqueous phase using an ultrasonic bath

with the pH adjusted to the desired value²⁵⁾. After adding iso-octane as the oil phase and stirring the suspension for a conditioning period of five minutes, the mixture is placed in a small cell where the aqueous phase and organic phase are allowed to separate and the two liquids collected separately in beakers. The amount of molybdenite in the organic and aqueous phases can be determined simply by drying and weighing the samples. The recovery of molybdenite by oil flotation as a function of pH is given in **Fig. 11**, which shows that oil flotation recovery is nearly 100 percent at pHs below approximately 4 or 5. In alkaline solutions, the recovery decreases, due to the more negative zeta potentials on both the molybdenite and the oil droplets.

Here again, oil flotation can be used to follow how conditions change the oil-water-solid contact angles, which were measured on freshly cleaved faces of a molybdenite crystal. The angle of contact between a free iso-octane droplet was measured across the water phase with a microscope-goniometer. At pH 4, the contact angle was determined to be about 150 degrees and in alkaline solutions it decreased to 100 degrees. Since this process involves the attachment of a solid particle immersed in an aqueous phase to an oil droplet, the process is again governed by interfacial tensions in accordance with Equation 8. For correlation purposes, we want a parameter that increases with increasing flotation recovery, which means simply plotting the results in terms of the quantity $(1 - \cos \theta)$. The results given in **Fig. 11** show very close correlation between the contact angle of oil and the oil flotation recovery. For this type of system, if the contact angle is known for one condition, then it should be possible to estimate the contact angle for any other recovery.

Liquid-Liquid Extraction of Nano-Particles

How the addition of a surfactant controls the wettability of nano-sized particles can be assessed by determining the distribution of particles between water and hexane. Fuerstenau and Colic^{26} investigated the wettability of 100-nm particles of anatase and hematite using this technique. First, the oxide particles are equilibrated with the surfactant at the desired pH in water, then 5 ml of hexane is added to the aqueous dispersion, and the vials agitated for one hour. After phase separation, the oxide content in each phase can be determined either gravimetrically or by a light scattering technique. The results presented here are for monodisperse spherical hematite particles (α -Fe₂O₃) that were prepared by thermal hydrolysis of



acidified solutions of ferric chloride. Their diameter was 120 ± 20 nm, and after thorough washing their point of zero charge (the pzc) was found to occur at pH 9.5. Since the hematite surface is positively charged at pH 3, the surfactant needed to control wettability under these conditions must be anionic, in this case sodium dodecylsulfate (SDDS). In Fig. 12, the percentage of hematite extracted into the hexane phase is plotted as a function of the concentration of SDDS in the aqueous solution. This plot shows that the conditions for maximum hydrophobicity of these nanosize particles is quite narrow. In Fig. 12, the electrophoretic mobility of these same particles is plotted as a function of SDDS concentration at pH 3 (here mobilities have not been converted to zeta potentials). Both of these plots can be explained in terms of dodecylsulfate adsorption.



Fig. 12 The effect of sodium dodecylsulfate on the wettability of hematite particles at pH 3 and 0.001 M sodium nitrate, expressed in terms of the percentage of hematite particles transferred into hexane from the aqueous phase. Also plotted is the electrophoretic mobility of the particles as a function of the surfactant concentration under the same conditions, showing maximum hydrophobicity when the mobility is zero (adapted from Fuerstenau and Colic [26]).

At pH 3, the ionic strength is millimolar, so adding SDDS at 10⁵ M does not change ionic strength and the electrophoretic mobility (which is directly related to the zeta potential) remains constant while adsorption is controlled only by the attraction of an anion by the positive oxide surface in exchange for nitrate ions (from the acid) in the double layer. However, when the hydrocarbon chains of adsorbed surfactant ions begin to associate at the surface, the zeta potential (mobility) decreases sharply. Under these conditions, the ionic heads are oriented to the surface and the hydrocarbon chains out towards the solution, causing the particles to become increasingly hydrophobic in this region. With further increase in the SDDS con-



centration, the zeta potential becomes zero when the number of adsorbed ions exactly equals the positively charged surface sites. Maximum hydrophobicity occurs when the mobility or zeta potential and the net interfacial charge are all zero. With increased addition of the SDDS, continued adsorption of the surfactant ions takes place in reverse orientation because the heads of the surfactant ions are now repelled from the negatively interface (as shown by the reversal of the zeta potential). Thus, the particles become hydrophilic again, preferring the aqueous phase over the organic phase, as can be seen by the decrease in extraction into hexane. These experiments show that conditions for maximum hydrophobicity of nanosized particles can be determined simply by finding conditions under which the surfactant brings the zeta potential to zero. To ensure full wetting through formation of an adsorbed bilayer, high concentrations of the surfactant must be added to the solution so that a first layer with the charged heads of the surfactant ions being oriented down and a second layer with charged heads being oriented towards the aqueous solution. To accomplish this, the surfactant concentration in solution should be raised above the critical micelle concentration (the CMC) of the given surfactant.

Bubble-Particle Pickup and Induction Times

For bubble-particle attachment the liquid film between the solid and the gas must thin and rupture. The stability of such films is controlled by electrical double layer forces, attractive van der Waals dispersion forces, repulsive hydration forces, and the existence of attractive hydrophobic forces between particles and air bubbles. Wetting films are not stable on hydrophobic surfaces and hence the attachment between a particle and an air bubble is almost instantaneous. However, partially hydrophobic surfaces interact with water molecules through hydrogen bonding, giving rise to a liquid film that may exhibit some stability over a finite period so that a certain amount of time may be required to achieve the formation of a contact angle. In mineral flotation, the minimum time required for thinning and rupture of the liquid film leading to a stable bubble-particle interface is called the induction time. Perhaps the simplest method devised was the bubble pickup apparatus of Cooke and Digre²⁷⁾. Their device was essentially a test tube with a stopper in the top through which a glass tube extends to near the bottom. On top of the glass tube a rubber hose was attached and clamped at the upper end, with the rubber hose acting as an air chamber for generating bubbles. In their investigation, which was concerned with how oleate and calcium salts controlled the wettability of quartz, they used minus 1-mm quartz particles: 0.05 g of wet quartz in 30 ml of aqueous solution. This would also yield a rough measure of induction times, which ranged from about 10 seconds down to 1 second in their system. They found complete pickup, that is when all particles adhered to a bubble that had been pressed against the particle bed and withdrawn, was readily discernible with an induction time less than one second when the contact angle was about 60 degrees in their system. Partial pickup occurred when the contact angle was in the 20-degree range. With this simple device, they were able to correlate the limits of full pickup conditions with solution chemistry reasonably well²⁷.

The Cooke bubble-particle pickup apparatus provides more or less yes/no information on conditions for mineral-bubble attachment. Various devices have been designed and built over the years to measure the very short induction times that relate directly to flotation kinetics, and these operate similarly to the bubble pickup device but with the contact time being controlled electronically. A fairly simple apparatus in which a captive bubble is moved against a bed of particles for successively longer periods of time until particles become attached to the bubble has been developed by Yoon and Yordon²⁸⁾. In their device, the vertical movement of the bubble holder is controlled by a power driver. An electronic pulse generator controls the driver, which allows both the amplitude and time of contact to be set. Contact time in this device can be varied between 30 microseconds and 2 seconds. Typically, a captive bubble of 2 mm diameter is produced on the end of a capillary tube and the particle bed raised until the particles are about 0.1 mm beneath the bubble. Generally, experiments are carried out with particles fractionated between two consecutive sieves. The bubble is pushed downward by the power driver for the set time and the bubble is observed through a microscope to determine if any particles are attached to the bubble.

Fig. 13 is an example of the dependence on solution conditions of the measured induction times for a naturally hydrophobic bituminous (Cambria #78) $coal^{29}$. In this case, the induction time measurements were carried out in 0.002 M sodium nitrate as a function of pH with 100 × 150 mesh (106 × 150 μ m) particles with the Yoon-Yordon induction time apparatus²⁸. In this Fig. the zeta potential of the coal, as calculated from electrophoretic mobilities, is also plotted as a function of pH. The zeta potential reverses sign at pH 4.7, indicating that the adsorp-



Fig. 13 Correlation of the effect of pH on the induction time and zeta potential of as-received 100×150-mesh Cambria #78 bituminous coal in 0.002 M sodium nitrate as a function of pH (adapted from Jia [29]).

tion of hydrogen and hydroxyl ions is responsible for the charging of the surface of the coal particles. At pH 4.7, the double layer on the coal particles is absent. Clearly, maximum hydrophobicity of Cambria #78 coal, as represented by the minimum in induction time, corresponds to conditions where the zeta potential of the coal is zero. At this pH, the electrical double layer does not have any effect on film thinning processes at the interface.

Other work has been published with measurements of induction times on quartz particles as a function of the concentration of dodecylammonium chloride at constant pH^{28} . The results show that there is a marked decrease in induction time under conditions where hemimicelles form, that is conditions that lead to greater hydrophobicity of particles, and that the induction time increases sharply as the critical micelle concentration in solution is reached. Under these conditions, the quartz surface is covered with the equivalent of a bilayer of adsorbed aminium ions and is fully hydrophilic. This is important for finding optimal conditions for planarization in electronic wafer processing, for example.

Immersion/Sink Time

The 'sink time' was originally defined by Draves and Clark³⁰⁾ as the time taken by a skein of cotton to sink after it had been immersed in a surfactant solution. A variation of this test is to measure the concentration of a surfactant required to give a 'sink time' of 25 seconds. The procedure was later modified by Walker et al.³¹⁾ to determine the wetting ability of various surfactants for coal dusts. In this technique coal particles were dropped individually onto the surface of surfactant solutions of progressively dilute concentrations. The most dilute concentration in which coal would sink 'instantaneously' was determined. These



authors did not define the term 'instantaneously'. Results of such measurement would be sensitive to the operator. Other variations of this technique have also been used. Some investigators^{32, 33, and 34)} reported the time for wetting a given amount of powder, whereas others have reported wetting rates³⁵⁾. Also there are differences in the manner in which time of wetting was measured. Some investigators have determined the time for the last trace of powder to be wetted^{32, 36)} whereas others have determined the time for the vast majority of the particles to sink³⁴⁾. The sink time method has been used by investigators to measure the wettability of a wide variety of solids: organic chromium pigment^{37, 38)} flour sulfur and molybdenite³⁹⁾. Some difficulties in accurate determination of sink time are likely to occur for powders that are heterogeneous with regard to their wettability.

Wetting Rate

To overcome some of the difficulties mentioned in the previous paragraphs, Mohal and Chander⁴⁰⁾ modified the Walker method to develop a procedure for determining the 'wetting rate' of powders. They used the pan of a microbalance placed beneath the surface of the liquid to measure the amount of powder wetted as a function of time. A schematic of the apparatus is given in **Fig. 14**. A barrier was placed at the surface to direct the particles towards the center of the pan and prevent them from contacting the sides of the pan. A fixed weight of the powder, typically 40 mg, was placed on a spatula attached to a vibro-feeder.



Fig. 14 A schematic of the wetting rate measurement apparatus (after Chander et al., [1987]).

The powder was dropped from a height of 0.5 cm above the barrier within a period of 1 second and the mass of the wetted powder was recorded as a function of time. The rate of wetting was estimated from the slope of the mass vs. time plot as illustrated in **Fig. 15**. Results were obtained for wetting a sample




Fig. 15 The wetting rate test results for a sample of coal (hvA bituminous) wetted by a surfactant solution (4×10⁴ M Triton X-100). The results are typical of those observed in many experiments (after Chander et al., [1987]).

of hvA bituminous coal with an aqueous solution of 4 $\times 10^4$ M Triton X-100 (an ethloxylated octyl phenol). The authors used the results to demonstrate that differences in the choice of the criterion for wetting can lead to different values for wetting rates. The linear portion of curve A corresponds to the condition in which wetting rate is constant and is defined as the 'initial wetting rate'. If the definition by Kost et al.³⁴ is used, the rate would be based on wetting of the vast majority of particles, which is schematically shown by line B in Fig. 15. Similarly, if one uses the definition in which the criterion of wetting is the disappearance of the last traces of particles, which is illustrated by line C in the figure, the lowest rate of wetting is measured. The main advantage of the wetting rate approach is that the wetting behavior of heterogeneous systems can be determined unambiguously.

For heterogeneous systems one could define two separate wetting rates if the powder was a mixture of materials with different wettabilities, or one could determine a wetting rate distribution, from slope of the plot if different particles exhibited a range of wettabilities. Mohal and Chander⁴⁰⁾ observed several types of wetting rate curves that are illustrated in **Fig. 16**. Different types of wetting curves were obtained depending on the coal type and concentration of the wetting agent. The main disadvantage of this technique is that the particle size for experimentation must be in a narrow range of values. If the particles



Fig. 16 A schematic representation of the types of wetting curves obtained by various combinations of type and concentration of the surfactant, and the type of hydrophobic characteristics of the solid (after Chander et al., [1987]).

are too large, gravity will sink the particles, and if they are too small dispersion will prevent settling of particles on the balance pan.

Imbibition Time

Mohal and Chander⁴¹⁾ determined the imbibition time of powders by microscopic observation of particles as they pass from air into liquid. A high-speed motion analysis system was used to photograph the sequence of events during imbibition of particles into a liquid. By analyzing the photographs the *imbibition time*, the time taken by a particle to be fully imbibed into the liquid was measured, to a resolution of 83 μ s (microseconds). A sequence of frames for quartz (hydrophilic) and coal (hydrophobic) is shown in Fig. 17. The quartz particle is wetted by water and it pulls the interface downwards due to hydrodynamic resistance and surface tension as seen in frames 1-7 on the left in Fig. 17. In subsequent frames, 8-12 on the left, the particle has gone into the liquid and the interface relaxes and moves upwards. The hydrophobic coal particle has an initial downward pull due to the kinetic energy of the particle, frames 1-5 on the right, but the particle moves slightly upwards once the kinetic energy is dissipated, frames 6-12 on the right. In this case the coal particle remains floating at the interface.

The imbibition times for quartz and coal samples are presented in **Fig. 18** as a frequency distribution.



Fig. 17 A sequence of photographic frames (1-12) showing imbibition of quartz (left) and coal particles (right) into liquid water. The quartz particle has a downward pull at the liquid-air interface (frames 1-7 on the left). In subsequent frames (8-12 on the left), the particle has gone into the liquid and the interface relaxes and moves upwards. The hydrophobic coal particle has an initial downward pull due to kinetic energy of the particle (frames 1-5 on the right) but the particle moves slightly upwards once the kinetic energy is dissipated (frames 6-12 on the right) (after Mohal and Chander [41]).



Fig. 18 Frequency distributions of the imbibition times for quartz and coal. The quartz was wetted by water, whereas the hvA bituminous coal was wetted by a mixture of 60% (by volume) methanol in water (after Mohal and Chander [41]).

Crushed quartz particles are wetted by water and the measured time corresponded to the time to travel a distance of one diameter under gravity. Wetting of coal by a liquid of lower surface tension (60% metha-



nol in water) gave three distinct peaks which were identified with ash-minerals (mainly hydrophilic), a hydrophobic component that gave imbibition times of the order 80 ms, and a middling fraction with an imbibition time of about 3 ms. The results clearly show that this method could be used to determine the distribution of wettability in a given sample. One can consider that the distribution would be 'a true distribution' because the procedure involves observation of one-particle-at-a-time in the sample set. Thus, any distortions due to particle crowding at the interface are eliminated. Some of the techniques described in previous paragraphs suffer from this disadvantage.

Another way to represent the imbibition time distribution is to present the data as a cumulative plot. An example is given in **Fig. 19** for wetting of three different coals by a liquid containing 4×10^4 M Triton N-101 (an ethoxylated nonylphenol). In separate wetting tests, wetting rates of 24 mg/s, 21 mg/s and 14 mg/s were measured for the hvA bituminous coal, anthracite, and sub-bituminous coals, respectively. These results confirmed at least a qualitative correlation between imbibition time and wetting rate.



Fig. 19 Cumulative frequency distributions of the imbibition times for a hvA bituminous coal, anthracite and a sub-bituminous coal. The wetting liquid was an aqueous solution of 4×10⁴ M Triton N-101 (after Mohal and Chander [41]).

Atomic Force Microscopy

Direct measurement of the forces acting between particles, which is challenging because the forces are weak and the surface separations must be controlled and measured to with 0.1 nm, has now become

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quite widely done. The impetus for doing this came from the development of the surface force apparatus (SFA) in the late 1960s by Tabor, Winterton and Israelachvili⁴²⁾ for measuring van der Waals forces between molecularly smooth mica surfaces in vacuum or in air. Later modifications have permitted making measurements in liquids and with other molecularly smooth materials. The interaction forces between two curved surfaces of mica mounted in cross-cylinder configuration are measured using highly sensitive force-measuring springs and the separation distance is determined by an optical technique (usually to better than 0.1 nm). The force is measured through the expansion and contraction of a piezoelectric crystal.

An extension or offshoot of the SFA is the atomic force microscope, readily available commercially, where the force is measured not between two macroscopic surfaces but between a fine tip and a flat surface. Several different researchers have attached micron-sized quartz or other spheres to the AFM tip and measured long-range electrostatic repulsive forces and hydrophobic attractive forces. Yoon et al.⁴³⁾ measured interaction forces between silanated glass spheres and a silanated silica plate and observed major attractive forces with increasing contact angles. In a recent AFM study, Zhang and Yoon⁴⁴⁾ measured the interaction force between glass spheres (12 to 20 μ m diameter) and a silica plate in the presence of alkyltrimethylammonium chlorides (CTAC) with 12, 14, 16 and 18 carbon atoms in their alkyl chains. Contact angles were also measured on the flat silica plates. The experiments were carried out at various surfactant concentrations, with maximum hydrophobicity appearing to occur under conditions where the amount of CTAC adsorbed in the Stern layer exactly equals the surface charge, namely when the zeta potential is brought to zero, that is, the point of zeta reversal, pzr. At higher concentrations, where the zeta potential would have reversed sign, electrical double layer repulsion forces reduce the total interaction force. Fig. **20** is a plot of their results giving the force-distance curves for the glass sphere/silica plate system with the four different surfactants at the concentrations of their strongest attractive forces, at what must be the pzr for each of these systems. These curves are fitted to a single-exponential force law, namely:



Fig. 20 Normalized force / separation distance curves to illustrate the effect of chain length of alkyltrimethylammonium chloride surfactants on the hydrophobic force acting between a glass sphere and a silica plate. Each surfactant is at the concentration that gave maximum hydrophobicity (after Zhang and Yoon [44]).

$$F / R = -C \exp(-H / D)$$
 (25)

where F is the interaction force, R is the radius of the glass sphere, H is the separation distance between the glass sphere and the silica plate, and C and D are fitting parameters. In this system, C was found to be a constant with a value of 1.35. D is considered to be the decay length. As can be seen by the plots given in **Fig. 20**, the attractive force between the hydrophobic sphere and plate extends farther out as the chain length of the surfactant is increased, meaning that the apparent hydrophobic force is greater, the longer the chain on the surfactant. **Table 3** summarizes the results for conditions of strongest attraction with

 Table 3
 Summary of the results for measuring attractive force curves by AFM measurements between a glass sphere and a silica plate with alkyltrimethyl-ammonium chloride solutions, including the concentration for maximum attractive force (the pzr), the decay length of the attractive forces, the contact angle on the silica plate, and the CMC of the surfactants (after Yoon et al.,43)

Surfactant	Solution	Contact Angle,	D, nm	Critical Micelle
	Conc., M	degrees		Conc. M
C12TAC	1×10^{-3}	47	3	1.8×10^{-2}
C14TAC	1×10^{-4}	51	6	4.0×10^{-3}
C16TAC	3×10^{-5}	58	14	$1.3 imes 10^{-3}$
C18TAC	5×10^{-6}	64	32	$4.0 imes 10^{-4}$

the four surfactants. This table clearly shows, as expected, that the longer the chain, the lower the bulk concentration required to attain maximum hydrophobicity. Since micelle formation in solution results from the same hydrophobic phenomena, the critical micelle concentration (CMC) of the four surfactants is also give in Table 3. The bulk concentration of a given surfactant required to achieve maximum hydrophobicity at the surface is about one-hundreth the CMC. Even though hydrophobic attraction changes markedly, the magnitude of the contact angles under those conditions does not change very much. These results suggest, once more, that the most powerful way to find the condition for maximum hydrophobicity due to the adsorption of a surfactant is to ascertain conditions under which the zeta potential is brought to zero, namely to determine the pzr from electrophoresis measurements.

Conclusions

Wetting of a solid refers to the displacement of one fluid by another at the solid surface and is determined by the different interfacial tensions involved. The balance among these surface forces defines the contact angle which is typically used to characterize wetting behavior. While interfacial tensions between fluid phases (liquid-gas, liquid-liquid) are readily measured, those involving a solid are not generally amenable to direct measurement. Consequently, prediction of contact angles based on the properties of the individual phases is not generally possible, although estimates can be made under certain conditions.

Control of wetting characteristics is desirable for many applications. Surface-active agents can be used to enhance wetting (reduce contact angle) by lowering the liquid-gas or liquid-liquid interfacial tension. Adsorption of appropriate reagents at the solid surface can enhance the wetting of lyophobic solids or reduce that of lyophilic surfaces. Characterization of wetting behavior is critical to the selection of appropriate reagents for specific applications.

Contact angles on solids are commonly measured by direct observation of drops or bubbles in contact with the surface. Unfortunately, this approach is impractical for very small particles and it cannot necessarily be assumed that the wettability of a fine particle is the same as that of the polished surface of a large piece of the same material. Measurements on compacted powders involve uncertainties due to surface irregularities and liquid penetration. The relative



disposition of a particle between the two phases at a liquid-gas or liquid-liquid interface can be used to determine an effective contact angle (the actual angle if the particle is a sphere). Since the method is based on the assumption that gravity is negligible relative to the surface forces, its use is generally limited to particles smaller than about 1mm. Measurements on particles as small as 0.1 mm have been reported. Measurements of the extent and/or rate of penetration of liquid into packed beds of powder can provide estimates of contact angles. Uncertainties in the estimates arise primarily from problems in the reproducible preparation and characterization of uniform particle beds.

Appropriately chosen indirect methods for characterizing wetting behavior can offer advantages in simplicity of measurement and direct relevance to specific applications. Methods such as immersion/sink time, wetting rate and imbibition time are directly applicable to problems associated with the dispersion of powders in liquid. Film flotation, the Hallimond tube, liquid-liquid extraction and particle-bubble pickup and induction time provide information of direct relevance to solid-solid separation processes based on selective wetting control. In some cases, the indirect methods can yield estimates of contact angles or quantities such as the Zisman critical surface tension.

The limited ability to predict wetting behavior based on material properties continues to be a primary constraint in practical applications. Development of a more complete understanding of the quantitative role of the various interaction forces in establishing interfacial tensions is a critical need. At the same time, improved procedures for the measurement of criteria such as contact angles, especially on fine powders, are needed to establish the basic parameters necessary for predictions to be made.

Nomenclature

A, A_1	Cross-sectional areas defined in Fig. 3	$[m^2]$
A_b	Cross-sectional area of a particle bed	[m ²]
с	Geometric factor defined in Equation 16	$[m^5]$
С	Parameter in Equation 25	$[N m^{-1}]$
D	Decay length of attractive forces	[m]
$f(\gamma c)$	fraction of particles with critical surface	
	tension yc	[-]
F	Interaction force	[N]
h	Height of liquid column	[m]
Η	Separation distance	[m]
т	Mass of liquid in column	[kg]
r_p	Effective mean pore radius in a powder bed	[m]
R	Particle radius	[m]



R f	Geometric factor defined in Equation	[m]
S_v	Specific surface area of powder	$[m^{-1}]$
t	Time	[s]
$\alpha_{_{ m HB}}$	Fraction of hydrophobic sites on a surface	[-]
$\alpha_{_{\rm HL}}$	Fraction of hydrophilic sites on a surface	[-]
γ _c	Critical surface tension	[N m ⁻¹]
γ _{LV}	Free energy of liquid-vapor interface	[N m ⁻¹]
$\gamma_{\rm SL}$	Free energy of solid-liquid interface	[N m ⁻¹]
γ _{sv}	Free energy of solid-vapor interface	[N m ⁻¹]
γw	Surface tension of wetting liquid	[N m ⁻¹]
ΔG_A	Free energy change for adhesional wetting	$[N m^{-1}]$
ΔG_{flo}	Free energy change for bubble attachment	[N m ⁻¹]
ΔG_I	Free energy change for immersional wettin	g [N m ⁻¹]
ΔG_S	Free energy change for spreading wetting	$[N m^{-1}]$
Δp	Capillary pressure in a powder bed	[Pa]
Δp_w	Capillary pressure for a wetting liquid	
	in a powder bed	[Pa]
3	Porosity of a powder bed	[-]
θ	Contact angle	[degrees]
heta HB	Contact angle on hydrophobic sites	[degrees]
θ	Contact angle on hydrophilic sites	[degrees]
μ	Liquid viscosity	[Pa s]
ρ	Liquid density	[kg m ⁻³]
$\sigma_{\gamma c}$	standard deviation of the distribution of	
	critical surface tension	$[N m^{-1}]$

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Crystalline Silica Particles Mediated Lung Injury[†]

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Abstract

Epidemiological studies have shown that the occupational exposure of crystalline silica can lead to silicosis and other lung injury. In this paper, we briefly summarize the various research works that have been conducted related to crystalline silica-induced toxicity. Firstly, a short description of the structure of quartz is presented, followed by the various types of silicosis that can be caused by inhalation of crystalline silica particles. Methods to characterize the particles and mechanisms of particle-cell interactions are also reported. The effect of physicochemical properties such as size, shape and surface functionality that influence the toxicity mechanisms are discussed, followed by a brief description on the effects of free radical generation due to quartz inhalation on biological targets (proteins, lipids and DNA). Finally, methods reported to modify the surface and reduce the quartz-induced toxicity are discussed.

Keywords: Quartz, Free radicals, Lung injury, Surface modifications, Toxicity

Introduction

The ancient Greeks¹⁾ first reported that inhaled crystalline silica can cause silicosis, which is one of the most important occupational diseases from silica inhalation. Reports on the toxicity of crystalline silica date back to the 1500s when metal diggers were known to wear protective equipments to avoid silica dust inhalation. The disease was initially referred to as *'pneumokoniosis'* which means *'dust in the lung'*, but later replaced with *'silicosis'* in 1870 by Visconti, who coined the term².

Quartz, one of the three crystalline forms of silica found in the earth's crust, is arranged in a stackedframework of Si-O tetrahedral units to make a 3d structure. Often, there are trace amounts of contaminating elements like aluminum, iron, lithium, magnesium, calcium, sodium and potassium associated with the structure³⁾ which play a very important role to influence the biological activity of the material. Quartz was established as a Group I carcinogen by the International Agency for Research on Cancer (IARC) working committee in 1997⁴⁾. Despite various disagreements amongst the working group regarding this decision, it was concluded that there did exist sufficient evidence for carcinogenicity in experimental animals and humans caused by quartz inhalation. Moreover, it has also long been implicated with various other lung diseases⁵⁾, the progress of which has been shown to depend directly on the rate of quartz deposition in the lung⁶⁾.

However, carcinogenicity of quartz has also been shown to vary considerably across the different industries with similar quartz exposure⁷. As per the views of the IARC working committee⁴, the degree of quartz toxicity depends on the 'inherent' properties of the crystal or on other 'external factors' that can affect its biological activity. The 'inherent properties' of silica are determined by the state of its external surface (e.g. defects present, chemical functionalities) which again depends on the origin of the quartz. 'External factors' like contact, association

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and presence of contamination can trigger or inhibit silica carcinogenicity. Thus, the same quartz sample exhibits variable toxicity behavior, although the basic composition remains the same⁸⁻¹⁰. The potential influence of external factors¹¹ may be observed in the different events occurring from the deposition of quartz to the occurrence of silicosis and lung cancer.

Despite the substantial volume of research since the early 1950s, on the pathogenicity of quartzinduced diseases, the exact mechanism of action of crystalline silica is still debatable and inconclusive. There are several reports available from various medical investigations that describe the etiological and morphological facets of silica-induced diseases in detail. But quite frequently, these observations cannot be correlated to the insights obtained from chemical and biochemical processes of quartz toxicity.

The surface of quartz plays an important role in determining its biological effects, as cells and other biological molecules first come in contact with the surface^{7, 12}. Thus, in order to understand the basic molecular mechanisms of quartz-induced toxicity, it is crucial to first study the biochemical reactions associated with the surface chemistry of the inhaled crystalline silica particles. There are inherent difficulties in finding a clear-cut molecular mechanism mainly due to two reasons¹²:

- O Most experimental studies on silicosis were conducted using silica samples which were not wellcharacterized. Thus although the available epidemiological data focuses on the quantitative aspects in details, frequently there is no correlation with qualitative issues like the physicochemical characteristics of the inhaled particles.
- Several particle-cell interactions occur during silica inhalation, leading to specific biological responses manifested by the surface. The varying molecular mechanism at each step lead to differences in surface functionalities. This again leads to variations in the physiochemical characteristics of the dust. Thus, the overall pathogenicity of the inhaled particle becomes more difficult to be interpreted¹³⁾.

This communication is an attempt to summarize from the past and recent literature the effects of different physicochemical parameters that affect the pathogenic mechanism of silica-induced diseases in the lung, present a hypothesis on the toxicity mechanism of crystalline silica and gives a short discussion on some established ways that have been reported to reduce crystalline silica-mediated toxicity in the

lungs.

Structure of Silica in Relation to Cytotoxicity

Silicon dioxide (SiO₂) or silica is the earth's most abundant mineral, occurring in nature in several crystalline forms. The most common crystalline forms of silica are α and β -quartz, α and β -tridymite, α and β -cristobalite¹⁴). α -quartz is the most common and thermodynamically stable form at room temperature which is converted reversibly to β -quartz upon heating¹⁵). The different polymorphic forms are known to exhibit different levels of toxicity. The majority of the population is exposed to α -quartz and hence most toxicity experiments are conducted using this polymorph of silica¹²).

Most quartz samples are associated with trace quantities of metal impurities that play a crucial role in determining its cytotoxic behavior^{3, 16}, as mentioned before. These impurities have a tendency to concentrate along certain crystallographic planes or defects inside the solid material, thereby affecting the relative ease of cleavage or fracture along those particular planes¹⁵. The differences in the relative frequency at which the cleavage planes occur on the surfaces of the polymorphic structures affect their toxicity behavior. Adsorption of impurities from the environment also influences the surface properties of the particles¹⁵. Moreover, the respirable particle sizes of the inhaled particles are also known to cause variation in the biological activity.

The basic difference between inhaling silica particles from other non-toxic particulates is that the latter is engulfed by the macrophages when it reaches the lung and transported through the lymphatic system to lymph nodes and rejected. But the silica particles when taken up by the macrophages can potentially kill the cell and lead to interstitialisation¹⁷⁾. This phenomenon has been discussed in greater details in the subsequent sections. There are many *in vitro* and *in vivo* evidences that demonstrate the particle-cell interactions occurring in the lung^{3, 11, 18-21}. The toxicity investigations associated with silica inhalation in the last 25 years can be classified into the following main categories:

(a) Acellular Tests – These investigations helped to ascertain the role of the different physiochemical parameters of the crystalline silica and correlated it to toxicity results obtained from cellular tests (in vitro and in vivo experiments). For example, the effect of surface-chemistry of well-character-



ized samples on the toxicity behavior has been reported by a number of investigators²²⁾. Although these tests are inexpensive, the results obtained are frequently inconclusive¹²⁾.

- (b) In Vitro Experiments The effect of crystalline silica dusts on different cell lines (macrophages cells, epithelial cells and fibroblasts) have been studied in terms of cell viability, membrane integrity²³⁾, inhibition of cell growth, transformation, release of cytokines^{21, 24)} and other inflammatory mediators^{25:27)}. Although these *in vitro* models are not able to incorporate all variables from *in vivo* tests, they do provide valuable information that help in developing the process and determining optimal doses in a cost and time-effective manner.
- (c) In Vivo Experiments Most in vivo tests have used rats, mice, hamsters and sheep to test for pathogenic activity in cells and tissues either after silica inhalation or by a comparatively faster and more economical process of intratracheal /intraperitoneal instillation in the lungs^{18, 28)}. A standard but not 'so pure' quartz sample – namely DQ 12 was developed in the 1970s to standardize and compare animal test results²⁹⁾. Data generated from *in vivo* tests include: lung weight and histomorphology, weight of silica retained in the lung, amount of internalized silica, presence of lipids and proteins in the lung and fibrogenicity.
- (d) Epidemiology Studies These studies consist of detailed scientific investigations into critical factors that affect the health and illness of a large set of population. Data obtained from such studies serve to provide the foundation and reason for administrative decisions made in the interest of public health and medicine. Recent epidemiological studies have shown a high risk of silicosis in workers with 30 years or more work experience in the ceramic industry³⁰.

Diseases associated with Silica Exposure

The Silicosis and Silicate Disease Committee has extensively studied the various diseases associated with silica inhalation. Silicosis is manifested as four pathologically distinct units¹²⁾ namely: chronic silicosis (nodular pulmonary fibrosis), acute silicosis (alveolar proteinosis), accelerated silicosis and complicated silicosis.

• Chronic silicosis (nodular pulmonary fibrosis): This ancient form of the occupational disease is associated with long period of exposure to low levels of silica dust. This is the most common type of silicosis progressing slowly into a fibrotic disease that causes injury to the lung parenchyma. Chronic silicosis may become fatal due to insufficient gaseous exchange, heart failure or infections.

- Acute silicosis (alveolar proteinosis): This form of silicosis is observed after 1-3 years of exposure to high concentration of silica dust as in environments where mechanical processes like sandblasting, drilling etc are carried out. Acute silicosis is very often fatal due to the irreparable damage caused in alveolar lining cells from the accumulating surfactants, cell debris and proteinaceous matter.
- \circ Accelerated silicosis: This form of silicosis is developed due to an exposure of high concentration of silica dust over a shorter period of time ($\sim 5 - 10$ years). In this case, the process of inflammation, scarring, and development of symptoms occur much faster than in chronic silicosis.
- Asymptomatic silicosis: In this form of silicosis the early onset of the disease does not present any symptoms, thereby making it very difficult to diagnose.

Certain other outcomes of silica inhalation include an increased susceptibility to bacterial and fungal infections, an increase in the incidence of autoimmune diseases and lung cancer (bronchogenic carcinoma).

Methods to Characterize Silica Surfaces

When compared on the basis of equivalent weights or surface areas, toxicity of silica exceeds other nonfibrous mineral dusts¹⁵⁾. Initially, a large number of theories based on the reactions of the silanol groups on the particle surface or hydrogen donation to form complexes with phospholipids in cell membranes, were formulated. These theories could not adequately explain the mechanism of toxicity in silica. The formation of silica free radicals on the particle surface is quite possibly the most important factor in the cytotoxicity of silica. The highest production of radicals occurs on a freshly fractured surface and with aging of the silica dust the radical formation decreases³¹⁾. The toxicity effects of other surface properties like the charge, shape and surface area are yet to be extensively investigated.

In a recent study, to determine the crucial parameters that influence quartz toxicity²⁸⁾, Warheit *et al* have shown that the toxicity behavior is dependent on surface characteristics in rats but not on particle size. Similarly, another critical analysis that considered all physicochemical characteristics like particle size,



specific surface areas, experimental uncertainties³²⁾ indicated a slight difference between the cytotoxicity of the three most common crystalline forms of silica (quartz, cristobalite and tridymite) when compared on the basis of equal number of particle number and surface area. The toxicity of crystalline silica can be markedly reduced by surface-modifications using a coating on the particle surface⁷⁾. Examples of coatings used for this purpose include: organosilane, surfactant, polyvinylpyridine-N-oxide (PVNO)^{12, 33, 34)} and a number of aluminum^{8, 12, 33)} compounds. Further details on the surface modification techniques to reduce the toxicity are described later.

A number of characterization techniques¹⁵⁾ have been developed to identify, quantify and make an attempt at correlating the measurable characteristics of crystalline silica particles to their cytotoxicity. These techniques include¹⁵⁾: electrophoretic mobility, thermally stimulated luminescence (TSL), electron spin resonance (ESR), composition profiling with energy dispersive X-Ray analysis (EDXA), laser microprobe mass analysis (LAMMA) and infrared spectroscopy (IR).

Interactions between Silica and Biological Molecules

The first step to establish the mechanism of action of any toxic material in the physiological environment is to determine the primary target cells that are injured or whose function gets altered. In this case, it has been well-established that the inhaled silica particles on reaching the terminal respiratory tract and the alveolar space, activates the alveolar macrophages and an inflammatory response follows. The mechanism by which the alveolar macrophage participates in the inflammatory response, leading to fibrosis in the lung is still debatable.

At least two overall cellular mechanisms³⁵⁾ could be possible. Firstly, the alveolar macrophages may become cytotoxic after phagocytosis of the particles and release certain 'factors' that may alter or damage cells (e.g. epithelial cells) from the surrounding environment. It may also initiate an inflammatory response, which may become chronic due to the continuous release of the silica particles from the macrophage lysate followed by further engulfment by the macrophages to continue the lytic-cycle¹¹⁾. In the second model, the interaction between the silica particles and the alveolar macrophages is non-lytic. It may activate one or more intracellular signaling^{35, 36)} pathways that lead to the release of inflammatory 'mediators'. The two cellular models may not be mutually exclusive, i.e. one or both may be dominant at a given stage of inflammatory response.

For successful clearance, the macrophages engulf the silica particles and migrate to the mucociliary escalator to leave the lung with their particle-burden, while releasing certain inflammatory mediators in the process. Anything interfering with this chain of events, can lead to the phenomenon of *interstitialisation*¹⁷⁾. It is an unwanted outcome where the particles can no longer be cleared by the normal pathways and either remains back in the interstitium to chronically stimulate cells or transfer to the lymph nodes. This



Fig. 1 Schematic representing the uptake of quartz particles inside the lung, cleared through the normal pathway (left) and particles that are interstitialised (right). Reprinted from Reference 17 with permission from Elsevier.



has been schematically represented in **Fig. 1**¹⁷. Generally, two events¹⁷ can lead to the failed clearance of any particulate materials deposited in the lung: (a) Presence of toxic particles that may lead to macrophage toxicity (b) Particle Overload.

- (a) Presence of toxic particles Presence of intrinsic toxic particles like quartz can stimulate the inflammatory mediators at a low dose and damage cells at higher doses, leading to acute and chronic inflammation¹⁷⁾.
- (b) Particle Overload¹⁷ If the number of respirable particles deposited in the lung is enormously high, due to high airborne mass concentrations, then the phenomenon of particle-overload occurs. Due to phagocytosis of a large volume of particles, the clearance ability of the macrophage gets affected. This leads to its inability to transport the large number of particles that gets deposited on the surface of the lung. The particles that remain left-behind start interacting with the epithelial cells and finally transfer across the epithelium (Fig. 1) and start accumulating in the interstitium. Continuous exposure under such conditions, shall lead to chronic inflammation, increase in the epithelial permeability, proliferation and clearance-retardation, fibrosis and finally cancer.

Effects of Physicochemical Parameters on Toxicity Behavior

Particle Size and Shape

Brown et al³⁷⁾ studied the particle size effect on toxicity of quartz in MET 5A mesothelial cells. The quartz particles used for the study varied between $0.8 \,\mu$ m to $3 \,\mu$ m, consisting of three categories ultrafine particles (below $0.8 \,\mu$ m), fine particles ($0.8 \,\mu$ m to 3μ m) and coarse particles (above 3μ m). It was reported that the toxicity behavior was highest for ultrafine particles and decreased with increase in particles size. In order to study the effect of particle agglomeration, the ultrafine particles were purposely agglomerated in cell-media to sizes above 3μ m. It was shown that the toxicity was reduced and became compareable to the coarse particles. An increase in percentage cytotoxicity values was observed with increasing particle concentration (25, 100 and $400 \mu \text{ g/}$ ml used for dosing the cells. The values of cytotoxicity for the different quartz particles at various particle concentrations, following 24 hour exposure, are shown in Fig. 2^{37} .

Similar experiments were carried out using amor-



Fig. 2 LDH Values reported for quartz, after 24 hours exposure, with varying particle size and increasing particle concentration. Reprinted from Reference 37 with permission from Springer.

phous silica of two different shapes: silica rods and silica spheres. Although no significant differences in cytotoxicity was recognized in this case, the authors also report that this could be due to enhanced agglomeration in rod-shaped particles as compared to their sphere-shaped counterparts. It is generally agreed^{38, 39)} that the shape of various inhaled particles play a significant role to influence the toxicity. Thin and long fibers are typically more toxic and biopersistent. Variations from the equiaxed to acicularshaped structure lead to an increase in toxicity which could evolve due to various forms of mechanical aggravation to cells and difficulties encountered by the cells to phagocytose the particles in the lungs.

Surface Functionalities

The surface reactivity¹²⁾ of crystalline silica particles has been shown to affect its biological activity. The particle surface on encountering the lung lining fluids, biological molecules and cells interact to generate free radicals in several ways. The silanol groups (Si-OH) and the ionized silanol groups (Si-O) on the surface play a crucial role in the interaction between the particles and the membranes. The regular SI-O tetrahedral arrangement on the surface of the particle is interrupted if the quartz is comminuted, generating both homolytic and heterolytic cleavages of the SiO bonds that constitute the basic quartz structure. Homolytic cleavages generate the Si* and Si-O* radicals whereas heterolytic cleavage produces the charged Si⁺ and Si-O⁻ groups. Inside the lung lining fluid or in the tissue fluid in the physiological environment, the products of homolytic cleavages give rise to reactive oxygen species (ROS) like hydroxyl radical (OH°) and hydrogen peroxide (H₂O₂) while



products of heterolytic cleavages interact with the membranes.

Presence of various common metals like iron, aluminum and copper may help to decrease the toxicity of quartz on one hand, but can also add to the oxidative stress by taking part as catalysts in Fenton Reactions on the other. Several investigators have demonstrated that aluminum salts present in minerals found together with quartz can lower quartz toxicity. Moreover, inhaling 300 mg/m^3 aluminum hydroxide for 30minutes per day for an exposure period of 12 months could successfully attenuate the fibrogenic response in rats. Similarly, in the sheep instillation model of silicosis, lungs of sheep instilled with quartz along with aluminum lactate were found to demonstrate reduced pathology scores and lessened cellular activity in the broncheoalveolar lavage (BAL). Presence of iron salts along with quartz has also been shown to reduce the toxicity in erythrocytes by protecting them against the quartz-mediated injury. However, the state of the metal is an important factor. For example, metallic iron has the inhibitory effects, but when present as ferrous or ferric salt contamination could lead to damage due to its role in assisting the ROS formation in Fenton Reaction. In that case, inhaling a mixture of freshly fractured quartz and iron will become more pathogenic than freshly fractured quartz all alone.

It is widely accepted that reactive oxygen species (ROS) and reactive nitrogen species (RNS) released from phagocytic cells are involved in inducing inflammation DNA damage and cancer. ROS and RNS generated due to exposure to quartz have long been implicated with lung diseases. Yamano *et al* reported an elevated level of the oxidative DNA lesions 8-hy-droxydeoxyguanosine (8-OHdG) in the lung tissue obtained from rats exposed to quartz. Other investigators have found 8-OHdG induction more concentrated in the lung alveolar regions, and a possible role of isolated neutrophils in the induction of 8-OHdG in lung type II epithelial cells *in vitro*.

Surface Properties and Mechanism of Toxicity

Hydrogen Bonding – Hydrogen bonding has been implicated in inducing silica toxicity by several authors for a long time^{40, 41)}. The silanol on the surface of the particle binds to macromolecules via H-bonding. The formation of the bond is determined by the matching between silanol group distribution on the surface and its matching to hydrogen molecule acceptor sites on the biomolecule. Macromolecules that bind

tightly onto the surface can mediate the toxicity in at least two ways: (a) May prevent any direct contact between the particle-surface and the biological molecules, thereby reducing the toxicity (b) May act to modify the surface, forming 'non-self' structures that act as antigens on which the immune system starts attacking. Thus there is enhanced toxicity in this case.

Surface Charges – Surface charges can be generated in different ways that could be mechanical and/or chemical¹⁴⁾. The presence of charges on the surface of ground quartz dust has been observed from electron microscopic images. Generally, the positive charge on the quartz surface originates from mechanical treatments while low humidity atmospheres tend to increase the magnitude of charges¹²⁾. The tendency of the dust to stick tightly to the glass container can be reduced only by heating to very high temperatures (above 800°C). The silicon-oxygen bonds also get cleaved if the dust is ground¹²⁾. A heterolytic rupture on the dust results in the formation of a negative charge on the oxygen atom and a positive on silicon (Fig. 3). The presence of these charges can influence the adsorption of endogenous matter and contribute towards particle-cell adhesions.

Hydrophilicity /Hydrophobicity – The hydrophilicity of the surface contributes towards its membranolytic behavior⁴²⁾. The more hydrophobic a surface, less is its tendency to lead to cell membrane lysis. Moreover, hydrophobic moieties tend to get phagocytosed more readily by the macrophages and the process of phagocytosis is directly dependent on the relative hydrophobicity between the particle and the phagocyte in question. The surface of the crystalline silica particle contains patches of hydrophilic and hydrophobic areas¹²⁾. The silanol groups impart hydrophilicity while the siloxane groups contribute towards making the surface hydrophobic. The degree of hydrophilicity also differs between the different samples of quartz¹²⁾. For example, a completely hydrated silica surface is more hydrophilic while one which has been heated to higher temperatures (converts the silanes to siloxanes) becomes more hydrophobic^{43, 44)}. Quartz and the other crystalline polymorphs of silica are more hydrophobic in comparison to its amourphous counterparts.

*Freshly Fractured Surfaces*⁴⁵⁾ – Cleaving the siliconoxygen bond, either by homolytic or a heterolytic cleavages, leads to the formation (**Fig. 3**) of dangling bonds^{12, 15)} and surface charges¹⁵⁾. These products are very reactive in nature and tend to recombine among themselves and form reactive bridges or react with





Fig. 3 Schematic to represent the formation of dangling bonds and surface charges from hemolytic and heterolytic cleavage of the silicon/oxygen bonds in crystalline silica particles. Figure taken from Reference 12 with permission.

the environment to form reactive oxygen species at the surface and in sub-surface layers. The potential reactions¹²⁾ that occur in the presence of oxygen due to reaction with quartz at the surface are:

Si $^{\circ}$ + O ₂ \longrightarrow	Si O ₂	(at room temperature)	(1)
Si $O^{\circ} + O_2 \longrightarrow$	Si O3	(at 77 K)	(2)
$Si^{+} + e^{-} + O_2$			
\rightarrow Si ⁺ O ₂ (at room temperature)			

If the process of grinding or cleaving the quartz surface is carried out in a liquid medium, the radicals generated depend on the reactivity between the solvent/ solute and the cleaved Si-O bonds¹²⁾. For example, presence of pure water prevents the formation of oxygen radicals whereas hydrogen peroxide tends to accelerate it and in some case induce the formation of hydroxyl radicals in parallel to the formation of other radicals.

Free Radical Release - It is hypothesized that the cytotoxicity and pathogenicity of silica dust is due to free radicals^{19, 46)} generated at the cleavage planes of silica, which make them more reactive to the lung tissues and thereby accelerates the onset of pulmonary diseases. In aqueous media, the Si° and Si-O° radicals formed on the quartz cleavage forms generate highly reactive hydroxyl radicals (OH°) which are detected and quantified using ESR spectroscopy15, using a OH° spin trap, like DMPO (5,5 dimethyl-1-pyrroline-N-oxide)^{15, 47,} ⁴⁸⁾. Many investigators have confirmed the release of OH° on the surface which can undergo a relatively fast decay to cause even greater damage ⁴⁷⁾. This can be correlated to the acute lung injury caused in lungs of workers involved in mining, drilling activities etc. It is important to note that aged metal-free quartz does not release any significant quantity amount of radicals. But as mentioned before, the presence of free metals, can lead to radical formation⁴⁷⁾ even on liquid-solid interfaces, that take part in Fenton-type reactions⁴⁸⁾.

Biological Targets of Particle-Cell Interactions

Certain biomolecular targets¹²⁾ that provide a simple and rapid approach to study the effect of crystalline silica on the cell membranes are:

- (a) Membranolysis
- (b) Induce Macrophage Cytotoxicity
- (c) Lipid Peroxidation
- (d) Free radical mediated DNA damage
- (e) Free radical mediated Protein Modifications
- (a) Membranolysis Recent investigations have shown that membranolysis is correlated to the number of silanol groups that occur on the surface of crystalline silica. On heating a cristobalite dust, there is a progressive condensation of silanol into siloxanes. On comparing the different samples, the fibrogenicity remained unchanged but there was a drastic increase in the retention of particles in the lung as well as particle uptake in cells for the sample heated to a high temperature. The site for membranolytic activity is the lysosomal membrane in macrophages, which on phagocytosis of silica particles form the phagolysosomes. The adsorption of proteins and lipids form a coating that can protect the outer cell membrane from the reactive sites on the particle surface. This coating is stripped off by the lysosomal enzymes during internalization, thus exposing the phagolysosomal membrane to the reactive particle-surface. The membrane is then lysed due to molecular interactions between the particle and membrane components.
- (b) Induced cytotoxicity in macrophages: It is important to study the cytotoxic effects of silica in macrophages, as they form the first line of defense mechanism and play an important role in the pathogenic process. Lactate dehydrogenase (LDH) release from macrophage cells is a good indicator of cytotoxicity, especially from crystalline polymorphs of silica. Several investigators have demonstrated the acute toxicity of quartz using % LDH as a scale. This test is extremely effective for quartz and there are various instances when quartz is used as a positive control⁴⁹ for



LDH experiments on other particles.

- (c) Lipid Peroxidation: Lipid peroxidation $^{47, 50)}$ is the oxidative degradation of lipids in cell membranes in the presence of oxygen and transition metal ions or enzymes. It is an autocatalytic process by which free radicals extract electrons from the lipids in cell membranes resulting in cell damage. It has been established as a biomarker of cellular oxidative stress. The three stages of lipid peroxidation are: initiation, propagation and termination. Initiation consists of extraction of H atoms by ROS like OH°, from fatty acids in the cell membrane leaving behind an unpaired electron⁵¹. During propagation, the lipid radical combines with oxygen to form more radicals, leading to a series of autocatalytic chain reactions. The free radicals produced finally combine together during termination. Lipid peroxidation is quantified by measuring the breakdown products.
- (d) Free-radical mediated DNA damage: Generally, amino acid sequences of cellular proteins occur in the nuclear DNA (nDNA) or in the mitochondrial DNA (mtDNA) double helix. Although DNA is a very stable molecule, the mtDNA and nDNA can undergo gradual chemical decomposition over its lifetime. Indirect evidences have implicated that oxidative damage from ROS generation^{47, 50)} in nDNA and mtDNA can lead to inflammation, neurodegenerative diseases, apoptosis, cancer and aging. ROS can cause base modifications (oxidation and deamination), base loss, single and double strand breaks, and cross-linking in DNA. $O_2^{\circ -}$ and hydrogen peroxide (H₂O₂) do not react readily with DNA, but OH° reacts readily with all 4 DNA bases. The ability of crystalline silica to cause DNA damage has been investigated using DNA strand breakage assay.
- (e) Free-radical mediated Protein Modifications: The main amino acid residues of oxidative degradations are histidine, proline, tryptophan, cysteine, tyrosine and to a lesser extent arginine, lysine and methionine⁵²⁾. OH° is the main radical that initiates the radical chain reactions in proteins by extracting hydrogen atom⁵⁰⁾. In addition to protein fragmentation, OH° can also facilitate the generation of protein-protein cross-linkages and induce the formation of higher molecular weight compounds. Methods to detect and measure the oxidative damage in proteins include: protein carbonyl assays and amino acid analysis.

Surface-Modifications to Reduce the Toxic Potential of Silica

It has been noticed that modifying the quartz surface using polymeric coatings like PVPNO^{12, 33, 34)}, aluminum salts^{8, 12, 33)}, tetrandine and other surface functionalization techniques can reduce the toxicity of quartz. Moreover, thermal treatments have also been shown to lead to a general loss of biological activity.

- Polymer Coating: An effective inhibitor of quartz induced silicosis is PVPNO (poly-vinyl-pyridine-N-oxide)^{12, 33, 34)}. The unique cytotoxicity of silica is attributed to the silanol groups (-SiOH) on the particulate surface which are good hydrogen donors and can easily form hydrogen bonds with various biological macromolecules that can efficiently accept hydrogen due to the presence of hydrogen acceptors like nitrogen or oxygen groups with lone pair electrons. So Schlipkoter⁵³⁾ and collaborators postulated that it is possible to mask the -SiOH groups on the particle surface by using hydrogen acceptor molecules like PVPNO. The coated silica would then be theoretically rendered non-toxic, thereby no longer being able to interact strongly with biological molecules. PVPNO, with a chemical name (C7H7NO)_n has a molecular weight ranging from 30,000 - 200,000 kDa and can effectively reduce the in vitro cytotoxicity of crystalline silica and its in vivo fibrogenicity.
- *Aluminum Salts*: It has been shown that the administration of aluminum salt^{8, 12, 33)} can effectively reduce the adverse effects of crystalline silica. Haldane⁵⁴⁾, in 1917, put forth that the non-fibrogenicity of some 'quartz containing dusts' could be due to the presence of certain clay silicates that help to reduce the toxicity. A couple of decades later, it was reported in the study of Denny *et al*⁵⁵⁾ that inhalation of aluminum dusts can inhibit the pathogenic response of silica. The reduction in the solubility of quartz was demonstrated by a number of investigators^{12, 33)} using aluminum powder and aluminum lactate⁵⁶⁻⁶⁰⁾.
- *Tetrandine*: This chemical has been reported to retard and reverse the fibrotic lesions formed due to silicosis in rats⁶¹. Tetrandine has been in use in China for a long time as an 'antifibrotic' drug, although its mechanism of action is quite unclear. Current studies have indicated that it possesses anti-oxidant properties that can effectively inhibit lipid-peroxidation and act as a scavenger for hy-

droxyl and superoxide radicals inside the body⁶², thereby protecting the cells from oxidative damage.

- Thermal treatments¹²: As mentioned before, the silanol groups present on the surface of quartz are converted to siloxane bridges, when the structure is heated to high temperatures. Cristobalite samples were obtained by heating a sample of pure quartz dust to 800°C and found to be fibrogenic in property. But the same samples were non-fibrogenic when heated to 1300°C. Probably, heating to 800°C was not sufficient to eliminate all hydrophilic patches that exist on the surface of quartz¹². Loss of the pathogenic potential of silica occurred due to removal of all hydrophilic regions, when heated to 1300°C.
- Other surface functionalization techniques¹²): The surface properties of quartz can be engineered to attach certain organosilanes with terminal hydrophobic groups⁶³. The modified surfaces show an improvement in the fibrogenic properties. This decrease in fibrogenicity has also been observed in p-amino groups. It is obvious that surface functionalization techniques cannot be used to prevent or treat silicosis but could help us to understand silica pathogenicity better.

Summary

Inhalation of crystalline silica has been shown to cause silicosis from results of epidemiological studies. Physicochemical factors associated with silica dust contribute towards the development of chronic inflammation that may subsequently lead to acute silicosis. The surface activity of crystalline silica particles can influence the generation of free radicals as well as affect particle uptake by macrophage cells in lungs. The undesirable effect of the generated free radical is cell-specific and depends on the form and concentration present in lungs. If not regulated properly, an excess of free radical can disrupt the normal cell functioning and continued exposure can result in pulmonary injuries. Surface modification of crystalline silica particles with polymer coatings, aluminum and tetrandine, thermal treatments as well as other functionalization techniques can reduce in vitro and in vivo toxicity.

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Particle Technology in Chemical Mechanical Planarization[†]

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Abstract

In order to keep pace with Moore's law, multilevel metallization has become the process of choice. Having a planar wafer surface before every successive step in multilevel metallization is important. The Chemical Mechanical Planarization (CMP) process is used in the semiconductor industry to achieve planar surfaces at every step of the multi-level metallization. In CMP, planarization is achieved primarily due to material removal by the use of abrasive particle slurries. In addition to the slurry chemistry, slurry performance is also dictated by the properties of the abrasive particles. A better understanding of the properties of abrasive particles and particle abrasion mechanisms will lead to better CMP. Some of the challenges in particle modeling, slurry stabilization and particle induced lubrication as well as recent developments in engineered particles for CMP are discussed in this paper.

Keywords: CMP, Multilevel metallization, Abrasive particles, Modelling

1. Introduction

Since the invention of the integrated chip (IC) by Jack Kilby in 1959, one of the main objectives of the semiconductor industry has been to increase the number of transistors on the IC in order to improve the processing performance. This fact is also corroborated by Gordon Moore's observation, now famously known as Moore's law: "The number of transistors occupying a given space doubles every two years" ¹⁾. The 65nm node technology, which indicates the minimum DRAM ? pitch, is the current norm in the IC industry and the 45nm node technology is slated for production in 2010²). For sub-0.5 μ m feature sizes, one of the barriers to improved performance is the interconnect delay. The RC time delay (a measure of interconnect delay due to resistance R and capacitance C of the metal line) is the total time taken by the voltage at one end of metal line to reach \sim 63% of the total applied step input at the other end³.

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 Corresponding author TEL: +352-8461194 FAX: +352-8461196 E-mail: bmoudgil@erc.ufl.edu The time delay increases with decrease in thickness of metal and dielectric and is independent of the line width. Thus, performance benefits expected from device scaling are offset by the interconnect delays. Hence one of the strategies employed to reduce the interconnect delay, apart from decreasing the metal resistivity and dielectric constant, is to reduce the line length. Multilevel Metallization (MLM) is employed for forming metal interconnections and its use also helps in reducing the line length, by dividing the



Fig. 1. Schematic of CMP process; ω_s and ω_p refer to angular velocity of carrier and platen respectively. (Fig. 1 from reference 7; Reproduced by permission of the MRS Bulletin.)

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interconnect length over multiple levels as opposed to a single plane. With the reduction in line dimensions, maintaining a planar surface topography after each subsequent processing step becomes important in MLM; an uneven surface topography created during each step in MLM presents challenges such as overexposures during photolithography thus changing the crucial dimensions and line contact interruptions among others. Many techniques such as reactive-ion etch and etch-back, spin on deposition and etch-back, flow-anneal processing are available for planarization, but compared to them chemical mechanical planarization is a relatively simple process and the only technique able to achieve excellent local as well as global planarization ⁴⁾⁻⁶⁾.

Chemical Mechanical Planarization (CMP) is commonly used in the semiconductor industry to achieve smooth and planar surfaces on wafers by chemical and mechanical means⁴⁾. The main components of the CMP process are wafer, pad and slurry. Semiconductor wafer is the surface which needs to be planarized. Pad helps in transferring the mechanical forces to the wafer surface as well as helps in transport of slurry and materials removed from the wafer. Slurry is an aqueous suspension which contains chemicals providing chemical action like modifying the surface layer, and abrasive particles which provide the mechanical action for material removal. The wafer moves in a pre-set geometric pattern against the polymeric pad, which is generally porous with embedded groves, onto which the slurry is fed; material removal occurs from the wafer surface rendering it smooth⁷). In the case of tungsten, the hardness and Young's modulus values of surface layer of tungsten are~22.5GPa and~450GPa respectively; while those for tungsten oxide (WO₃) are \sim 7.5GPa and \sim 125 GPa respectively⁸⁾. It is easier to abrade softer tungsten oxide as compared to tungsten. In tungsten CMP the chemical aspect comes into play by converting the surface layer of tungsten to tungsten oxide with the help of oxidizing agents such as ferricyanidephosphate⁹⁾ while the abrasive particles provide the mechanical aspect of abrading the softer surface layer. The chemical aspect can also come into play through what is known as the 'chemical-tooth action'¹⁰, where the dissolution products from the substrate are adsorbed onto the particle surface and there is a net positive removal away from the surface. In case of glass polishing by ceria abrasives¹⁰, ceria forms bonds with silica which are ruptured due to particle movement away from the bonding site; also dissolved silica is adsorbed onto the abrasive particles, eventually leading to silica build-up on ceria particle surface and material removal from the substrate.

In 2005, the CMP consumables market for slurries, pads and pad-conditioning agents was worth US\$1.1 billion and is expected to grow to US\$1.9 billion by 2009¹¹; the CMP slurry market alone was estimated to be US\$522 million in 2005¹² with anticipated growth over the next few years to US\$1 billion where-in lies the opportunity and challenges for the whole particle community. In the following sections some of the particle technology related issues in CMP are discussed.

2. Particle Based Modeling Approach in CMP

The major pad properties affecting the polishing process are its composition, reactivity, roughness and hardness. Slurry aids in modification, removal and transport of the wafer surface material. The substrate being polished will also have its unique inherent properties. CMP modeling hence is a challenging task due to the sheer number of variables involved. Most of the modeling efforts in CMP are inspired by Preston's equation¹³⁾. It relates the material removal rate (MRR) of a glass substrate to the pressure applied and to the relative velocity between the pad and the substrate being polished, as given by the following equation

 $MRR = K_{p}PV$

Where,
$$K_{p}$$
 = Preston coefficient

P = Pressure

V = Velocity

Preston's equation is empirical in nature and the exact effect of process variables, e.g. abrasive hardness and size, on K_{ℓ} is unclear. Brown developed a simple particle based, two body abrasion model for metal polishing ¹⁴. It considers single abrasive particle penetration into the metal surface using Hertz elastic contact theory and relates the MRR as

$$MRR = \frac{1}{2E} PV$$

Where, *E*= Young's Modulus of the wafer surface

For glass polishing, it was observed by Cook that Brown's model overestimated the polishing rates by over one order of magnitude ¹⁰⁾. This discrepancy was attributed to probable changes in the mechanical properties of the surface due to formation of a layer on it. These preliminary models are too simplistic with very limited applicability. In actuality the abrasion in CMP is a three-body problem, where pad and wafer slide against each other with particles inbetween; and material removal occurs due to the





Fig. 2.1: Abrasive Rolling (on left); Abrasive Sliding (on right) (Reprinted from reference 16; Reproduced by permission of ECS — The Electrochemical Society).

cutting action of abrasives on the soft chemicallymodified wafer surface ¹⁵⁾. This section takes a look at some of the recent models developed taking into account the above mentioned factors.

2.1 Abrasive rolling/sliding model

During polishing, the abrasive particle comes in contact with the pad as well as the wafer. This model¹⁶ proposes that at low pressures the friction at the substrate-abrasive interface is higher, causing the abrasive particles to roll against the wafer substrate; this leads to negligible material removal. As the pressure increases, the friction at the pad-abrasive interface increases and beyond a threshold pressure the abrasives start being dragged by the pad across the substrate causing a sliding motion of the particles leading to appreciable material removal. Choi et al ¹⁷⁾ have corroborated this model on the basis of insitu friction force measurements during polishing. For a given applied load, the higher the interaction at the pad-abrasive-substrate three-point interface, the higher the material removal due to sliding friction resulting from motion of the abrasive particles. On the other hand, as the interaction at the padabrasive-substrate three-point interface decreases due to lower effective contact area, material removal decreases as a consequence of reduced friction due to rolling motion of the abrasive particles. For a given load, sliding occurs at low solids loading or smaller abrasive sizes and, rolling occurs at high solids loading or large abrasive sizes. This model needs further quantification for determining the threshold pressure where rolling motion changes to sliding motion.

2.2 Abrasive contact-area and indentation-volume model

This model proposed by Mahajan *et al*¹⁸⁾ is based on the observations of the oxide CMP using silica particles. Depending on the solids loading and particle size, the material removal occurs via either contact-area mode or the indentation volume mode according to this model.

The higher the concentration of abrasive particles and the smaller their size, the more the abrasive surface area comes into contact with the substrate being polished. In the contact-area mode, smaller particles and higher solids loading would lead to a high MRR. The larger the particles and smaller the solids loading, the more the pressure exerted per particle. In the indentation-volume mode, large particles at lower solids loading would create a bigger indentation volume in the substrate leading to higher MRR. Indentation volume refers to the volume of the surface recesses caused due to the particles. The mathematical expressions for this model follow from the relation developed by Brown *et al*¹⁴⁾

 $A \propto C_0^{1/3} \phi^{-1/3}$

 $V \propto C_0^{-1/3} \phi^{4/3}$

Where, A = total contact area

V =total indentation volume

 C_0 = solids loading

 ϕ = particle size

Mahajan et al ¹⁸⁾ do not give any conditions when the material removal process would cross the threshold between the two modes.

2.3 Abrasive size distribution model¹⁹⁾

Most of the CMP models assume a uniform particle size, however Luo and Dornfeld¹⁹⁾ considered the effect of abrasive size distribution in their model. This model is an extension of their previous work²⁰⁾ based on the concept of active abrasives capable of material removal. It is assumed that the polishing pad has uniform asperities and the active abrasives must be located on the contact area between pad and substrate; also the active abrasives must be larger than the gap formed between pad and wafer substrate due to intermediate presence of a large abrasive particle. This model has been shown to correlate the experimental results obtained by Bielmann *et al*²¹⁾ for tungsten CMP using alumina particles. The MRR has been shown to be proportional to abrasive size by the



following relation

$$\begin{split} MRR & \propto N \, \frac{A_{avg}^2}{D_{avg}^3} \\ \text{Where, } N = \text{number of active abrasives} \\ D_{avg} = \text{average abrasive size} \\ \sigma = \text{standard deviation of the abrasive size} \\ \text{distribution} \\ A_{avg} = (D_{avg} + 3 \, \sigma) = \text{average size of active} \end{split}$$



Fig. 2.3: Material Removal as function of standard deviation of the abrasive size (Reprinted from reference 19 with permission from IEEE; c 2003 IEEE).

The average size of active abrasives increases with standard deviation while the number of active abrasives required for maintaining the same contact area with the substrate decreases. The standard deviation range of abrasive size has been divided into a number dominant region and a size dominant region based on this model. In the size dominant region the active abrasive size as well as MRR increases with standard deviation, and the increase in size of active abrasives is faster than decrease in their number. In the number dominant region the number of active abrasives as well as MRR decreases with standard deviation, and the decrease in number of active abrasives is faster than increase in their size. The use of monodisperse abrasives in a slurry might lead to a low MRR if the standard deviation falls in the size dominant region. This model needs further expansion to obtain optimum value of standard deviation required to achieve effective material removal as well as to reduce scratches.

3. CMP Slurry Stabilization

Golini and Jacobs $^{22)}$ suggest that in polishing the abrasive particle size is generally less than 0.5 μm



Fig. 3: AFM images of the silica wafers polished with (A) baseline $0.2 \,\mu$ m 12wt% monosize silica slurry and (B) slurry with dry aggregates (Reprinted from reference 24 with permission from Elsevier).

as opposed to microgrinding. Also, mono-dispersed abrasive particle size distribution (PSD) leads to a very smooth surface, while poor abrasive PSD control leads to excessive surface scratching¹⁰. Basim et al.^{23), 24)} has showed that the formation of soft-agglomerates or presence of a small percentage of large size abrasive particles in the CMP slurry leads to increase in surface roughness as well as number of surface defects, which can be directly correlated to the size as well as concentration of the soft-agglomerates and large-particles. The initial particle size in CMP slurries is very less and also filtration systems are used before the slurry reaches the polisher, hence the observed defects on the wafer can be attributed to formation of agglomerates during CMP process ²⁵⁾. Thus, the stability of CMP slurries with respect to particle agglomeration is an important issue in order to achieve effective planarization.

3.1 Challenges in CMP slurry stabilization

The CMP slurries present a unique challenge for stabilization due to their chemistries and extreme pH ^{4), 26), 27)}. The slurry should have adequate viscosity in order to maintain an adequate flow rate during the polishing ⁴⁾. The slurry is also subjected to high





Fig. 3.2a: C_{12} TAB, C_{10} TAB, and C_8 TAB surfactants at 32, 68, and 140 mM concentrations in the presence of 0.6 M NaCl at pH 10.5: slurry particle size (stability) and material removal rate responses (Reprinted from reference 27 with permission from Elsevier).

shear and normal forces^{4), 27)}. Electrostatic Stabilization is not sufficient in the high ionic strength environment, because the charge screening will render electrostatic repulsion ineffective, which can lead to formation of agglomerates and increased defectivity. Steric Stabilization and Electrosteric Stabilization using Poly (-mer or -electrolyte) may increase the viscosity of the slurry, thereby affecting its flow rate²⁸; this may also lead to localized slurry concentration gradient on the wafer, thereby leading to uneven etch and removal rates, and defectivity. There have been some recent attempts to stabilize the CMP slurry using polymer / polyelectrolyte^{29), 30)} and, though material removal selectivity was shown to increase, it was found that the viscosity of the solution increased as well as the abrasive PSD became uneven; defectivity studies ³⁰⁾ suggest an increase in within-wafer non-uniformity, with an increase in the molecular weight of the polymer. Thus, CMP slurries warrant either new stabilization mechanisms or a synergistic combination of different stabilization mechanisms. Amphiphilic surfactant molecules have been shown to fit the criterion to disperse particles in conditions similar to CMP slurry ²⁸⁾, hence researchers have focused on surfactants for achieving dispersion in CMP slurries ²⁵⁾⁻²⁷⁾.

3.2 Lubrication in stabilized CMP slurries

Adler *et al*²⁸⁾ showed that resistance to elastic deformation of surfactants is the primary stabilization mechanism occurring in high ionic strength silica slurries (pH~4) similar to CMP slurries, which were stabilized using surfactant molecules. It was observed that the particle agglomeration was found to decrease as sufficient amount of surfactant became available to cover the particle fully, which was also shown to decrease the defectivity as measured by the surface roughness²⁵⁾⁻²⁷⁾. In CMP slurries stabilized using C_nTAB surfactant molecules, Basim *et al*²⁷⁾ observed that the slurry stability increased as the surfactant chain length increased due to interparticle repulsion; but it led to a lowering of material removal rates (**Fig. 3.2a**).

It was seen that when the surfactant was added to the baseline slurry in the absence of salt, the lateral (frictional) force between the particle and substrate remained constant even though the loading (normal) force was increased; this explains the possible lower material removal rates observed. When salt was added, it was observed that the lateral force increased beyond a certain loading force, which



Fig. 3.2b: AFM friction force measurements on silica wafer with 7.5- μ m-size particle attached to the tip for solutions containing C₁₂TAB, C₁₀TAB, and C₈TAB surfactants at 32, 68, and 140 mM concentrations in the absence of salt at pH 10.5 (on left) and in the presence of 0.6 M salt in the solution (on right) (Reprinted from reference 27 with permission from Elsevier).



can be explained due to charge screening between the negatively charged silica and positive surfactant headgroup leading to surfactant desorption from the particle at higher loading force (**Fig. 3.2b**). Thus it was shown that along with particle-particle interactions, particle-substrate interactions should also be considered in formulation of stable CMP slurries.

4. Engineered Abrasives for CMP Slurries

Apart from the chemistry of slurry involved, slurry performance is also governed by the properties of the abrasive particles. Just to name a few, hardness, chemical composition, shape and density of the particles control the slurry behavior as well as affect the CMP performance. Though ceria is better in material removal of silica due to chemical-tooth action¹⁰ it can pose problems with respect to slurry stability due to its relatively high density of $\sim 7g/cc$ leading to clogged slurry flow lines³¹⁾. Also, it is difficult to control the size and shape of synthesized ceria abrasives. Similarly silica abrasives are ineffective in copper CMP; and alumina particles due to their relatively high hardness of 9-8 on mho's scale⁴⁾ are more susceptible to cause scratches during polishing. In order to overcome these problems and take advantages of some of the inherent properties of the abrasive material, researchers have engineered specific abrasives for CMP slurries.

4.1 Mixed abrasive slurries

Silica abrasives are known to have a minor effect on copper material removal, but are effective in polishing of tantalum and the protective oxide film formed on it due to chemical-tooth action ^{32), 33)}. In order to achieve comparable MRR of copper and tan-



Fig. 4.1: Copper and tantalum disk polish rates by slurries containing alumina/fumed silica particles dispersed in DI water at pH 4 with 3 wt % total particle loading (Reprinted from reference 34; Reproduced by permission of ECS — The Electrochemical Society).

talum during the second step CMP of wafer with copper interconnects having tantalum as diffusion barrier material, Jindal *et al* ³⁴⁾ used the mixed abrasive slurry of alumina and silica abrasives for CMP. The mean aggregate particle sizes for calcined alumina and fumed silica abrasives were 220 and 70-90nm respectively and, the slurry pH was maintained around 4.

When a slurry of 0.5% alumina and 2.5% silica maintained at pH of 4 was used, the smaller silica particles formed a sheath around the alumina particles due to electrostatic interactions. This led to decreased polishing action of alumina on copper. It was seen that MRR of copper and tantalum were of similar magnitude as compared to when abrasives were used independently.

4.2 Nanoporous abrasive slurries

Scratching and de-lamination of the wafer substrate materials, especially of low-k dielectric materials, are some of the major problems encountered in CMP. These problems can be overcome if the hardness of



Fig. 4.2a: Change in hardness (on left) and Hamaker constant (on right) of silica particles with porosity (Reprinted from reference 37).



the abrasive is reduced while maintaining its ability to chemically modify the wafer while polishing, this can be achieved by synthesis of porous abrasive particles³⁵.

The porous silica nanoparticles were synthesized by hydrolysis and condensation reaction using glycerol as porogen; on calcination of the dried particles, the traces of organic glycerol were removed creating a porous network in the particles³⁵. It was observed that the hardness decreased while the elasticity of the particles increased with porosity leading to lower scratching during CMP of black diamond³⁶.

The slurry formulated from these particles was



Fig. 4.2b: Change in number of scratches on black diamond, silica and silicon nitride substrates polished with 0.2μ m silica slurry (5wt% loading, pH 3) as a function of surface porosity of silica particles (Reprinted from reference 36).

also observed to be stable owing mainly due to a decrease in Hamaker constant of the porous particles³⁷⁾.

5. Summary and outlook

Though many facets are now known, the exact science of CMP is still not completely understood. The role of abrasive particles in CMP is just one of the parameters controlling the planarization process. The modeling effort in CMP mainly takes into account the mechanical aspects of the particle and surface and rarely is the chemical aspect considered. There is a need for developing the models taking both the chemical and mechanical aspects into account which can satisfactorily explain the experimental observations. The models need to incorporate parameters which would yield the degree of global planarity in addition to acceptable material removal rate. As in many particle industries, slurry stability is still an issue in CMP which is further magnified due to scratching problems created by particle aggregation. Particle technology needs to address the issue of designing abrasive particles that are able to provide stable slurries as well as achieve efficient planarization. Our understanding of the CMP process needs to be further enhanced in order to tailor the particles according to substrate and application requirements. Also new routes to utilize CMP for producing tailored surfaces using functionalized particles need to be explored. Lastly CMP is a means to an end and not an end in itself; so the particle community has an opportunity to apply the CMP knowledge to fields other than microelectronics.

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Flow Pattern in Hydrocyclones[†]

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Abstract

This paper presents a review of the flow pattern in hydrocyclones from a fluid dynamics perspective. Measurements attempt to establish the velocity and pressure distribution inside the equipment. With the experimental values of the velocity distributions, mass and linear momentum equations were solved using different approximations. The review starts with discussion of the principal experimental measurements in hydrocyclones and continues obtaining theoretical solutions to the equations with the simplest inviscid approach combining a free vortex with a sink, with rotational inviscid models, with models based on the exact solution of the Reynolds equation for highly idealized conditions and ends with solutions using different mathematical techniques such as asymptotic expansions, similarity solutions and boundary layer flows. When developments of the models can be found in the original papers they were not reproduced here, but in some cases they were include to relate them to a given fluid dynamic solution type.

Keywords: Hydrocyclone, Modeling, Cyclone, Flow pattern, Fluid dynamics

Introduction

A hydrocyclone is a classification devise consisting of a cylindrical or a cylindrical-conical body with a tangential



Fig. 1 Commercial type of a hydrocyclone and its interior parts. (1) Involuted entrance, (2) Vortex finder,
(3) Inlet head casting, (4) Cylindrical section, (5) Mounting flanges, (6) Cone casting, (7) Liners, (8) Apex valve, (9) Pneumatically operated apex orifice, (10) Feed and overflow adaptor. Courtesy Krebs Engineering.

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entrance and two opposite axial exits. The top exit is called *vortex* which consists of a tube, called *vortex finder*, extending into the cylindrical section of the vessel. At the bottom of the cone, the exit is called *apex*. **Fig. 1** shows a commercial hydrocyclone.

The feeding tube, which is of circular or rectangular cross-section, joins tangentially to the body of the hydrocyclone. Since the flow enters at the periphery and top of the equipment and leaves through the cyclone core, at the top and the bottom of the vessel, a three-dimensional fluid motion, called *vortex motion* must exist, with a tangential, axial and radial velocity. The vortex motion produces a zone of low pressure in the center of the equipment that sucks air from outside forming an air core of unknown nature. The shape of this air column has been described as cylindrical and conical but by simple observation these descriptions do not fit the real shape.

While in normal operation a hydrocyclone has axial and tangential velocities of the order of several meters per second, the radial velocity is one order of magnitude smaller. This very fact is the reason why the radial velocity distribution in the equipment is not very well known. In the presence of highly turbulent tangential and axial velocities, the fluctuations of these velocities are of the same order of magnitude as the radial velocity making it difficult to measure.

Flow patterns in hydrocyclones have been studied by many authors (Kelsall 1952, 1963; Ohasi and Maeda 1958; Knowles et al. 1973; Dabir and Petty 1984; Bhattacharyya 1880a, 1980b, 1984; Gu and Li 1987; Hsieh and Rajamani 1988a, 1988b, 1991; Rajamani and Hsieh 1988; Quian et al. 1989; Xu et al. 1990; Hwang et al. 1993). In this review we will analyze three of the most notable measurements.

The first and most cited velocity measurement was studied by Kelsall (1952, 1963) using small cyclones with diluted feeds containing fine aluminum particles. With proper illumination the motion of the particle were followed with a microscope having rotating objectives. The following figure shows the tangential, axial and radial velocity distribution obtained by Kelsall.

Kelsall (1963) describes his finding in the form: "Beneath the bottom of the vortex finder, envelopes of constant tangential velocity are cylinders coaxial with the cyclone, and, at any horizontal level, starting from near the conical wall, this component of velocity increases with decrease in radius according to the relationship $vr^n = K$, with 0 < n < 1, where *K* is a constant". This holds in the region near the center of the cyclone, where the velocity reaches a maximum value at a radius somewhat smaller than that of the inside of the vortex finder. As the radius is further decreased the tangential velocity decreases such that $v \propto r$.

The two most significant features of the vertical velocity distribution are the approximately conical envelope defining regions of zero vertical velocity. In regions between the conical wall and the zero velocity envelope, all liquid flows downwards towards the apex and between the envelope and the central axis, or wall of the air core column if present, all liquid flows upwards towards the vortex finder.

"The limited information about the inward radial velocity component tends to indicate that, at any horizontal level, near the conical wall the following expression is valid: $v_r = v_z \tan \theta$, where θ is the half angle of the cone."

Twenty years past since Kelsall's measurements until other measurements were made. During this time, the



Fig. 2 Tangential, axial and radial velocity components according to Kelsall (1963).



development laser Doppler velocimetry (LDV) improved significantly velocity measurements. Very accurate measurements of the tangential and axial velocity distribution were made by Hsieh and Rajamani (1984a, 1988). **Fig. 3** shows a schematic view of the laser Doppler velocimeter system and hydrocyclone used by Hsieh and Rajamani (1988).

The glass hydrocyclone was 75 mm inside diameter with an inlet diameter of 23 mm, vortex-finder of 23 mm, apex of 11 mm and total height of 244 mm. Over 200 hundred measurements were taken of the two velocity components, tangential and axial, at each location, 1mm radial direction and 10 mm axial direction. The fluid medium was water with small silicon carbide powder to enhance the data collection ability of the receiving optics. Due to the magnitude of the fluctuating component of the velocities (turbulence), which are of the order of 20 to 50 cm/s, as seen in **Fig. 4** for the tangential velocity, measurement of the radial velocity was not possible, since it was of the same order of magnitude as the turbulence. Therefore the radial velocity component was calculated from the continuity equation.

Fig. 5 shows the axial velocity measurements in the vortex-finder region. The asymmetry of the axial velocity predominates near the region of the inflow and gradually becomes almost symmetric in the lower part of the cone. Further, there is more than one reversal in the flow direction in the region between the vortex-finder and the hydrocyclone wall.

Fig. 6 shows the distribution for the three components of the velocity along the hydrocylone as measured and calculated by Hsieh and Rajamani (1988a).

Quian et al. (1989) also used LDV to measure the velocity distribution in a conventional and a water-sealed hydrocyclone, both of 82 mm diameter body, 12 mm internal diameter vortex finder and 6 mm internal diameter apex and a feed pressure of 0.9 kg/cm^2 .

In the cylindrical section the tangential and radial velocities are very small while the axial velocity is in the range of 0.5 m/s. In the conical section the value of the tangential velocity varied from 2 m/s, close to the wall, to approximately 4 m/s at its maximum value. They confirmed Kelsall's expression $v_{\theta}r^n = K$ and gave the values of the parameter n = 0.432 and the constant K = 7.95. They noted an air core of 8mm diameter rotating at 10300 rpm. For the axial velocity they obtained values around 1.5 m/s, which they approximated with the following expression $v_z = \ln(r/(a+br))$, where a and b are constant depending on the distance from the vortex finder, as seen in table 1. Finally, the radial velocity increased from close to zero near the hydrocyclone wall to around -4 m/s close to the air core. We must note that this result is opposite to that of Kelsall's and different to that of Hsieh and Rajamani.

The measurement of the velocity distribution in a hydrocyclone is the first step in predicting the flow pattern from a fluid mechanic point of view. The simplest approach is to use inviscid isochoric flows. The three dimensional nature of the flow produces a secondary an-isotropic flow near the entry region. Since the classification action of the equipment is performed below the level of the bottom of the vortex finder tube, an axial-symmetric simplifica-



Fig. 3 laser Doppler velocimeter system and hydrocyclone.





Fig. 4 Turbulent fluctuation of the tangential component, according to Hsieh and Rajamani (1988).



Fig. 6. Tangential, axial and radial velocity components according to Hsieh and Rajamani (1988a).

FINDER 37.5 30 mm 20 10 0 20 mm 30 37.5 10 ATT - 10 UTT V INLET [cm/sec] 20 100 ग्मा axlal valocity -50 - 30 mm 40 -0 50 CENTRAL AXIS

VORTEX

Fig. 5 Axial velocity profile in the inlet region, according to Hsieh and Rajamani (1988).

Distance from the vortex finder in mm	а	b
45	-6.906	1.429
75	-7.579	1.506
105	-6.924	1.670
135	-5.142	1.745
165	-3.482	1.733

tion of the flow is possible without loosing the main features of the vortex motion. To model the feeding of the hydrocyclone in an axial-symmetric model, a feeding ring substitutes the actual shape of the feeding tube. This imaginary device has a certain height that, in combination with the radial entry velocity, yields the volumetric flow into the equipment. The flow enters with a combination of a tangential and radial velocity, the ratio of which is dependent on the geometry of the real entry.

The fast inlet velocity, of the order of several meters per second, produces a highly turbulent flow in the equipment. The modeling of the turbulence is crucial in obtaining reasonable results of the flow patterns.



Fluid Dynamic Equations

The Navier Stokes equations have been for many years the starting point to solve fluid dynamic problems involving simple fluids, like liquids and gases at moderate temperature and pressure. For laminar incompressible flows they may be represented by the equations:

$$\frac{\partial \rho v}{\partial t} + \nabla \cdot \rho v v = \nabla \cdot T + b, \qquad \nabla \cdot v = 0$$
(1)

where ρ and v are the density and velocity of the fluid and T and b are the tensor and external force field respectively. To study specific problems it is necessary to set a boundary value problem stipulating boundary conditions.

The turbulent flow of a Newtonian fluid is modeled with the instantaneous and the time averaged velocity, stress and external force fields of the Navier-Stokes equations $v = \overline{v} + v'$, $T = \overline{T} + T'$ and $b = \overline{b} + b'$. Integrating the resulting equations for a short time, Reynolds Equations are obtained:

$$\frac{\partial \rho \bar{v}}{\partial t} + \nabla \cdot \rho \bar{v} \bar{v} = \nabla \cdot \left(\bar{T} - \rho \overline{v' v'} \right) + \bar{b}, \qquad \nabla \cdot \bar{v} = 0$$
⁽²⁾

where \overline{v} , \overline{T} and \overline{b} are the mean velocity, mean stress tensor and mean body force fields, while v' is the fluctuating velocity field, ρ is the constant fluid density and $-\rho \overline{v'v'}$ are the Reynolds stresses. In most cases, research workers have used Reynolds equations to model the hydrocyclone. The choice of constitutive equations for the stress tensor and Reynolds stresses and the mathematical tools used to solve the equations will be reviewed in this paper.

Unfortunately the Navier Stokes equations or the Reynolds equations, depending on the case, are non-linear and, therefore, difficult to solve. There are three approaches to solve these boundary-value problems:

(1)Exact solutions. The first and most common approach to solve these equations is to find exact solutions for highly idealized situations for which the non-linear terms vanish due to the geometry or symmetry of the flow. These solutions are rarely valid for real configurations, but often give an indication of the flow and pressure distribution to be expected in the real problem.

(2) Extreme solutions. The difficulties encountered in obtaining general solutions to the flow equations have shown that it is advantageous to divide the flow into categories depending on the relative value of the several terms of the equations and to neglect the terms of lower order of magnitude. To perform this task the Navier Stokes equations are written in dimensionless form:

$$\frac{1}{St}\frac{\partial v^*}{\partial t^*} + \nabla^* v^* \cdot v^* = -\frac{1}{Ru}\nabla^* p^* + \frac{1}{Re}\nabla^{*2}v^* + \frac{1}{Fr}b^*, \qquad \nabla^* v^* = 0$$
(3)



Fig. 7 Tangential, axial and radial velocity components according to Quian et al (1989).



with
$$St = \frac{t_0 u_0}{L}, \quad Ru = \frac{\rho u_0^2}{p_0}, \quad Re = \frac{\rho u_0 L}{\mu}, \quad Fr = \frac{u_0^2}{Lg}$$

where the stress tensor *T* was expressed as the sum of a pressure *p* and an extra stress modeled as a Newtonian fluid, *L*, t_0 , u_0 and p_0 are characteristic parameters of the flow and *St*, *Ru*, Re and *Fr* are the Strouhal, Ruark, Reynolds and Froude dimensionless numbers and the asterisk indicates dimensionless field variables. The Reynolds number is the ratio of the convective to the diffusive forces in the flow and therefore, it is a good parameter to divide the flow into three categories:

(a) Euler's isochoric flows

Euler's isochoric flows, or inviscid flows, are obtained if the convective forces are much greater than the diffusive, or viscous, forces. In this case the Reynolds number is infinite, making the second term in the right hand side of (3) vanish:

$$\rho \frac{\partial v}{\partial t} + \nabla v \cdot v = -\nabla p + b, \qquad \nabla \cdot v = 0$$
(4)

(b) Stokes flow

Stokes flow is obtained if the convective forces are much smaller than the viscous forces. In this case the Reynolds number is very small ($Re \rightarrow 0$), making the second term in the left hand side of (3) negligible:

$$\rho \frac{\partial v}{\partial t} = -\nabla p + \mu \nabla^2 v + b , \qquad \nabla \cdot v = 0$$
(5)

(c) Prandtl's flow

Prandtl's flow, or boundary layer flow, is obtained when the Reynolds number is high but convective forces are of the same order of magnitude as the diffusive forces.

Inviscid Isochoric Models

Many research workers have suggested an inviscid isochoric flow for the hydrocyclone, that is, the flow of an ideal fluid. The reason for this is that, for hydrocyclones, the tangential velocity shape is very close to a free vortex, as can be seen from the experimental observations. Within ideal flows, we can distinguish rotational and irrotational flows. The field equations for inviscid isochoric flows are:

$$\nabla \cdot v = 0$$
 $\nabla B = v \times \omega$ $B = \frac{p}{\rho} + \frac{1}{2}v^2$ (6)

where *v*, *w* and *p* are the velocity, vorticity and pressure fields and *B* is the Bernouilli. Body forces have been neglected.

1. Irrotational inviscid isochoric flow (Potential flow model)

For potential flow the field equations become:

 $\nabla \cdot v = 0 \qquad \qquad \nabla \times v = 0 \qquad \qquad \nabla B = 0$

Combining these equations we get:

$$v = -\nabla\phi$$
, $\nabla^2\phi = 0$, $\frac{1}{2}v^2 + \frac{p}{\rho} = \text{constant}$ (7)

where ϕ is the velocity potential. For cylindrical plane flows the Laplace equation is valid:

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} = 0, \qquad p(r) = p(R) - \frac{1}{2} \rho \left(v_R^2 + v_{\theta R}^2 \right) \left(1 - \frac{v_r^2 + v_{\theta}^2}{v_R^2 + v_{\theta R}^2} \right) \tag{8}$$

$$v_r = -\frac{\partial \phi}{\partial r}$$
, $v_\theta = -\frac{1}{r} \frac{\partial \phi}{\partial \theta}$ (9)

All measurements of the flow patterns in hydrocyclones (Kelsall 1952, Hsieh and Rajamani 1988a, Quian et al. 1989) have shown that the tangential velocity has the form of a free vortex from the cyclone wall in the direction of the axis. Near the axis, the tangential velocity resembles that of a solid body rotation. For the radial velocity, there is no agreement between the different measurements, as can be seen in figures 1 to 3. The best assumption that can be made, from Hsieh and Rajamani's measurement, is that the radial flow is similar to a sink close to the cyclone wall but is proportional to the radius closer to the cyclone axis. Taking these observations into consideration, the simplest model for the hydrocyclone is a combination of a free vortex and a rigid motion with a sink. This combination is also called a *forced vortex with a sink*.

Consider the flow in a hydrocyclone, working without an air core, divided into two regions, the vortex core for $0 \le r \le R_c$, where the flow is a rigid body motion with constant angular velocity $w = v_{\theta} (R_c)/R_c$ and the exterior region $R_c \le r \le R$, where the flow is a free vortex with a constant circulation $\Gamma = 2 \pi R v_{\theta R}$. The total flow rate into the cyclone per unit length is $\hat{Q} = 2 \pi R v_R$.

Region R_c≤r≤R:

The solution of equations (8) and (9) in this region yields a free vortex and a sink for the tangential and radial velocity respectively:

$$v_{\theta} = \frac{\Gamma}{2\pi r}, \qquad v_r = -\frac{\hat{Q}}{2\pi r} \tag{10}$$

From Bernouilli's equation:

$$p(r) - p(R) = \frac{1}{2}\rho \left\{ v^2(R) - v^2(r) \right\}$$

Since $v^2 = v_{\theta}^2 + v_r^2$, substituting the values of (10) at *r* and *R*, yields

$$p(r) = p(R) - \frac{\rho}{2} \left(\frac{\Gamma}{2\pi R}\right)^2 \left\{ 1 + \left(\frac{\hat{Q}}{\Gamma}\right)^2 \right\} \left\{ 1 - \left(\frac{R}{r}\right)^2 \right\}$$
(11)

Region $0 \le r \le R_c$

In this region a forced vortex and a sink represent the tangential and the radial velocity respectively:

$$v_{\theta}(r) = \omega r, \qquad v_r = -\frac{\hat{Q}}{2\pi r} = -\left(\frac{\hat{Q}}{\Gamma}\right)\left(\frac{R}{r}\right)$$
(12)

where *w* is the angular velocity of the rigid motion. At $r = R_c$, the velocity fields of both regions intersect, that is, $wR_c = \Gamma/2 \pi R_c$, from which R_c can be calculated as:

$$R_c = \left(\frac{\Gamma}{2\pi\omega}\right)^{1/2} \tag{13}$$

Fig. 8 shows the tangential and radial velocity profiles for the *forced vortex with a sink* model.

For a rigid body motion the pressure can be calculated from, $\nabla B = (2\rho\omega^2 r)e_r$, where e_r is the unit vector in the direction of the radius pointing outwards. Integrating from R_c to r yields:

$$p(\xi) + \frac{1}{2}\rho v^{2}(\xi)\Big|_{\xi=R_{c}}^{\xi=r} = \rho \omega^{2} \eta^{2}\Big|_{\eta=r}^{\eta=r}, \qquad p(r) = p(R_{c}) + \frac{1}{2}\rho v^{2}(R_{c}) - \frac{1}{2}\rho v^{2}(r) + \rho \omega^{2} r^{2} - \rho \omega^{2} R_{c}^{2}$$

Replacing v from (12) gives:

$$p(r) = p(R_c) + \frac{1}{2}\rho\omega^2 \left(r^2 - R_c^2\right) + \frac{1}{2}\rho\left(\frac{\hat{Q}}{\Gamma}\right)^2 \left\{ \left(\frac{R}{R_c}\right)^2 - \left(\frac{R}{r}\right)^2 \right\} \text{ for } 0 \le r \le R_c$$
(14)

Fig. 9 shows the pressure distribution.

Several authors, for example Fontain and Dijsman (1953), suggested models of this type.





Fig. 8 Tangential and radial velocity profiles for a potential flow model of a hydrocyclone for Γ =7.065, Q=0.1413 and ω =50.



Fig. 9 Pressure distribution for a potential flow model of a hydrocyclone for Γ =7.065, Q=0.1413 and ω =50.

2. Rotational inviscid isochoric model

For steady flow $\dot{B}=\nabla B \cdot v$, therefore, from equation (6) $\dot{B}=v \times w \cdot v\equiv 0$, which indicates that Bernouilli is constant along streamlines. Then, in *spherical coordinates* (ξ, ϕ, θ) we can write:

$$v_{\xi}\frac{\partial}{\partial\xi}\left(\xi\sin\phi v_{\theta}\right) + \frac{v_{\phi}}{\xi}\frac{\partial}{\partial\phi}\left(\xi\sin\phi v_{\theta}\right) = 0 \tag{15}$$

therefore, $\xi \sin \phi v_{\theta} = f(\psi)$ is constant along a streamline, where $f(\psi)$ is the vorticity function, which must be a constant at the wall. Bloor and Ingham (1973, 1974, 1975, 1984) assumed that the tangential velocity was a free vortex everywhere, that is, $v_{\theta} = f(\psi)/\xi \sin \phi$. Using the stream function to satisfy the continuity equation the velocity components may be written in the form:

$$\frac{\partial}{\partial\phi} \left(\frac{1}{\phi} \frac{\partial\psi}{\partial\phi} \right) = -\xi^4 f\left(\psi\right) \tag{16}$$

Assuming a vorticity function of the form $f(\psi) = F \psi^{-5/3}$, Bloor and Ingham obtained the following velocity distributions:

$$v_r = -A \frac{r^{3/2}}{z^2} v_{\phi} = \frac{k}{r} v_z = \frac{1}{2} A r^{-1/2} \left\{ 3\alpha - r(r/z) \right\}$$
(17)
where
$$k = \frac{0.8QR}{A_i}$$
 and $A = \frac{Q}{2\pi (d_v/2)^{3/2} (\alpha - d_v/2\ell)}$ (18)

and Q is the volume flow rate to the hydrocyclone, A_i is the feed inlet area, d_v is the external diameter of the vortex finder tube and ℓ is the distance form the apex to the lower part of the vortex finder tube. Fig. 10 shows the tangential and radial velocity, while Fig. 11 shows the axial velocity distribution, according to Bloor and Ingham.

Bryshaw (1978) explored other vorticity functions for equation (16). Using *cylindrical coordinates*, he derived the following boundary conditions for the stream function $f(\psi)$ at the entry section, at the underflow and at the overflow respectively:

$$\frac{1}{R^2} \frac{d^2 \psi}{dz^2}, \qquad \frac{1}{r^2} \left. \frac{d^2 \psi}{dr^2} \right|_{r=R_{\mu}} - \left. \frac{1}{r^3} \left. \frac{d\psi}{dr} \right|_{r=R_{\mu}}, \qquad -\frac{1}{r^2} \left. \frac{d^2 \psi}{dr^2} \right|_{r=R_{\mu}} + \left. \frac{1}{r^3} \left. \frac{d\psi}{dr} \right|_{r=R_{\mu}}$$
(19)

He found that a gamma function and an exponential function were suitable for $f(\psi)$ and gave rise to different particle selectivity curves, with the gamma function showing a sharper separation. Fig. 12 shows a plot of different vorticity function as given by Bryshaw (1978).

Models Based on the Exact Solutions of Reynolds Equation

In general, the turbulent velocity distribution in a hydrocyclone is three dimensional, as we have already discussed, but the flow can be approximated, except for the region close to the entrance, as an axial-symmetric mo-



Fig. 10 Velocity distribution for the isochoric rotational flow model of a hydrocyclone according to Bloor and Ingham (1974).









Fig. 12 Three different vorticity functions according to Brayshaw (1978).

tion. Kelsall (1952) was the first author to determine the essential features of the flow pattern in the hydrocyclone. With a fair degree of approximation, his work shows that the radial and tangential velocities depend on the *r* coordinate only. Then, neglecting the body forces, Reynolds equations in cylindrical coordinates, with the turbulence represented by a constant eddy viscosity v_{ε} much greater than the kinematical shear viscosity v_{t} , can be written in the form:

$$\frac{\partial}{\partial r}(rv_r) + \frac{\partial}{\partial z}(rv_z) = 0 \tag{20}$$

$$v_r \frac{\partial v_r}{\partial r} - \frac{v_\theta^2}{r} = \frac{1}{\rho} \frac{\partial p}{\partial r} + v_\varepsilon \frac{\partial}{\partial r} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r v_r \right) \right\}$$
(21)

$$\frac{v_r}{r}\frac{\partial}{\partial r}\left(rv_{\theta}\right) = \mathbf{v}_{\varepsilon}\frac{\partial}{\partial r}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{\theta}\right)\right\}$$
(22)

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = v_e \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{\partial^2 v_z}{\partial z^2} \right\}$$
(23)

The approach followed by the different authors to solve this set of equations depends on the assumptions made by them with respect to the form and dependence of these equations. Their guideline was the experimental velocity distribution obtained by authors such as Kellsal (1952), Knowles et al (1973), Hsieh and Rajamani (1988a) and Quian et al (1989). We will organize this section based on these assumptions.

1. Models with $v_r = v_r$ (r), $v_{\theta} = v_{\theta}$ (r) and $v_z = 0$

All early authors (Rietema and Krajenbrink 1958, Rietema 1961, Van Dujin and Rietema 1983 and Upadrashta 1987) considered a cylindrical hydrocyclone with the feed entering through the entire cylindrical mantel at r=R and having a radial velocity v_R and a tangential velocity $v_{\theta R}$ at the entrance, see Fig. 13.

Thus, the flowrate into the hydrocyclone is given by $Q=2 \pi RLv_R$ and the circulation at r=R is $\Gamma(R)=2 \pi Rv_{\theta R}$, where *L* is the height of the cylinder. The boundary conditions for a hydrocyclone with and without an air core were respectively:

With air core:

$$v_{\theta}(R) = v_{\theta R}, \ v_r(R) = v_R, \ v_r(0) = 0$$
(24)

Without air core:





Fig. 13 Physical model of a cylindrical hydrocyclone.

$$v_{\theta}(R) = v_{\theta R}, \ v_r(R) = v_R, \ v_r(R_a = R_o) = 0$$
 (25)

where R_a is the radius of the air core and R_o is the radius of the overflow opening.

Rietema and Krajenbrink (1958) analyzed two cases, the hydrocyclone with and without an air core. Since the feed to the hydrocyclone entered through the whole cylindrical mantle they assumed no axial velocity. This is equivalent to assume that a linear sink evacuates the fluid at the cylinder axis. Then, from the continuity equation (20) and boundary condition (25) for r=R, the radial velocity becomes:

$$v_r = R v_R / r \tag{26}$$

Introducing equations (25) and (26) into equation (22), they solved for $v_{\theta}(r)$ with the radial Reynolds number, defined by $\text{Re}=Rv_R/v_e$, as a parameter. Their solutions are given in equations (27) and (28) and also in **fig. 14** and **15**. For a cylindrical hydrocyclone with an air core the size of the overflow R_o:

$$v_{\theta}^{*} = \begin{cases} \frac{\text{Re}R_{o}^{*2-\text{Re}} - 2r^{*2-\text{Re}}}{\text{Re}R_{o}^{*2-\text{Re}} - 2} & \text{for } \text{Re} > 0 \neq 2\\ \frac{1 - 2\ln R_{o}^{*}/r^{*}}{1 - 2\ln R_{o}^{*}} & \text{for } \text{Re} = 2\\ 1 & \text{for } \text{Re} = \infty \end{cases}$$
(27)

For a cylindrical hydrocyclone without an air core:

$$v_{\theta}^{*} = \begin{cases} \frac{R_{o}^{*2-\text{Re}}(2-\text{Re}-2\exp(-\text{Re}/2)) + \text{Re}\exp(\text{Re}/2) r^{*2-\text{Re}}}{R_{o}^{*2-\text{Re}}(2-\text{Re}-2\exp(-\text{Re}/2)) + \text{Re}\exp(\text{Re}/2)} & \text{for} \quad \text{Re} > 0 \neq 2 \text{, } 1 > r^{*} > R_{o}^{*} \\ \frac{1+2\ln(R_{o}^{*}/r^{*}) - \exp(1)}{1+2\ln R_{o}^{*} - \exp(1)} & \text{for} \quad \text{Re} = 2 \text{, } 1 > r^{*} > R_{o}^{*} \\ \frac{R_{o}^{*2-\text{Re}}(2-\text{Re}) + \left(1 - \exp\left(-r^{*}/R_{0}^{*}\right)^{2}(\text{Re}/2)\right)}{R_{o}^{*2-\text{Re}}(2-\text{Re}-2\exp(-\text{Re}/2)) + \text{Re}\exp(\text{Re}/2)} & \text{for} \quad \text{Re} > 0 \neq 2 \text{, } R_{o}^{*} > r^{*} > 0 \\ \frac{\exp(1 - (r^{*}/R_{o}^{*})) - \exp(1)}{1 + 2\ln R_{o}^{*} - \exp(1)} & \text{for} \quad \text{Re} = 2 \text{, } R_{o}^{*} > r^{*} > 0 \\ 1 & \text{for} \quad \text{Re} = \infty, \quad 1 > r^{*} > 0 \end{cases}$$

Comparing their result with experimental information, Rietema and Krajenbrink concluded that the correct radial Reynolds number for this problem is close to Re \approx 3. In other words, that the turbulent eddy viscosity should be a constant of the order of $v_e \approx 3 \times 10^{-4}$ m/s. In a further analysis, these authors indicate that, if wall effect were taken into account, the tangential velocity would depend on the *z* coordinate.

In 1961, Rietema published a study assuming that the radial velocity was constant $v_r = v_R$ in the whole flow field. He claimed that this assumption was based on Kelsall's measurements. (As a matter of fact Kelsall's experiments show that the radial velocity is proportional to the radial distance from the axis). With $v_r = v_R$, Rietema solved equa-



tion (21) and pointed out that these results were valid for a conical hydrocyclone with a Reynolds number of $Re\approx$ 10 (turbulent kinematical eddy viscosity of $\nu_e = 10^{-4} \text{m}^2/\text{s}$). His solution, for a dimensionless air core of $R_a^* = 0.15$, is given in equations (29) to (31) and in **Fig. 14**.

$$v_{\theta}^{*} = C_{2}(\text{Re}) - C_{1}(\text{Re}, R_{a}^{*}) \exp(-\text{Re} r^{*}) \left(\frac{r^{*}}{\text{Re}} + \frac{1}{\text{Re}^{2}}\right)$$
(29)

with
$$C_1(\operatorname{Re}, R_a^*) = \frac{\operatorname{Re}^2}{-(1 + \operatorname{Re})\exp(-\operatorname{Re}) + ((R_a^{*2}/2) + R_a^*\operatorname{Re} + 1)\exp(-\operatorname{Re} R_a^*)}$$
 (30)

and
$$C_2(\text{Re}) = 1 + C_1(\text{Re}R_a^*)\exp(-\text{Re})\left(\frac{1}{\text{Re}} + \frac{1}{\text{Re}^2}\right)$$
 (31)

In 1962, Rietema solved the same set of equations and boundary conditions (8) for $v_r = (v_R/R)r$, in accordance to Kelsall's measurements. His solution was (see Fig. 17):

$$v_{\theta}^{*} = \frac{1}{r^{*}} + \frac{C_{3}(\operatorname{Re}, R_{a}^{*})}{r^{*}} \left[\exp\left\{-\left(1/2\right) \operatorname{Re}\right\} - \exp\left\{-\left(1/2\right) \operatorname{Re} r^{*2}\right\} \right]$$
(32)

with
$$C_3(\operatorname{Re}, R_a^*) = \frac{1}{\{1 + (1/2)\operatorname{Re} R_a^{*2}\} \exp(\operatorname{Re} R_a^{*2}) - \exp\{-(1/2)\operatorname{Re}\}}$$
 (33)

In a final work Van Duijin and Rietema (1983) went back to their 1958 solution, but now using the equations for a mixture of a solid and a fluid.

One additional work was done on the same line as Rietema's. Upadrashta and Venkateswarlu (1983) and Upadrashta et al. (1983) analyzed the flow of a non-Newtonian pseudo-plastic fluid in a hydrocyclone. His analysis was justified since concentrated suspensions, such as those used in the mineral industries, are of this type. Based on the measurements of Kelsall (1952), (which were made with water) they assumed that the radial velocity had the form $v_r = (v_R/R)r$. Introducing this term and a constitutive equation for the non-Newtonian fluid, they obtained the following expression for the dimensionless tangential velocity and the dimensionless air core radius respectively:

$$v_{\theta}^{*} = \frac{1}{r^{*}} \left[1 - \frac{1}{\operatorname{Re}_{m}} \frac{2^{n'} \left(1 - n'\right)}{n'} \left\{ \left(\frac{1}{r^{*}}\right)^{2n'} - 1 \right\} \right]^{2}$$
(34)

$$R_a^* = \left\{ \frac{1}{\operatorname{Re}_{\mathrm{m}}} \frac{2n' \left(2n'+1\right) \left(1-n'\right)}{2n' \left(1-n'\right)+n' \operatorname{Re}_{\mathrm{m}}} \right\}^{1/2n'}$$
(35)

For the case of a Newtonian fluid, n'=1, and (34) reduces to a free vortex.



Fig. 14 Tangential velocity profile according to Rietema and Krajenbrink (1958) for a cylindrical hydrocyclone with a dimensionless air core the size equal to the overflow $R_a^{*}=R_a^{*}=0.15$.



Fig. 15 Tangential velocity profile according to Rietema and Krajenbrink (1958) for hydrocyclone without air core and a dimensionless overflow opening of $R_{\phi}^{*}=0.15$.





Fig. 16 Tangential velocity profile according to Rietema with $R_a^* = 0.1$ (1961).

ig. 17. Tangential velocity profile according to Rietema with $R_{\circ}^{*}=0.15$ (1962).

2. Models with $v_r = v_r(r)$, $v_\theta(r)$ and $v_z(r,z)$

The problem with the previous models is that they do not consider explicitly the axial velocity. Furthermore, their solutions serve only to calculate the centrifugal force, but give no clue as to how the particles are separated and how the particles and fluid are evacuated from the equipment. Furthermore, the authors were not concerned if their models satisfy the continuity equation. The conclusion is that, if the velocity distributions are to be used in hydrocyclone modeling, it is essential to incorporate the axial component of the Reynolds equation in the dynamic process.

Integrating the continuity equation (20) yields:

$$rv_r(r) = -\int \frac{\partial rv_z(r,z)}{\partial z} r dr + K$$
(36)

Since, by assumption, the radial component of the velocity is a function or *r* only, it is clear from (36) that the axial velocity gradient $\partial v_z/\partial z$ must be independent of *z*, that is, the most general form of the axial velocity should be (Donald and Sullivan 1960):

$$v_z = f(r)z + g(r) \tag{37}$$

Case 1.: *f*=0; *v*_z=*g*(*r*)

Consider first the case when the axial velocity is an arbitrary function of *r* independent of *z*, than:

$$v_z = g(r), \ \frac{\partial v_z}{\partial z} = 0 \text{ and } v_r = \frac{Rv_R}{r}$$
(38)

Equation (38) implies that the radial flow becomes infinite at the cylinder axis; therefore a singularity is introduced into the equations if the axis of symmetry is included in the domain. In that case, no solution exists for which the tangential velocity diminishes as the radius diminishes, reaching a finite value at the axis. On the other hand, for a hydrocyclone with an air core of radius R_a , the tangential velocity distribution has the following form:

$$v_{\theta}^{*} = \frac{1}{r^{*}} \frac{(2/\text{Re}) (r/R_{a})^{-(R_{a}-2)} - 1}{(2/\text{Re}) (R_{a}/R)^{-(R_{a}-2)} - 1}$$
(39)

Since the function g(r) is arbitrary, assume the following form for the dimensionless axial velocity, which compares favorably with experimental data:

$$v_z^* = 1 - 1.8\sin^6\left(\frac{r - 0.5}{R}\right)$$
(40)

Fig. 19 shows the tangential and axial velocity distributions given by equations (39) and (40).

Consider the case of an axial velocity as a linear function of *z*, with g(r) an arbitrary function of *r*. The problems analyzed by Rietema (1961) and Upadrashta et al (1987) correspond to this case. Rietema assumed a constant radial velocity ($v_r = v_R$), which implies that $f(r) = v_r/r$. For this case, g(r) can be an arbitrary function of *r*. Then,





Fig. 18 Tangential velocity profile according to equation (34) for a power law fluid with n'=0.5 and R_a^* =0.15.



Fig.19 Tangential and axial velocity profile with v_z^* given by (40).

$$v_r = v_R$$
, $v_\theta = v_\theta(r)$ and $v_z = \frac{v_R}{r}z - 1.8\sin\frac{6r - 0.5}{R}$ (41)

Their axial velocity distribution is given in Fig. 20.

Collantes et. al. (2000) applied this case to a flat bottom hydrocyclone, with f and g as arbitrary functions of r to be determined. Introducing the general form of the axial velocity into the field equations and eliminating the pressure, the following set of equations is obtained for f(r) and g(r):

$$\frac{d}{dr}\left\{v_r(r)\frac{df(r)}{dr} + f^2(r) - v_{\varepsilon}\frac{1}{r}\frac{d}{dr}\left(r\frac{df}{dr}\right)\right\} = 0$$

$$\frac{d}{dr}\left\{v_r(r)\frac{dg(r)}{dr} + f(r)g(r) - v_{\varepsilon}\frac{1}{r}\frac{d}{dr}\left(r\frac{dg}{dr}\right)\right\} = 0$$
(42)

To satisfy the continuity equation a stream function ψ was defined, such that:

$$v_r(r) = \frac{1}{r} \frac{\partial \psi}{\partial z} \equiv \frac{q(r)}{r} \text{ and } v_z = -\frac{1}{r} \frac{\partial \psi}{\partial r} \equiv -\frac{1}{r} \frac{dq}{dr} z + g(r)$$
 (43)

Defining the dimensionless variable $\eta = (r/R)^2$, and introducing these expressions into (42) the following equations were obtained for $q(\eta)$ and $g(\eta)$:





Fig.20 Axial velocity profile according to equation (41).

$$\frac{dq(\eta)}{d\eta} \frac{d^2q(\eta)}{d\eta^2} - q(\eta) \frac{d^3q(\eta)}{d\eta^3} = 0$$

$$\frac{d}{d\eta} \left\{ q(\eta) \frac{dg(\eta)}{d\eta} \right\} - \frac{d}{d\eta} \left\{ \frac{dq(\eta)}{d\eta} g(\eta) \right\} = 0$$
(44)

The viscous terms were neglected in equation (42). This is the same assumption made by Bloor and Ingham (1976), which gave good results for the axial velocity (see previous section). A solution to this ordinary differential equation system, compatible with the boundary conditions for a flat bottom hydrocyclone, where the feed enters the equipment through a ring of height L_A in the upper part of the cylinder, see **Fig. 21**, is:

Finally, the velocity distributions for zone I and II are: Zone I

$$v_r(r) = -\frac{Q}{2\pi r L_A} \left[\frac{Q_o}{Q} \left[1 - \exp\left\{ -5.6 \left(\frac{r}{R_o} \right)^2 \right\} \right] - \sin\left\{ \beta \left(\frac{r}{R} \right)^2 \right\} \right]$$
(45)

$$v_{z}(r,z) = \frac{Q}{\pi R^{2}} \left[\beta \cos\left\{ \beta \left(\frac{r}{R}\right)^{2} \right\} + \left[5.6 \frac{Q_{o}}{Q} \left(\frac{R}{R_{o}}\right)^{2} \exp\left\{ -5.6 \left(\frac{r}{R}\right)^{2} \right\} - \beta \left(\frac{r}{R}\right)^{2} \right] \frac{z}{L_{A}} \right]$$
(46)



Fig. 21 Schematic representation of the flat-bottom hydrocyclone according to Collantes at all (2000).



$$v_{\theta}(r) = \frac{\Gamma_R}{2\pi r} \left[\frac{1 - \exp\left\{-\frac{1}{2}\operatorname{Re}\beta\left(\frac{r}{R}\right)^2\right\}}{1 - \exp\left(-\frac{1}{2}\operatorname{Re}\beta\right)} \right]$$
(47)

where $\beta = \pi + \arcsin(Q_u/Q)$, and where Q, Q_u and Q_0 are the volume feed and the overflow rate respectively, and R is the hydrocyclone radius. All the volume flowrates are taken positive. Note that in (45) the factor $-Q/2 \pi L_A r \equiv v_R R/r$ and in (46) and (47) $Q/\pi R^2 \equiv 2v_R L_A/R$ and $\Gamma_R/2 \pi r = v_{\theta R} R/r$. **Zone II**

$$v_r(r) = -\frac{Q}{2\pi \left(L - L_A\right) r} \left[\sin\left\{\beta \left(\frac{r}{R}\right)^2\right\} + \frac{Q_u}{Q} \left[1 - \exp\left\{-5.6\left(\frac{r}{R}\right)^2\right\}\right] \right]$$
(48)

$$v_{z}(r,z) = -\frac{Q}{\pi R^{2}} \begin{bmatrix} 5.6 \frac{Q_{u}}{Q} \left(\frac{R}{R_{u}}\right)^{2} \exp\left\{-5.6 \left(\frac{r}{R}\right)^{2}\right\} - \left\{\beta \cos\left(\frac{r}{R}\right)^{2}\right\} \\ +5.6 \frac{Q_{u}}{Q} \left(\frac{R}{R_{u}}\right)^{2} \exp\left\{-5.6 \left(\frac{r}{R}\right)^{2}\right\} \frac{z}{L-L_{A}} \end{bmatrix}$$
(49)

$$v_{\theta}(r) = \frac{\Gamma_R}{2\pi r} \left[\frac{1 - \exp\left\{\frac{\text{Re}}{2}\beta\frac{L_A}{L - L_A}\left(\frac{r}{R}\right)^2\right\}}{1 - \exp\left(\frac{\text{Re}}{2}\beta\frac{L_A}{L - L_A}\right)} \right]$$
(50)

In (48) $Q/2\pi (L - L_A)r = v_R R L_A/r(L - L_A)$ and in (49) $Q/\pi R^2 \equiv 2v_R L_A/R$. In both zones the pressure distribution can be calculated from:

$$p(r,z) = p_0 - \frac{\rho}{2} \left\{ v_r(r)f'(r) + f^2(r) \right\} z^2 - \rho \left\{ v_r(r)g'(r) + f(r)g(r) \right\} z + \rho \int \frac{v_\theta^2}{r} dr - \frac{1}{2}v_r^2(r)$$
(51)

From the exact solutions of the Reynolds equations, as given in this section, and from the conclusions of the several research workers that have modeled the hydrocyclone in this manner, we can conclude that the radial velocity depends strongly on the shape of the axial velocity. One can obtain completely different radial velocities distributions by choosing appropriate axial flows. Nevertheless, the shape of the tangential velocity, as a combination of a free vortex and a rigid motion, is insensible to the form of these axial and radial velocities. Only the maximum value of the tangential velocity and its position varies as the radial velocity changes. It is important to note that none of the radial velocities chosen by Rietema or Upadrashta have associated axial velocities that resemble the experimental ones.

For the axial velocity to be a consequence of the radial velocity, it must be a function of r and at least a linear function of z. Finally, we can indicate that, in modeling the hydrocyclone, the selection from several solutions to the field equations by comparing the size of the maximum of the tangential velocity with experimental values is not the proper way to go. The three, or at least two, velocity components must be compared and especially the axial velocity must be reasonable.

Case 3.: Models with $v_{\theta} = v_{\theta}$ (r), $v_r = v_r$ (r, z) and $v_z = v_z(r,z)$

The more recent experimental data of Hsieh and Rajamani (1988) and Quian et al (1989) confirm that the radial and axial velocities are functions of the radial and axial coordinates.

Bloor and Ingham (1974, 1983) analyzed the inviscid isochoric flow within a hydrocyclone, as we already saw. Assuming a free vortex for the tangential velocity, they obtained the radial and axial component as functions of the radial and axial coordinates. Since these velocities compared favorably with Kelsall's experimental information, Bloor and Ingham used the resulting axial and radial velocities to recalculate the tangential velocity from Reynolds' s equations with variable eddy viscosity.

Consider the tangential component of Reynolds's equation:

$$\frac{v_r}{r}\frac{\partial}{\partial r}(rv_\theta) + v_z\frac{\partial v_z}{\partial z} = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{v_\varepsilon r^3\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{\partial}{\partial z}\left(v_\varepsilon\frac{\partial v_z}{\partial z}\right)\right\}$$
(52)





Fig 22 Simulated tangential velocity distribution according to Collantes et al (2000). Comparison with experimental data from Chiné and Concha (2000).



Fig. 23 Simulated axial velocity distribution, according to Collantes et al. (2000).

Using dimensionless coordinates: $r^* = r/R$, $v^*_{\ \theta} = v_{\ \theta}/v_{\ \theta R}$, radial and axial velocities given by $v_r = -A\frac{r^{3/2}}{z^2}$ and $v_z = (1/2)A(1/r^{1/2})(3a - 5(r/z))$, and assuming that the eddy viscosity has the following form: $v_{\varepsilon} = v_t/z^2$ (necessary for the tangential velocity to be independent of *z*), Bloor and Ingham obtained from (15) with boundary conditions $v^*_{\ \theta}(1) = 1$ and $v^*_{\ \theta}(0) = 0$:

$$v_{\theta}^{*} = \frac{1}{r^{*}} \gamma \left(\frac{4}{5}, \frac{2}{5}, r^{*5/2} \lambda_{\text{Re}}\right) / \gamma \left(\frac{4}{5}, \frac{2}{5}, \lambda_{\text{Re}}\right)$$
(53)

where *r* is the incomplete gamma function, λ_{Re} is a type of Reynolds number defined by $\lambda_{\text{Re}} = AR^{5/2}/v_t$ and where v_t is fluid kinematical viscosity. The assumption that $v_{\varepsilon} = v_t/z^2$ implies that the length scale ℓ of the turbulence in the



Prandtl's mixing length theory, $\nu_{\varepsilon} = \ell^2 \left| K + \frac{\partial v_{\theta}}{\partial r} - \frac{v_{\theta}}{r} \right|$, varies as $\ell = h(r)/z$ (Bloor and Ingham 1983). Fig. 25 gives the new tangential velocity distribution.

In 1987 Bloor and Ingham made a further analysis of the swirling flow in hydrocyclones without underflow in terms of the vorticity function. They started from the continuity equation in spherical coordinates and the Bernouilli equation:

$$\nabla \cdot v = 0, \quad \nabla B = v \times w \tag{54}$$

where *B* is the Bernouilli and *w* is the vorticity defined by $w = \nabla \times v \ w = \nabla xv$. In component form:

$$\frac{\partial}{\partial\xi} \left(\xi^2 v_{\xi} \sin \phi \right) + \frac{\partial}{\partial\phi} \left(\xi v_{\phi} \sin \phi \right) = 0$$
(55)

$$w_{\xi} = \frac{1}{\xi \sin \phi} \frac{\partial}{\partial \phi} \left(v_{\theta} \sin \phi \right); \ w_{\phi} = -\frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi v_{\theta} \right); \ w_{\theta} = \frac{1}{\xi} \left(\frac{\partial}{\partial \xi} \left(\xi v_{\phi} \right) - \frac{\partial v_{\xi}}{\partial \phi} \right)$$
(56)

To satisfy the continuity equation a stream function was used with components:



Fig. 24 Radial velocity distribution for zone I and II, according to Collantes et al. (2000).



Fig. 25 Tangential velocity distribution according to Bloor and Ingahm (1976).



$$v_{\xi} = \frac{1}{\xi^2 \sin \phi} \frac{\partial \psi}{\partial \phi} \quad \text{and} \quad v_{\phi} = -\frac{1}{\xi \sin \phi} \frac{\partial \psi}{\partial \xi}$$
 (57)

The θ , ξ and θ component of vorticity were obtained from the ϕ and θ component of equation (56). The solution to the stream function led to the following velocity distributions:

$$v_{\theta} = \frac{R}{r} v_{\theta R} \left(1 - \frac{2\psi}{R^2 v_z} \right)^{1/2}$$
(58)

$$v_r = 2\sigma \sin\phi \left[\left\{ \csc^2\alpha + \ln(\tan\alpha/2) - \csc\alpha \cot\alpha \right\} \cos\phi - \left\{ \cos\phi \ln(\tan\alpha/2) \right\} \right] + \frac{r^2 \cos\phi \left(\cos^2\phi - \cos^2\alpha - \sin^2\phi \right)}{\sin^2\phi \left(1 - 5\cos^2\phi \right)}$$
(59)

$$v_{z} = 2\sigma \sin\phi \left[\left\{ \csc^{2}\alpha + \ln(\tan\alpha/2) - \csc\alpha \cot\alpha \right\} \cos\phi - \left\{ \cos\phi \ln(\tan\alpha/2) \right\} \right] + \frac{r^{2}\cos\phi(\cos^{2}\phi - \cos^{2}\alpha - \sin^{2}\phi)}{\sin^{2}\phi(1 - 5\cos^{2}\phi)} + 2\sigma \left[\begin{bmatrix} \left\{ \csc^{2}\alpha + \ln(\tan\alpha/2) - \csc\alpha \cot\alpha \right\} \sin^{2}\phi \\ -\sin^{2}\phi \ln(\tan\phi/2) + \cos\phi - 1 \\ + 2r^{2}\frac{\cos^{2}\phi - \cos^{2}\alpha}{1 - 5\cos^{2}\alpha} \end{bmatrix} \right]$$
(60)

where
$$\sigma = -\pi R^2 v_{\theta R}^2 / Q v_z$$
 (61)

Bloor and Ingham (1987a, 1987b) show that their solution compared well with experimental values of Kelsall (1952) and of Knowles et al (1973). They indicate that the way the entry conditions are modeled has a profound effect on the nature of the flow. See **Fig. 26**.

Hwang et al (1993) extended the work of Bloor and Ingham (1987a) to include underflow through the apex. To do this, they use a stream function for the sink in the form:

$$\psi_1 = \frac{Q\cos\phi\cos\alpha}{2\pi(1+Q_o/Q_u)(1-\cos\alpha)} \tag{62}$$

With this modification the velocity distributions become: (see Fig. 27):

$$v_{\theta} = \frac{R}{r} v_{\theta R} \left(1 - \frac{2\psi}{R^2 v_z} \right)^{1/2}$$

$$v_r = -\frac{Q \sin \phi}{2\pi R^2} \left[\frac{1 + \Lambda}{\eta^2} \frac{1}{1 - \cos \alpha} + 2\sigma \left[\frac{D(\alpha)}{\sin^2 \alpha} \cos \phi - 1 - \cos \phi \ln \left\{ \tan \left(\phi/2 \right) \right\} \right] \\ + \frac{Q \cos \phi}{2\pi R^2} \left\{ \frac{D(\alpha)}{\sin^2 \alpha} \sin \phi - \frac{D(\alpha)}{\sin \phi} \right\} \right]$$

$$v_z = -\frac{Q \cos \phi}{2\pi R^2} \left[\frac{1 + \Lambda}{\eta^2} \frac{1}{1 - \cos \alpha} + 2\sigma \left[\frac{D(\alpha)}{\sin^2 \alpha} \cos \phi - 1 - \cos \phi \ln \left\{ \tan \left(\phi/2 \right) \right\} \right] \\ - \frac{Q \sin \phi}{2\pi R^2} \left[2\sigma \left\{ \frac{D(\alpha)}{\sin^2 \alpha} \sin \phi - \frac{D(\alpha)}{\sin \phi} \right\} \right]$$
(63)

where *Q* is the feed volume flowrate, *R* is the radius of the cylindrical part of the hydrocyclone, σ is given by (61), $\Lambda = Q_0/Q_u$ is the flow partition between overflow and under flow streams and where is the operator $D(\circ)=1-\cos(\circ)+\sin^2(\circ)\ln(\tan(\circ)/2)$.

Similarity Solution of Reynolds Equations

Mikaylov and Romensky (1974) solved Reynolds equations for the flow within a hydrocyclone assuming axial symmetry and self-similarity, with the similarity variable $\eta = z/r \equiv z^*/r^*$, independence of v_{θ} from z and an air core modeled given by the following equation:





Fig. 26 Velocity distribution according to Bloor and Ingham (1987b) compared with experimental values by Kelsall (1952) and by Knowles et al (1973).



Fig. 27 Simulated velocity distribution compared with measurements according to Hwang et al (1993).



$$\frac{d_a}{R} = 0.64 \frac{d_o}{R} \tan\left(\frac{\alpha}{2}\right)^{0.3} \tag{65}$$

Defining the dimensionless variables, $r^* = r/R_{\text{max}}$ and $v^*_{\ \theta} = v_{\ \theta}/v_{\ \theta \text{max}}$, where the characteristic variable R_{max} is the value of r where the tangential velocity has its maximum $v_{\ \theta \text{max}}$, they obtained the following set of field equations,

$$\frac{v_{\theta}^*}{r^*} = \frac{1}{2} \frac{\mathrm{d}p^*}{\mathrm{d}r^*} \tag{66}$$

$$\frac{v_r^*}{r^*} \frac{\mathrm{d}}{\mathrm{d}r^*} \left(r^* v_r^* \right) - \frac{r^*}{z^*} v_z^* \frac{\mathrm{d}v_\theta^*}{\mathrm{d}r^*} = \frac{1}{2r^{*2}} \frac{\mathrm{d}}{\mathrm{d}r^*} \left(r^* T_{r\theta}^{*E} \right) \tag{67}$$

$$\frac{1}{r^*}\frac{\mathrm{d}}{\mathrm{d}r^*}\left(r^*v_r^*\right) - \frac{r^*}{z^*}\frac{\mathrm{d}v_z^*}{\mathrm{d}r^*} = 0 \tag{68}$$

They give the solutions to these equations in the form:

$$v_{\theta}^{*} = \frac{1}{\left(1 + \frac{1}{b^{2}}\left(r^{*} - \frac{1}{r^{*}}\right)^{2}\right)^{0.5}} \tag{69}$$

$$v_{z}^{*} = Cv_{\theta}^{*} \frac{\mathrm{d}}{\mathrm{d}r^{*}} \left(r^{*}v_{\theta}^{*}\right) + \frac{0.5}{r^{*}v_{\theta}^{*}} \frac{z^{*}}{r^{*}} \frac{\mathrm{d}}{\mathrm{d}r^{*}} \left(r^{*}T_{r\theta}^{*E}\right) + f\left(r^{*}, z^{*}\right)$$
(70)

$$v_r^* = \left\{ v_{\theta}^* \frac{r^*}{z^*} - \frac{\left(r^* v_{\theta}^*\right)^2}{r^*} \right\} \left\{ \frac{C_1}{z^*} + g\left(r^*\right) \right\} + C_2$$
(71)

$$\Delta p = 2 \int \frac{v_{\theta}}{r^*} \mathrm{d}r^* + C_3 \tag{72}$$

The constants depend on the geometry of the hydrocyclone and on the boundary conditions. To obtain the solution they modeled the extra stress $T_{r\theta}^{*E}$ empirically from measurements of the velocity distributions:

$$\frac{\mathrm{d}}{\mathrm{d}r^*}\left(r^{*2}T_{r\theta}^{*E}\right) = C_4 r^* v_{\theta}^* h\left(r^*\right) \tag{73}$$

The authors claim good agreement with their own experimental information. However, in setting up the equations, they eliminate terms arbitrarily in the dimensionless field equations. It is not clear the reason for some elimination since, in the *r* and *z* components of the field equations they eliminated terms of the order of $O(10^{-2})$, while in the θ component they eliminated terms of the order of $O(10^{-3})$. Furthermore, in the *z* component, they eliminate the pressure gradient $\partial p^*/\partial z^*$, which is of the order of O(1). Their results are given in **Fig. 28**.

Nepomnyashchii and Pavlovskii (1977, 1980), made a dimensional analysis of the integral angular momentum equations and, using the similarity theory, concluded that the velocity components and the pressure within a hydrocyclone could be expressed as an expansion in series of functions of the similarity variables:

$$v_{\theta}^{*} = z^{*-3/2} \varphi_{1}(\eta) + \operatorname{Re}^{-1} z^{*-1} \varphi_{2}(\eta) + \dots$$
(74)

$$v_z^* = z^{*-3/2} f_1(\eta) + \operatorname{Re}^{-1} z^{*-1} f_2(\eta) + \dots$$
(75)

$$v_r^* = \operatorname{Re}^{-1} z^{*-1} F_1(\eta) + \dots$$
 (76)

$$p^* = z^{*-3}g_1(\eta) + \operatorname{Re}^{-1} z^{*-5/2} + \dots$$
(77)

where $v_{\theta}^* = v_{\theta}/v_{\theta R}, v_z^* = v_z/v_{zR}, v_r^* = v_r/v_{rR}$ and $p^* = (p - p_0)/\rho v_{\theta}^2$

In this case, the Reynolds number is defined in terms of the tangential characteristic velocity $v_{\theta R}$. Inserting the expressions for the velocities into the field equations yields as the first term in the expansion:





Fig. 28 Velocities and pressure distributions according to Mikhailov and Romenskiy (1974).

$$\varphi_1(\eta) = C_1 \eta^{-3/2}, \quad f_1(\eta) = C_2 \eta^{-3/3}, \quad g_1(\eta) = -\frac{1}{3} C_1^2 \eta^{-3}, \quad F_1(\eta) = A_1 \eta^{-1},$$
(78)

$$\varphi_2(\eta) = D_1 \eta^{-2} + D_2 \eta^{-1}, \quad f_2(\eta) = B_2 \eta^{-1}, \quad g_2(\eta) = E_1 \eta^{-7/2} + E_2 \eta^{-7/2}$$
 (79)

$$A_1 = -\frac{20C_1^2 + 63C_2^2}{8C_1^2 + 42C_2^2}, \quad D_1 = -\frac{21C_1C_2}{8C_1^2 + 42C_2^2}, \quad E_1 = -\frac{6C_1^2C_2}{4C_1^2 + 21C_2^2}, \quad E_2 = -\frac{4}{5}C_1D_2$$
(80)

$$I = \frac{(R-R_a)H_1}{RR_a} + \frac{H_2}{R_a} - \cot\alpha \ln\left\{\frac{R}{R-H_2 - n\alpha}\right\}$$
(81)

$$C_{1} = \left(\frac{2}{2I}\right)^{1/2}, \quad C_{2} = \frac{Q_{o}}{2\pi R^{3/2} R_{v} v_{\theta R} \left\{ \left(\frac{R}{R_{v}}\right)^{1/2} - 1 \right\}} \quad \text{and} \quad D_{2} = \frac{\frac{15C_{1}^{2}C_{2}}{4C_{1}^{2} + 21C_{2}^{2}} \int_{s_{l}} \frac{dr}{r^{1/2}} dz}{\frac{6}{5}C_{1} \int_{s_{l}} \frac{dr}{r^{1/2}} dz}$$
(82)

where H_1 and H_2 are the height of the cylindrical and conical sections respectively, R_v is the outer radius of the vortex finder tube and R_a is the radius of the air core. With these values the velocities distributions are:

$$v_{z} = \frac{Q}{2\pi} \frac{\frac{R}{r} - \left(\frac{R_{o}}{R}\right)^{1/2} \left(\frac{R}{r}\right)^{3/2}}{\left\{1 - \left(\frac{R_{o}}{R}\right)^{1/2}\right\}^{2}}, \quad v_{\theta} = v_{F} \left(\frac{R_{F}}{3}\right)^{3/2}, \quad v_{r} = v_{F} \left(\frac{R_{o}}{R}\right) \frac{A_{1}}{C_{1}^{2/3} \operatorname{Re}} \frac{R}{r}$$
(83)

$$p = p_0 - \frac{1}{3}\rho v_F^2 \left(\frac{R_F}{r}\right)^3, \quad R_a = \frac{R_F}{R} \left\{\frac{\rho v_F^2}{3(p_{\max} - p_o)}\right\}^{1/3}$$
(84)

In these equations p_{max} is the maximum pressure in the apparatus and R_F is the eccentricity of the hydrocyclone feed, that is, the distance from the axis to the center of the inlet pipe.

This model does not satisfy the boundary conditions at the cyclone's wall, therefore, it can be considered to be valid far from wall only.

Davidson (1988) indicated that Boor and Ingahm's solution of equation (16) could be generalized in the form:

$$\Psi = (\xi \phi)^m \left(\alpha^\beta - \phi^\beta \right); \text{ with } \beta = 2 (2-m)$$
(85)

Unfortunately, no analytical solution of this form could be obtained. Instead, Davidson (1988) proposed a similarity solution, in cylindrical coordinates with the tangential velocity independent of the axial coordinate, of the form:



$$v_{z} = z^{n} F(r/z) , v_{r} = z^{n} G(r/z) , p = P(r) + \rho z^{2n} p_{0}(r/z)$$
(86)

$$\Psi = z^{n+2}H(r/z)$$
, $\frac{dH}{d(r/z)} = F(r/z)$, $G(r/z) = (r/z)^2 F - (n+1)H$ (87)

$$H = \gamma^{1/2} \left(r/z \right)_c^2 \times \left(d^2 - \phi^2 \right), \quad F = a \gamma^{1/2} \phi \left(d^2 - \phi^2 \right)^{-1/2}$$
(88)

where ϕ is a function obtained by solving the equation:

$$\sum_{k=0}^{k} a_i \phi^{2k-2i+1} = \frac{1}{4} \left(-1\right)^{k+1} \left\{ \left(\frac{r/z}{r/z_c}\right) - 0. \right\}$$
(89)

Davidson solved these equations numerically obtaining excellent agreement for the velocity distributions with n=0.5 (corresponding to m=3/2) compared to the experimental values of Knowles et al (1973) and Kelsall (1952). In this case the axial velocity is:

$$v_z = Ar^{-1/2} \{ 1.5\alpha - 2.5 (r/z) \}$$
(90)

where *A* is a constant. Fig. 29 shows this axial velocity:

Asymptotic Solutions of The Reynolds's Equations

According to Collantes and Concha (1998, 2000), the most general axial-symmetric model of a hydrocyclone, having the inflow through a cylindrical mantle, may be expressed in terms of a dimensionless axial-symmetric stream function Ψ and a dimensionless circulation Γ :

$$v_r = \frac{1}{r} \frac{\partial \hat{\psi}}{\partial z}; \quad v_z = -\frac{1}{r} \frac{\partial \hat{\psi}}{\partial r}; \quad v_\theta = \frac{\Gamma}{r}$$
(91)

with the radial Reynolds number $\text{Re}=Rv_R/v_e$, the dimensionless number $R_0=Lv_R/Rv_{\,\theta\,R}$, representing the ratio of the total flow Q to the hydrocyclone to the circulation $\Gamma(R)$ at the cyclone's outer edge, and the characteristic length $a = (R/\ell)^2$ as parameters. Appropriate values of ℓ are $\ell = L_A$ in zone I and $\ell = L - L_A$ in zone II. The following two equations represent the flow field with $\eta = (r/R)^2$, $\xi = z/\ell$, $\Gamma = rv_{\,\theta}/Rv_{\,\theta\,R}$, $\Psi = \hat{\Psi}/(Q/2\pi)$, L the length of the hydrocyclone and L_A the length of the hydrocyclone's feed:

$$\frac{\partial \psi}{\partial \xi} \frac{\partial \Gamma}{\partial \eta} - \frac{\partial \psi}{\partial \eta} \frac{\partial \Gamma}{\partial \xi} = \left(\frac{2\eta}{\text{Re}} \frac{\partial^2 \Gamma}{\partial \eta^2} + \frac{\alpha}{2\text{Re}} \frac{\partial^2 \Gamma}{\partial \xi^2}\right) \frac{\ell}{L_A}$$
(92)



Fig. 29 Axial velocity for the isochoric rotational flow model of a hydrocyclone according to Davidson (1988), compared with experimental data of Kelsall (1952). A) n = -0.5; b) n = -1.8.



(96)

$$\Gamma \frac{\partial \Gamma}{\partial \xi} = R_o \left[4\eta^2 \left\{ \frac{\partial \psi}{\partial \xi} \frac{\partial^3 \psi}{\partial \eta^3} - \frac{\partial \psi}{\partial \eta} \frac{\partial^3 \psi}{\partial \xi \partial \eta^2} - \frac{2\ell}{\operatorname{Re} L_A} \left(2\frac{\partial^3 \psi}{\partial \eta^3} + \eta \frac{\partial^4 \psi}{\partial \eta^4} \right) \right\} \right] + \alpha \left(-\frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \xi^2} + \eta \frac{\partial \psi}{\partial \xi} \frac{\partial^3 \psi}{\partial \eta \partial \xi^2} - \eta \frac{\partial \psi}{\partial \eta} \frac{\partial^3 \psi}{\partial \xi^3} - \frac{\ell}{\operatorname{Re} L_A} \left(4\eta^2 \frac{\partial^4 \psi}{\partial \eta^2 \partial \xi^2} + \frac{\alpha}{2} \eta \frac{\partial^4 \psi}{\partial \xi^4} \right) \right)$$
(93)

In hydrocyclone flow, the tangential velocity is two orders of magnitude greater than the radial velocity, therefore the dimensionless number R_0 is always small (of the order of 10^{-2}). For that reason it is convenient to solve equations (92) and (93) as a series expansion in R_0 :

$$\Gamma = \sum_{n=0}^{\infty} \Gamma_n(\eta, \xi) R_0^n \text{ and } \psi = \sum_{n=0}^{\infty} \psi_n(\eta, \xi) R_0^n$$
(94)

Replacing these terms into equations (93) yields:

$$\left(\Gamma_o \frac{\partial \Gamma_o}{\partial \xi}\right) R_o^0 + (\dots) R_o^1 + \dots = (\dots) R_o^1 + (\dots) R_o^2 + \dots$$
(95)

therefore: $\Gamma_0 = \Gamma_0(\eta)$

Zero order approximation

Collantes and Concha (1998, 2000) show that as a zero order approximation:

$$\psi_0 = f_{oo}(\eta) + \xi f_{01}(\eta) \tag{97}$$

$$\Gamma_{0} = \frac{\int_{0}^{\eta} \exp\left[\operatorname{Re} \times L_{A}/2\ell \int_{0}^{t} \left\{f_{01}(s)/s\right\} ds\right] dt}{\int_{0}^{1} \exp\left[\operatorname{Re} \times L_{A}/2\ell \int_{0}^{t} \left\{f_{01}(s)/s\right\} ds\right] dt}$$
(98)

It is convenient to divide the hydrocyclone into two zones: the inlet zone, which will be called zone I, and zone II below this, see **Fig.21**. Boundary conditions for equation (97) are obtained from the values of the stream functions $\xi=1$ at zone I and $\xi=0$ at zone II. Physically this means that for small values of R_0 , the stream function is totally specified by their boundary conditions. For a flat bottom hydrocyclone, such as shown in **Fig. 21**, the boundary conditions equivalent to setting $v_r(R)=v_R$, $v_r(0)=0$, $v_\theta(R)=v_{\theta R}$, $v_z(r,0)=Q/2\pi R_u^2$ and $v_z(r,L)=(Q-Q_D)/2\pi R_u^2$ were found to be:

In zone I:
$$f_{00}(\eta) = j(\eta), f_{01}(\eta) = \frac{Q_o}{Q} (1 - \exp(-100\eta)) - j(\eta)$$
 (99)

In zone II:
$$f_{00}(\eta) = -\frac{Q_o}{Q} \left(1 - \exp\left(-150\eta\right)\right), f_{01}(\eta) = j(\eta) + \frac{Q_o}{Q} \left(1 - \exp\left(-150\eta\right)\right)$$
 (100)

Where: $j(\eta) = 1445.32\eta^5 - 6166.26\eta^{4.5} + 11025\eta^4 - 10676\eta^{3.5} + 5964.80\eta^3 - 1829.91\eta^{2.5} + 220.59\eta^2 + 15.53\eta^{1.5}$ (101)

In the zero order approximation, which is with n=0, the circulation and stream functions are independent of R_0 . Γ is a function of η only and Ψ are a function of η and a linear function of ξ . This result coincides with the solution analyzed previously, where $v_z=f(r)+g(r)$. The results for the zero order approximation of velocity distributions are shown in **Fig. 30** to **32** (Collantes 2000, Collantes and Concha 2000).

Boundary Layer Models

In previous sections we have learned that the tangential and axial velocities have an order of magnitude of 1 m/s and that the tangential velocity is insensitive to the axial coordinate while the axial velocity depends on *z*. The radial velocity is two orders of magnitude smaller. Since the axial velocity is of the order of 1 m/s, the length of the hydrocyclone is of the order of 1 m and the kinematical viscosity is of the order of 10^{-4} m²/s, the axial Reynolds number





Fig 30 Dimensionless tangential velocity distribution for several values of the Reynolds number in the zero order approximation.



Fig. 31 Predicted radial velocity profile in a flat bottom hydrocyclone for the zero order approximations in zones I and II. (Collantes 2000, Collantes and Concha 2000).

is of the order of 10⁴. With this high Reynolds number it is only natural to think of the flow inside the hydrocyclone as divided into a viscous boundary layer close to the walls and an inviscid flow in the central region. The inviscid flow was thoroughly analyzed by Bloor and Ingham in several papers (1973,1974,1975a,1975b, 1984a, 1984b) yield-ing the velocity distribution. In later papers, Bloor and Ingham (1975b, 1976) studied the boundary layer along the lateral walls and at the top wall of a conical hydrocyclone giving the velocity distribution and volume flow within the boundary layer and the boundary layer thickness.

For equations (20) to (23), representing the Reynolds equations for the isotropic turbulent swirling flow in a cone, characterized with a turbulent eddy viscosity v_{ε} , consider:





Fig. 32 Tangential and axial velocity distribution at several heights of the hydrocyclone for the zero order approximation. Collantes (2000), Collantes and Concha (2000). Experimental points are from Chiné and Concha (2000).

1. The boundary layer at the lateral walls of a hydrocyclone

Since the length scale in the direction "y" perpendicular to the lateral wall is much smaller than in the direction "x" along the wall, it is convenient to make a coordinate transformation from (z, r) to (x, y) by means of:

$$z = x \operatorname{co} \alpha + y \quad \operatorname{n} \alpha, r = x \quad \operatorname{n} \alpha - y \operatorname{co} \alpha, \theta = \theta$$
(102)

where a is the semi angle of the hydrocyclone. In addition, it is convenient to define dimensionless variables:

$$x^* = \frac{x}{L_x}, y^* = \frac{y}{L_y}, v_x^* = \frac{v_x}{u_x}, v_y^* = \frac{v_y}{u_y}, v_\theta^* = \frac{v_\theta}{u_x}, p^* = \frac{p}{p_0}, \frac{\partial}{\partial x^*}(\circ) = L_x \frac{\partial}{\partial x}(\circ), \frac{\partial}{\partial y^*}(\circ) = L_y \frac{\partial}{\partial y}(\circ)$$
(103)

With these considerations the field equations become: Continuity equation:

$$\frac{\partial}{\partial x^*} \left(x^* v_x^* \right) + \left(\frac{L_x}{L_y} \frac{u_y}{u_x} \right) \frac{\partial}{\partial y^*} \left(x^* v_y^* \right) - \cot \alpha \left(\frac{u_y}{u_x} \right) \frac{\partial}{\partial y^*} \left(y^* v_y^* \right) + \left(\frac{L_y}{L_x} \right) \frac{\partial}{\partial x^*} \left(y^* v_x^* \right) = 0$$
(104)



 x^* component:

$$v_{x}^{*}\frac{\partial v_{x}^{*}}{\partial x^{*}} + \left(\frac{L_{x}}{L_{y}}\frac{u_{y}}{u_{x}}\right)v_{y}^{*}\frac{\partial v_{x}^{*}}{\partial y^{*}} - \frac{\sin\alpha v_{\theta}^{*2}}{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha} = -\left(\frac{p_{0}}{\rho u_{x}^{*2}}\right)\frac{\partial p}{\partial x^{*}} + \left(\frac{L_{x}}{L_{y}}\frac{u_{y}}{u_{x}}\right)\frac{\partial^{2}v_{x}^{*}}{\partial x^{*2}} + \frac{1}{\operatorname{Re}}\left(\frac{L_{y}}{L_{x}}\right)\frac{\partial^{2}v_{x}^{*}}{\partial y^{*2}} + \frac{1}{\operatorname{Re}}\left(\frac{L_{y}}{L_{x}}\right)\frac{\partial v_{x}^{*}}{\partial y^{*2}} + \frac{1}{\operatorname{Re}}\left(\frac{\sin\alpha \cos\alpha \frac{u_{x}}{u_{y}}v_{y}^{*}}{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha} + \frac{1}{\operatorname{Re}}\left(\frac{\sin\alpha \cos\alpha \frac{u_{x}}{u_{y}}v_{y}^{*}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}} - \frac{1}{\operatorname{Re}}\left(\frac{\sin^{2}\alpha v_{x}^{*}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}\right)^{2} + \frac{1}{\operatorname{Re}}\left(\frac{\sin\alpha \cos\alpha \frac{u_{x}}{u_{y}}v_{y}^{*}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}\right)^{2} + \frac{1}{\operatorname{Re}}\left(\frac{\sin\alpha \cos\alpha \frac{u_{x}}{u_{y}}v_{y}^{*}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}\right)^{2} + \frac{1}{\operatorname{Re}}\left(\frac{1}{\operatorname{R$$

 θ component:

$$v_{x}^{*}\frac{\partial v_{\theta}^{*}}{\partial x^{*}} + \left(\frac{L_{x}}{L_{y}}\frac{u_{y}}{u_{x}}\right)v_{y}^{*}\frac{\partial v_{\theta}^{*}}{\partial y^{*}} - \frac{\sin\alpha v_{\theta}^{*} - \left(\frac{u_{y}}{u_{x}}\right)\cos\alpha v_{y}^{*}}{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha} = \frac{1}{\operatorname{Re}}\frac{\partial^{2}v_{\theta}^{*}}{\partial x^{*2}} + \frac{1}{\operatorname{Re}}\left(\frac{L_{x}}{L_{y}}\right)\frac{\partial^{2}v_{\theta}^{*}}{\partial y^{*2}} + \frac{1}{\operatorname{Re}}\frac{\cos\alpha\left(\frac{L_{x}}{L_{y}}\right)v_{\theta}^{*}}{\left(x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right)^{2}} + \frac{1}{\operatorname{Re}}\frac{\sin\alpha\frac{\partial v_{\theta}^{*}}{\partial x^{*}} - \cos\alpha\left(\frac{L_{x}}{L_{y}}\right)\frac{\partial v_{\theta}^{*}}{\partial y^{*}}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}$$
(106)

y^{*} component:

$$v_{x}^{*}\frac{\partial v_{y}^{*}}{\partial x^{*}} + \left(\frac{L_{x}}{L_{y}}\frac{u_{y}}{u_{x}}\right)v_{y}^{*}\frac{\partial v_{y}^{*}}{\partial y^{*}} - \frac{\left(\frac{u_{y}}{u_{x}}\right)\cos\alpha v_{\theta}^{*}}{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha} = -\left(\frac{p_{0}}{\rho u_{x}^{2}}\right)\left(\frac{L_{x}}{L_{y}}\frac{u_{y}}{u_{x}}\right)\frac{\partial p^{*}}{\partial y^{*}}$$

$$\frac{1}{\operatorname{Re}}\frac{\partial^{2}v_{y}^{*}}{\partial x^{*2}} + \frac{1}{\operatorname{Re}}\left(\frac{L_{x}}{L_{y}}\right)\frac{\partial^{2}v_{y}^{*}}{\partial y^{*2}} + \frac{1}{\operatorname{Re}}\frac{\sin\alpha\frac{\partial v_{y}^{*}}{\partial x^{*}} - \cos\alpha\left(\frac{L_{x}}{L_{y}}\right)\frac{\partial v_{y}^{*}}{\partial y^{*}}}{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha} + \frac{1}{\operatorname{Re}}\frac{\sin\alpha\cos\alpha\left(\frac{u_{x}}{u_{y}}\right)v_{x}^{*}}{\left\{x^{*}\sin\alpha - \left(\frac{L_{y}}{L_{x}}\right)y^{*}\cos\alpha\right\}^{2}}$$

$$(107)$$

A study of order of magnitude of the terms shows that:

$$\left(\frac{L_x}{L_y}\right)^2 = \operatorname{Re}, \quad \left(\frac{u_x}{u_y}\right)^2 = \operatorname{Re}, \quad \left(\frac{L_x}{L_y}\frac{u_y}{u_x}\right) = 1$$
 (108)

Substituting into the previous equations and neglecting all terms with powers to the Re⁻¹, the boundary layers equations in dimensional form for the swirling flow in a cone are:

$$\frac{\partial}{\partial x}\left(xv_{x}\right) + \frac{\partial}{\partial y}\left(xv_{y}\right) = 0 \tag{109}$$

$$v_x \frac{\partial v_\theta}{\partial x} + v_y \frac{\partial v_\theta}{\partial y} = v_\varepsilon \frac{\partial^2 v_\theta}{\partial y^2} \tag{110}$$

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + v_\varepsilon \frac{\partial^2 v_x}{\partial y^2}$$
(111)

$$\frac{\partial p}{\partial y} = 0 \tag{112}$$

Since the pressure is independent of *y*, the pressure gradient in equation (111) can be written in terms of the velocity outside the boundary layer, according to Bernoulli's equation.

Bloor and Ingham (1976) used the velocities obtained for the inviscid flow (see previous analysis) as boundary conditions at the boundary layer limit. These equations are:

$$v_{x} = v_{x}(R) \left(\frac{x}{x_{0}}\right)^{-1/2}, \quad v_{\theta} = \frac{Rv_{\theta}(R)}{r} \frac{\gamma\left(\frac{4}{5}, \frac{2}{5}\frac{Lr}{R^{5/2}}\right)}{\gamma\left(\frac{4}{5}, \frac{2}{5}L\right)}$$
(113)

where $x_0 = \ell / \tan a$ and *R* is the radius of the cylindrical portion of the hydrocyclone. They obtained solutions to equations (109) to (112) with boundary conditions (113) using the approximate integral method of von Polhausen. Defining the new similar variable $\eta = y/\delta(x)$, where $\delta(x)$ is the thickness of the boundary layer, they described the velocity distributions in the form:



$$\frac{v_x}{v_x(R)} = 2\eta - \eta^2 + a(x)\eta (1-\eta)^2, \quad \frac{v_\theta}{v_\theta(R)} = 2\eta - \eta^2$$
(114)

Substituting these expressions into the von Karman integrals of the field equations results in two ordinary differential equations, the result of which indicate that the dimensionless thickness of the boundary layer $\delta^*(x^*)$ increases from $x^*=0$ to $x^*=0.5$, then stays constant and finally diminishes to 0 at $x^*=1$. At the points of maximum thickness the boundary layer has the form:

$$\delta_m = \frac{1.88x_0}{\mathrm{Re}^{1/2}} \tag{115}$$

where $x_0 = \ell / \tan \alpha$.

2. Boundary layer at the top wall of a hydrocyclone

Equations (109) to (112), but in the variables (r, θ , z) are:

$$\frac{\partial}{\partial r}(rv_r) + \frac{\partial}{\partial z}(rv_z) = 0 \tag{116}$$

$$v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} - \frac{v_\theta^2}{r} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \frac{1}{\rho} \frac{\partial T_{r_z}^E}{\partial z}$$
(117)

$$\frac{v_r}{r}\frac{\partial}{\partial r}(rv_\theta) + v_z\frac{\partial v_\theta}{\partial z} = \frac{1}{\rho}\frac{\partial T_{\theta_z}^E}{\partial z}$$
(118)

$$0 = \frac{1}{\rho} \frac{\partial p}{\partial z} \tag{119}$$

with boundary conditions:

$$v_r(r,0) = 0 \qquad v_\theta(r,0) = 0$$

$$v_r(r,\delta(r)) = V_r \qquad v_\theta(r,\delta(r)) = V_\theta$$
(120)

Since the pressure is independent of *z*, the pressure gradient in equation (117) can be written in terms of the velocity outside the boundary layer, according to Bernoulli's equation: $Vr\partial Vr/\partial r - V_{\theta}^2/r = -(1/\rho)\partial \rho/\partial r$. Using the method of von Karman integrals, Bloor and Ingham (1975b) approximated the velocity distribution with the following functions of a similar variable ξ :

$$v_r = V_r \xi^{1/7} \left\{ \gamma \left(\frac{15}{7} - 2\gamma \right) \xi + \left(\gamma - \frac{8}{7} \right) \xi^2 \right\}; v_\theta = \frac{1}{7} V_\theta \xi^{1/7} \left(8 - \xi \right)$$
(121)

where $\xi = z/\delta(r)$

Smith (1962) analyzed the stability of the boundary layer in the vortex flow of a pneumatic cyclone. He explains that the flow is naturally unstable close to the wall, since in this region the angular momentum diminishes with increasing radius. The instability manifests itself with the intermittent burst of fluid from the boundary layer moving radially inwards where it diffuses and loses identity. These burst makes the flow in the cyclone very turbulent even if there is no turbulence convected into the equipment by the incoming fluid or produced by the interaction of the incoming fluid with the flow in the cyclone. This turbulence, resulting from the unstable boundary layer is inherent in any device employing a rotating flow within a stationary container. On a conical wall, the secondary flows and the generation of turbulence occur in combination. During a burst, the heavy particles are left behind forming the streaks that are observed commonly in dust separation cyclones. The lighter particles are dragged by the fluid and re-mix into the main flow. This is a mechanism of re-dispersion of small particles trapped in the boundary layer. Although these mechanisms were observed in pneumatic cyclones, they can also explain the high turbulent motion in hydrocyclones and the re-dispersion of small particles.

Kumari and Nath (1985) studied the unsteady laminar motion in the boundary layer of nozzles, diffusers and hydrocyclones. They concluded that the tangential velocity at the edge of the boundary layer is of a non-free vortex type, in contrast to the steady flow. In the flow through hydrocyclones the swirl flow dominates the axial flow, which increases approaching the apex.





Fig. 33 Discharge volume flow rate $Q_{\rm D}$ versus total head H for axial or tangential inlet of water of 0.9×10^{-3} m³/s. Also shown is the curve for a tangential inflow of 0.24×10^{-3} m³/s and axial inflow of 0.66×10^{-3} m³/s.

The Air Core

The role of the air core in the performance of a hydrocyclone was not recognized until 1987, when Plitt and coworkers commented that it relates to the flow transition from a spray discharge to roping. That same year Davidson et al (1987) indicated that as the slurry viscosity increased, the angular velocity dropped in the hydrocyclone and the air core contracts. Castro (1990) found that the water split is mainly controlled by the air core size for an apex/ vortex ratio and, therefore, under such conditions the water split is governed by those operating conditions and variables which affect the air core. Bustamante (1991) found that working a hydrocyclone with water only might be used to predict roping conditions. He performed tests in which, for a fixed apex/vortex ratio, he measured the underflow rate for increasing values of the feed rate. Those conditions for which no underflow was obtained because the air core obstructed completely the apex, coincided with the onset of roping when the hydrocyclone was operated with pulp (Barrientos et al 1993, Concha et al 1996). This late recognition of the importance of the air core in the operation of a hydrocyclone is strange, since research workers had developed models for the air core size in vortex motions long before.

Binnie and Hookings (1957) analyzed the drainage of water from an open cylindrical tank with a controlled axial and tangential inflow and a free discharge at the bottom and center of the tank. They observed a relationship between the total head and the discharge rate that depended on the ratio of tangential to radial inflow. They also observed a critical pressure head that could maintain an air core. **Fig. 32** shows such curves.

When a combination of tangential and axial inflow of constant ratio was used, they observed an interesting phenomenon of surging. This effect was related to the forming and breaks down of the air core. Consider the tank full up to a total head of 0.16 m with a tangential inflow rate of 0.24×10^{-3} m³/s and an axial inflow rate of 0.66×10^{-3} m³/s. The total inflow was maintained at 0.9×10^{-3} m³/s. The curve for the total head versus the discharge flow rate is also given in **Fig. 32**. At *H*=0.16m, the ratio of tangential to axial inflow rates of 0.37 is not sufficient to maintain an air core and the entire discharge leaves through the exit pipe with a flow rate of 2.3×10^{-3} m³/s. Since this outflow is larger than the inflow of 0.90×10^{-3} m³/s, the container begins to loose water and the total head and discharge rate diminish until H becomes *H*=0.06m. This is the lowest total head at which a coreless discharge is



possible with the given inflow ratio of 0.37 and, once again, an air core forms suddenly diminishing abruptly the discharge rate to 0.57×10^{-3} m³/s. This outflow is now smaller then the inflow of 0.90×10^{-3} m³/s, and the water level will rise until the discharge rates equate the inflow rate. At this point, with a total head is *H*=0.16m, the air core again becomes unstable collapsing to a coreless outflow of 2.3×10^{-3} m³/s. Then, a new cycle begins.

Binnie and Hookings (1957) obtained an approximate expression for the discharge rate in the above problem, by considering a potential flow. With the Bernouilli given by $B = p/\rho + (1/2)(v_{\theta}^2 + v_z^2)$, the total head is H=B/g, and the axial velocity at the interface, where p=0, is given by $v_z = (2gH - v_{\theta}^2)^{1/2}$. If the underflow and the air core radii are denoted by R_u and R_a respectively, the outflow volume is given by:

$$Q_u = \pi \left(R_u^2 - R_a^2 \right) v_z \tag{122}$$

and therefore:

$$Q_{u} = \pi \left(R_{u}^{2} - R_{a}^{2} \right) \left(2gH - V_{\theta}^{2} \right)^{1/2}$$
(123)

For an inviscid flow, the tangential velocity is a free vortex of the form $v_{\theta} = V_{\theta u}/r$, where $V_{\theta u}$ is the tangential velocity at $r = R_u$, and therefore, for $r = R_a$:

$$Q_{u} = \pi \left(R_{u}^{2} - R_{a}^{2} \right) \left(2gH - \left(V_{\theta u} / R_{a} \right)^{2} \right)^{1/2}$$
(124)

Binnie and Hookings argued that, for the stability of the flow, R_a should adjust itself so that the discharge is maximum, which means that $\partial Q_u / \partial R = 0$, and leads to the following condition:

$$4gHR_a^4 - V_{\theta u}^2 R_a^2 - V_{\theta u}^2 R_u^2 = 0$$
(125)

from which the radius of the air core is:

$$R_{a} = \left\{ \frac{V_{\theta u}^{4} + \left(V_{\theta u}^{4} + 16gHV_{\theta u}^{2}R_{u}^{2}\right)^{1/2}}{8gH} \right\}^{1/2}$$
(126)

Equation (125) we can also be written in the form:

$$4gHR_{a}^{4} - 2V_{\theta u}^{2}R_{a}^{2} = V_{\theta u}^{2}R_{a}^{2} + V_{\theta u}^{2}R_{u}^{2} - 2V_{\theta u}^{2}R_{a}^{2} = 0, 2gH - V_{\theta u}^{2} = \frac{V_{\theta u}^{2}}{2R_{a}^{2}}\left(\frac{R_{u}^{2}}{R_{a}^{2}} - 1\right) \equiv v_{z}^{2}(R_{a})$$
(127)

This is the value of the axial velocity in the discharge tube. Introducing this value into equation (122), the flow rate through the discharge can be found:

$$Q_{u}^{2} = \frac{1}{2}\pi R_{a}^{2} V_{\theta u}^{2} \left\{ \left(\frac{R_{u}}{R_{a}}\right)^{2} - 1 \right\}^{3}$$
(128)

$$\left(\frac{Q_u}{T_u}\right)^2 = \frac{1}{8} \left(\frac{R_a}{R_u}\right)^2 \left\{ \left(\frac{R_u}{R_a}\right)^2 - 1 \right\}^3$$
(129)

where $\Gamma_u = 2 \pi R_u V_{\theta u}$ is the circulation at r=R. This equation was derived by Smith (1962) for the outflow of a hydrocyclone.

Davidson (1994) followed Binnie and Hookings approach to calculate the air core size, for one outlet at the underflow and for two outlets at the underflow and overflow. For one outlet he described the tangential velocity with the equation $v_{\theta} = A/r^n$. The Bernouilli can now be written in the form $B = p/\rho + v_z^2 + A^2/r^{2n}$. At the air core interface the pressure is zero, $r=R_a$ and $A=V_{\theta u}$, then:

$$v_z = \left(2B - V_{\theta u}^2 / R_a^{2n}\right)^{1/2} \tag{130}$$

So that the volume flow results:

$$Q_{u} = \pi \left(R_{u}^{2} - R_{a}^{2} \right) \left(2B - V_{\theta u}^{2} / R_{a}^{2n} \right)^{1/2}$$
(131)

Differentiating this expression with respect to R_a and equating the result to zero yields:

$$\frac{R_a}{R_u} = \left(\frac{nV_{\theta u}^2}{nV_{\theta u}^2 + 2V_z^2}\right)^{1/2} \tag{132}$$



For n=1, equation (129) derived by Smith (1962) is recovered:

For two outlets Davidson (1994) described the axial velocities with the following equations $V_{zu} = 2B - V_{\theta u}^2 / R_a^{2n}$ and $V_{zo} = 2B - V_{\theta o}^2 / R_a^{2m}$. The total flowrate is given by:

$$Q = \pi \left(R_u^2 - R_a^2 \right) \left(2B - V_{\theta_u}^2 / R_a^{2n} \right)^{1/2} + \pi \left(R_o^2 - R_a^2 \right) \left(2B - V_{\theta_o}^2 / R_a^{2m} \right)^{1/2}$$
(133)

After differentiating with respect to R_a , the radius of the air core becomes:

$$R_{a} = \left\{ \frac{nR_{u}^{2}V_{\theta_{u}}^{2}V_{zu} + nR_{o}^{2}V_{\theta_{o}}^{2}V_{zo}}{\left(2V_{zu}^{2} + nV_{\theta_{u}}^{2}\right)V_{zo} + \left(2V_{zo}^{2} + nV_{\theta_{o}}^{2}\right)V_{zu}} \right\}^{1/2}$$
(134)

For large $V_{\theta u}$, $R_a \rightarrow R_u$ and for large $V_{\theta 0}$, $R_a \rightarrow R_0$. Since R_u is smaller than R_0 the apex will be blocked first.

Davidson (1994) indicates that, using inviscid flow to calculate the air core size, equation (134) gives correct results when the fluid is water. For a suspension he assumes that a correction factor proportional to the ratio of the kinematical viscosity of the suspension v_s to the kinematical viscosity of the water v_w can be used for the air core radius as follows:

$$R_a|_{suspension} \approx R_a|_{water} \left(\frac{v_s}{v_w}\right)^{0.3}$$
(135)

Davidson (1994) further indicates that his equation for the air core size compares well with the experiments of Petersen (1993) and those of Kelsall (1952), Hsieh and Rajamani (1991) and Svarovsky and Marasinghe (1980). The agreement with the experiments of Steffens et al (1993) is only fair.

Mikhaylov and Romenskiy (1974) proposed the following equation for the air core in a conical hydrocyclone:

$$R_a = k_a d_o \left(\tan\alpha\right)^{0.30} \tag{136}$$

where 2 a is the angle of the conical section of the hydrocyclone and k_a is a constant.

Nepomnyashchii and Pavlobskii (1977) derived the following equation for the air core radius (see equation):

$$R_a = \frac{R_F}{R} \left(\frac{\rho v_F^2}{3\Delta p}\right)^{1/3} \tag{137}$$

where R_F and R are the eccentricity of the hydrocyclone feed and the hydrocyclone radius respectively, v_F is the inlet velocity of the feed.

Svarovsky (1984) presented this equation in dimensionless form:

$$\frac{d_a}{d_c} = \frac{d_F}{d_c} \left\{ \frac{1}{3Eu} \left(\frac{d_c}{d_F} \right)^4 \right\}^{1/3}$$
(138)

where d_a , d_F and d_c are the air core diameter, twice the inlet eccentricity and the hydrocyclone diameter respectively and Eu= $\Delta p/(1/2)\rho v^2$ is Euler's number.

Barrientos et al (1993) calculated the air core radius using the momentum jump balance for the normal stresses. Across the interface, a jump of the normal stresses exists and is given by the Young-Laplace equation:

$$[Tn \cdot n] = -2H\gamma \tag{139}$$

where the square brackets represent the jump of a property across the interface, *T* is the stress tensor, *n* is the normal unit vector to the interface, *H* is the main curvature of the air core and γ is the liquid surface tension. Assuming the air behaves as an ideal fluid rotating as a rigid body with density ρ_a and angular velocity ω_a and that the liquid is a Newtonian fluid with viscosity μ , equation (139) can be written in the form:

$$\frac{1}{2}\rho_a \omega_a^2 R_a^3 + \left(2\mu \left.\frac{\partial v_r}{\partial r}\right|_{r=R_a} - \Delta p_a\right) R_a - \gamma = 0$$
(140)

Introducing the dimensionless variables and making a study of order of magnitude of the resulting equation, they found the following equation for the air core:

$$R_a \approx \frac{\gamma}{2\mu\nu - \Delta p_a} \tag{141}$$

Based on this equation Concha et al (1996) and Castro et al (1996) developed empirical equations for the air core diameter in terms of the operating variables in a laboratory and industrial hydrocyclone respectively. Concha et al (1996) obtained the following equation for the air core:

$$d_a = \frac{3.03\gamma d_o}{270.3\mu_w \left(1 + \frac{1.18 \times 10^5}{\Delta P^{2.61}}\right) \left(\frac{d_u}{d_o}\right)^{-0.20} - 1.38 \times 10^{-3}}$$
(142)

In this equation γ is measured in N/m, μ_w is in kg/ms, ΔP is in Pa and d_a , d_o and d_u are in m. In this case ΔP is the total pressure drop in the hydrocyclone.

Castro et al (1996) obtained the following relationship:

$$d_a = \frac{103.6(d_u/d_o)^{0.89}}{6.3(\mu/\mu_w) \left(1 + \frac{0.98}{\Delta P^{1.15}} - \frac{1.41}{\Delta P^{1.57}}\right)}$$
(143)

where μ and μ_w are the viscosities of the pulp and the water respectively.

Ovalle and Concha (1955) studied the generation and propagation of waves at the air core-water interface of a conical hydrocyclone. They show that inside the hydrocyclone the flow is sub-critical (Froude number less than 1) and therefore in a favorable condition for the existence of ondulatory motions in the fluid. Through a hydraulic analogy consisting of a launder with a ramp where the water enters through the bottom at the left side, and overflows both at the left and the right of the upper part of the physical model, see **fig. 34**. The centrifugal force of the hydrocyclone is substituted by the gravitational force in the hydraulic model.

The flow in this hydraulic analogy was modeled as inviscid and irrotational obtaining the form of the free surface as:

$$\eta(x, y, t) = 2A\frac{k}{\omega}\sinh\left(k(y+h)\right)\cos\left(kx - \omega t\right)$$

where *A* is a constant, $\omega(t)$ and k(x) represent the temporal and the spatial behavior respectively. Fig. 35 shows some isobaric lines resulting from the calculations of the temporal evolution of the waves imposed over the free surface.

The authors concluded that the form of the free surface depends mainly on the global geometrical characteristics of the flow and possibly to a minor extent on physicochemical properties at the surface. They show that the waves propagating through the water-air interface of the air core will increase their amplitude as the hydrocyclone diameter becomes smaller (tsunami effect), so that the air core may become of the size of the apex, in which case instability is induced in the underflow. The apex would intermittently become blocked by the air core, inducing roping. Unfortunately the presence of waves in a conical hydrocyclone is inherent in the physics of the flow.

Conclusions

In spite of the fact that the experimental evidence on the flow pattern in hydrocyclones is based on studies with water or a single phase fluid, it can be said that the flow pattern in a hydrocyclone is well understood. From the known measurements that of Hsieh and Rajamani (1984a, 1988) is the most reliable one. From measurements and hydrodynamic modeling, the shape of the three velocity component has been established and the early discrepan-



Fig. 34 Hydraulic analogy of a conical hydrocyclone.





Fig. 35 Isobaric lines in the hydraulic model of a conical hydrocyclone.

cies solved. What is still not sufficiently clear is the shape of the air core and how it affects the flow pattern and the fluctuating component of the velocities.

The problem with the early models is that they did not consider explicitly the axial velocity. Furthermore, their solutions serve only to calculate the centrifugal force, but give no clue as to how the particles are separated and how the particles and fluid are evacuated from the equipment. Those authors were not concerned if their models satisfy the continuity equation. The conclusion is that it is essential to incorporate the axial velocity component together with the tangential and radial velocity, in the dynamic process.

From the exact solutions of the Reynolds equations and from the conclusions of the several research workers that modeled the hydrocyclone in this manner, we conclude that the radial velocity depends strongly on the shape of the axial velocity. One can obtain completely different radial velocities distributions by choosing appropriate axial flows and, therefore, it is essential to choose an axial velocity that approximates the experimental one. Nevertheless, the shape of the tangential velocity, as a combination of a free vortex and a rigid motion, is insensible to the form of these axial and radial velocities. Only the maximum value of the tangential velocity and its position varies as the radial velocity changes.

The axial velocity must be a function of r and at least a linear function of z. Finally, we can indicate that, in modeling the hydrocyclone, the selection from several solutions to the field equations by comparing the size of the maximum of the tangential velocity with experimental values is not the proper way to go. The three, or at least two, velocity components must be compared and especially the axial velocity must be reasonable.

The knowledge of the flow pattern in a hydrocyclone and the quantitative description of the velocity distributions are sufficient at the present to develop classification models in the hydrocyclone. A review of this subject will be presented in a future article.

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Three-Dimensional Monte Carlo Simulations of Density Relaxation[†]

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Abstract

The packing efficiency of granular materials is an important consideration in a variety of industrial settings. Here, the density relaxation problem is studied using three dimensional Monte Carlo simulations, which model the effect of regular taps applied to vessel having a planar floor filled with hard spheres. Results show that the equilibrium bulk solids fraction depends strongly upon the intensity of the taps, with relatively lower intensity taps producing more dense systems. A broad range of solids fractions are generated, starting from a loose configuration, rather like a 'poured' assembly, to a relatively dense structure having local crystalline order. Reasonably good agreement of the computed coordination number with experiments in the literature is found. Results show an enhanced tap-induced ordering effect of the floor on the local microstructure, which is reflected in the radial distribution function. For energetic taps, the solids fraction evolution fit well to a hyperbolic tangent model, while results at low intensity taps are described by an inverse log law.

Keywords: density relaxation, Monte Carlo simulation, solids fraction evolution, vibrated bulk solids

1. Introduction

The compaction and densification of granular matter is an issue of importance in the industrial sector in that an increase in packing efficiency in the processing of bulk solids is often desirable in reducing costs and in meeting consumer demands. However, in some situations, the compaction resulting from tapping or vibrations in handling operations and long term transport may be detrimental to the quality of the end product. Beyond these practical matters, the ability of a bulk solid to undergo a change in its bulk density due to external disturbances is a fundamental attribute of granular materials that is not well-understood. Indeed, the factors that have a bearing on the phenomenon (e.g., particle properties, containment geometry, environmental conditions, and the nature of the imposed disturbances) are rather broad and consequently the relationship between them requires further study.

The increase in bulk density experienced by contained granular materials subjected to taps and/or continuous vibrations (often referred to as 'density relaxation') has been well-documented in the early literature ^{6, 17-19, 33, 49, 50)}. From a broader perspective, research on this phenomenon has its foundations in the many fundamental studies on the packing of particles (for example, see 1, 3, 9, 10, 14, 16, 21, 25, 26, 40, 46-48, 53, 54)). In recognition of the importance of developing a better understanding of the nature of the granular state, and motivated in part by recent experiments ^{27, 37-39)}, density relaxation has received renewed interest as evidenced by the recent upsurge in both modeling and computational studies, such as ^{2, 11, 13, 20, 24, 29-32, 34, 42, 52}.

In this paper, the effect of discrete taps applied to a vessel of granular material is modeled using a Monte Carlo approach in three-dimensions. This meth-

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odology does not consider the detailed dynamical interactions between particles, as would be the case with dissipative molecular dynamics simulations ⁵⁶⁾. Rather, the effect of the intensity of the taps on the equilibrium bulk solids fraction is examined. In this regard, the intensities that were selected roughly correspond to relatively large accelerations of the vessel. A broad set of tap intensities was used, thereby allowing us to obtain a correspondingly wide range of solids fractions, from a loose configuration, rather like a 'poured' assembly, to a relatively dense structure with local crystalline order. The vessel itself was chosen to have a smooth (i.e., not bumpy) floor so as not to preclude the well-known 'ordering' effect of a flat plane on packing of uniform spheres ^{23, 41, 43)}.

The outline for the remainder of this paper is as follows. The next section presents the details of the simulation technique that was developed to evolve the system from an initial low solids fraction state to a denser configuration. We describe the means by which taps are applied to the system of particles, the physical interpretation of these taps, the computation of equilibrium averages and the convergence criterion used. Simulation results are presented in Section 3. Here, the progression of the bulk solids fraction with tap number is shown for various tap intensities, in addition to a study of the equilibrium solids fraction as a function of the tap intensity. These simulation results are also compared with various models from the literature. In Section 4, results on the microstructure are given and quantified through the contact number distribution and radial distribution function. Finally, the conclusions are presented in Section 5.

2. Simulation Methodology

In this section, the approach used to generate equilibrium assemblies of spheres is described. The quantity of interest is the bulk solids fraction v, which is calculated from the simulation data as the ratio of the total sphere volume to the volume occupied. In carrying out the calculations of v, the upper 20% of the packing was not included so as to minimize the influence of the top surface and to simplify the numerical procedure without a loss in accuracy. We remark that the heap formed ^{8, 15)} at the surface as a consequence of a granular material's angle of repose in a physical experiment was not a phenomenon that could be captured by our simulation method.

A Monte Carlo scheme was used to simulate the density relaxation process that occurs as a result of a



series of discrete taps applied to a 'box' containing Nspherical particles of diameter d. The computational domain (i.e. the 'box') is a rectangular parallelepiped having periodic boundary conditions in the lateral directions, which are hereby denoted as x and z. The lateral dimensions of the box $(12d \times 12d)$ are chosen to optimize CPU time. In order to model the effect of the taps on the particles, each sphere is subjected to a height-dependent, vertical displacement whose magnitude is controlled by the lift intensity γ . This expansion of the system allows a greater portion of the bulk mass to reside near the floor of the box. For each selected value of γ , the bulk solids fraction is traced as a function of the number of taps, and its equilibrium value $v_{\infty}(\gamma)$ is computed. The next section presents a detailed description of the Monte Carlo method.

2.1 Generation of the poured assembly

The simulation is initiated by randomly placing within the box *N* spheres that are subsequently allowed to collapse vertically under gravity to generate a configuration corresponding to a loose ('poured') assembly. The spheres are 'hard'; that is, in order to avoid overlap of the spheres, for each $i \neq j$, the distance $|\vec{r}_i - \vec{r}_j|$ between the centers $\vec{r}_i = (x_i, y_i, z_i)$ and $r_j = (x_i, y_i, z_j)$ of particles is always greater than $d + \varepsilon$, where $\varepsilon = 10^{-4}d$. The Metropolis³⁵⁾ algorithm is then used to advance the system to a stable configuration. A single Monte Carlo (MC) step in the Metropolis algorithm consists of the random selection of a particle (x_i, y_i, z_i), followed by its assignment to a trial position in accordance to the prescription,

$$\begin{cases} x_{i}' = x_{i} + \delta (1 - 2\xi_{x}) \\ y_{i}' = y_{i} + \delta (1 - 2\xi_{y}) \\ z_{i}' = z_{i} + \delta (1 - 2\xi_{z}) \end{cases}$$
(1)

Here, ξ_x , ξ_y , ξ_z , are random numbers sampled from a uniform distribution on [0, 1], and δ is a maximum allowed displacement. The procedure for selecting δ is described in the next paragraph. The trial position is accepted unconditionally as the new center coordinate if the change in the system potential

energy is negative, i.e., $\Delta E \equiv mg \sum_{i=1}^{N} (y'_i - y_i) < 0$. Otherwise, ($\Delta E \ge 0$) the trial position is accepted with

probability $e^{-\beta \Delta E}$. For the macroscopic particles that we are studying, β is very large ⁴⁵⁾ so that for all practical purposes, only downward displacements are allowed. Another particle is then selected at random, and the above procedure is repeated.

As the process described above advances through

many thousands of MC steps, the space between adjacent particles is reduced and the bulk density increases. If the maximum allowed displacement δ were set to a small fixed value $\delta / d << 1$ at the outset, the evolution of the system to a local equilibrium would be prohibitively slow. The situation would be the same if $\delta/d \sim 1$, since the percentage of accepted steps would be drastically reduced as the system density increases. In order to prevent this from taking place, δ is dynamically changed from a maximum value $\delta = d$ at the beginning of the process to a minimum $\delta = 10^{-3} d$, with its reduction determined by the accepted fraction of steps every 10⁴ MC steps. If more than half of the MC steps have been accepted, δ remains unchanged; otherwise δ is modified as follows: $\delta'=0.995 \delta$. While other algorithms in the literature may be more computationally efficient ^{12, 51}. this approach has a great deal of virtue in its simplicity.

The change in the bulk solids fraction is computed every one million MC steps and the Metropolis algorithm is terminated when

$$|v(n; \gamma) - v(n-10^{6}; \gamma)| < 0.001$$
 (2)

where $v(n; \gamma)$ is the bulk solids fraction at tap number n and lift intensity γ . To ensure that this stopping criterion did not cause premature termination, in many test runs we required the criterion in (2) to be satisfied twice before ending the process. In none of these instances was a premature termination observed, allowing us to satisfy (2) only once for many of the results presented below. In all of the case studies reported in this paper, the initial random assembly collapsed to a loose configuration having a bulk solids fraction in the range 0.56 to 0.58. In general, the poured assemblies filled the box to a height $H/d \cong 11$ for the system size considered in this work.

2.2. Tapping procedure

The poured assembly is dislodged from its local energy minimum by applying vertical position dependent displacements to each particle in accordance to

$$\gamma_i^{new} = \gamma_i^{old} \times \gamma \tag{3}$$

The factor γ represents the effect of a single tap so that in a qualitative sense, a greater impulse applied to the container corresponds to a larger value of γ . We remark that the form (3) for vertical displacements is equivalent to that used by Barker and Mehta ⁷, who also imposed random lateral displacements on the particles at each tap. The influence of applying this additional lateral displacement on



the equilibrium solids fraction is considered later in this paper. After expanding the vertical coordinates using (3), the system is allowed to settle using the Metropolis algorithm as described in the previous section. Satisfaction of the stopping criterion (2) to signal completion of a single 'tap' applied to the system typically required 17 to 20 million MC steps (~ 40 CPU seconds on our computers). **Fig. 1** shows a sequence of configurations, starting from the initial random placement, the 'poured assembly', its expansion via a single tap (3), and its state in accordance with the criterion (2). Note that the shading in this figure is only for the purpose of visualization.



Fig. 1 Snapshots of system: (a). Initial random configuration, (b). Poured assembly ($\nu = 0.568$), (c). Configuration after applying one tap, and (d). Final configuration at 1000 taps. Note that particles are shaded only for the purpose of visualization.

2.3. Equilibrium bulk solids fraction

A tapping cycle is initiated with the poured particle assembly as described in Section 2.1. A single experiment (or realization) consists of a sequence of individual taps (Section 2.2). As used here and henceforth, the term 'tap' refers to the expansion by (3) and subsequent relaxation. Each realization is carried out using a fixed lift intensity γ ; the total number of taps to obtain equilibrium depends on γ . For smaller values of γ , more taps were needed to reach an equilibrium solids fraction. Typical plots of bulk solids fraction against the number of taps N_T are shown in



Fig. 2 for two different realizations at $\gamma = 1.25$. The graphs exhibit an overall increase in the solids fraction with the number of taps, a general trend that was evident in all realizations. The convergence to the equilibrium configuration also exhibited dependence upon the choice of γ , which will be demonstrated in subsequent figures.

The ensemble averaged bulk solids fraction $\langle v(n; \gamma) \rangle$ was computed over *M* realizations. In order to identify the minimum number of realizations *M* so that a statistically correct equilibrium value was obtained, the standard deviation $\langle \sigma(n; \gamma) \rangle$ as a function of the tap number *n* was determined as

$$\langle \sigma(n;\gamma) \rangle = \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left[\nu_k(n;\gamma) - \langle \nu(n;\gamma) \rangle \right]^2}$$
(4)

where

$$\langle \nu(n;\gamma) \rangle = \frac{1}{M} \sum_{k=1}^{M} \nu_k(n;\gamma)$$
(5)

The behavior of $\langle \sigma(n; \gamma) \rangle$ was monitored by increasing the number of realizations *M* until, over a sufficient number of taps *N*_T,

$$\langle \sigma(N_{\rm T};\gamma) \rangle < 0.001$$
 (6)



Fig. 2 Bulk solids fraction ν versus tap number N_T for two independent realizations at tap intensity $\gamma = 1.25$. These plots show the typical evolution of the system.

which essentially defines equilibrium in the simulations. The behavior of the standard deviation $\langle \sigma (N_T; 1.25) \rangle$ depicted in **Fig. 3** demonstrates that criterion (6) is reached when of $N_T \sim 800$ for this value of γ . The ensemble averaged solids fraction as a function of *M* is shown in **Fig. 4** for the same case when N_T =1000. The vertical lines in the figure denote error bars in the ensemble averaged solids fraction. In general, it was found that M \cong 100 realizations were adequate to satisfy the criterion in (6).



Fig. 3 Standard deviation of the bulk solids fraction $\langle \sigma(n; \gamma) \rangle$ versus tap number N_T at tap intensity $\gamma = 1.25$ for 100 realizations. This demonstrates the convergence properties of the methodology.



Fig. 4 Dependence of the ensembled-averaged bulk solids fraction on the number of realizations *M* at tap intensity $\gamma = 1.25$ to exhibit the sensitivity of the system to the ensemble size. The vertical lines through the points are error bars.

3. Simulation Results

The value of the equilibrium bulk solids fraction depends on the lift intensity γ , which is roughly analogous to changing the intensity of the taps on the containment vessel in a physical experiment. As will be seen, the results demonstrate that it is possible to obtain a rather wide range of equilibrium solids fractions, from loosely packed assemblies to rather



dense configurations whose radial distribution functions contains peaks associated with the presence of crystalline structures. It is noted however that these dense configurations are largely promoted by the ordering influence of the plane floor - a phenomenon that we did not wish to preclude by using a bumpy base.



Fig. 5 Evolution of the ensemble-averaged bulk solids fraction $\langle v(n; \gamma) \rangle$ for tap intensity $\gamma = 1.25(\Delta), 1.3(\times), 1.35(\diamondsuit), 1.4(\bigcirc), 1.50(\degree)$. This demonstrates the effect of increasing γ on $\langle v(n; \gamma) \rangle$.

For the pouring phase of the simulation, we obtained 'poured' solids fractions in the range 0.560 to 0.580, corresponding to a random loose structures reported in the literature ^{27, 37, 40, 44}. Starting from the poured structure, taps are applied to the system following the procedure described in Sec. 2.2 and Sec. 2.3. The ensemble-averaged bulk solids fraction $\langle v(\mathbf{n}; \gamma) \rangle$ for lift intensities γ between 1.25 and 1.50 as a function of the tap number is shown in Fig. 5. For the purpose of clarity, only every twentieth data point is plotted; here each symbol represents the average bulk solids fraction over 100 realizations. It can be seen in the figure that taps of smaller intensity eventually yield larger equilibrium bulk densities. Simulations were also performed at $\gamma = 1.2$; however these results were not included in Fig. 5 because of the larger number of taps ($N_T \ge 2,000$) required to reach equilibrium. In fact, for $\gamma = 1.15$, we carried out 10,000 taps, which were not sufficient to satisfy the equilibrium criterion in (6). This is not unexpected given the trend shown in Fig. 6 for the number of taps required to reach 99.5% of the equilibrium solids fraction. The deviations (equations (4) and (5)) for γ = 1.25, 1.35 and 1.50 as a function of the tap number in Fig. 7 exhibit a clear-cut dependence on lift intensity γ . The peak observed in the $\gamma = 1.25$ case was observed to be a characteristic feature at small values of the intensity. However, as the lift intensity became smaller, the peak in the deviation grew so that it re-



Fig. 6 The number of taps required to attain 99.5% of equilibrium bulk solids fraction versus the tap intensity γ . A reduction of γ results in a greater number of taps to reach equilibrium.



Fig. 7 The standard deviation of bulk solids fraction $\langle \sigma(\mathbf{n}; \gamma) \rangle$ versus tap number N_T for tap intensity $\gamma = 1.25 (\Delta), 1.35 (\diamond)$ and 1.50 (*). Smaller values of γ yield higher variances.

quired significantly more taps to satisfy criterion (6). At the smaller intensities γ considered here, the system tends to visit a greater portion of the phase space in approaching its final lower energy state.

In order to determine if random lateral displacements of the particles in sync with vertical taps would significantly change the equilibrium bulk solids fraction, we modified our Monte Carlo procedure by incorporating this feature of Mehta et al.'s algorithm⁷. That is, in conjunction with the vertical motion prescribed by (3), each particle is assigned a random lateral displacement within a disk of radius ρ given by,

$$x' = x + \rho(1 - 2\xi_x), \qquad z' = z + \rho(1 - 2\xi_z)$$
 (7)

The parameter ρ is computed at each tap as the average (over N_{ρ} particles) of the minimum near-neighbor lateral distance,

$$\rho = \frac{1}{N_p} \sum_{k=1}^{N_p} r_k^{\min} \tag{8}$$

Here,
$$r_k^{\min} \equiv \min_{j \neq k} \left\{ \sqrt{(x_k - x_j)^2 + (y_k - y_j)^2} \right\}$$
, where

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the minimum is taken over all particles j whose centers are within two diameters from particle k. In **Fig. 8**, we compare the bulk solids fraction versus tap number at lift intensity $\gamma = 1.25$ with and without application of the random lateral displacements (7). The trends of the two graphs are very similar, and we observed steady-state values of the solids fraction that were statistically equivalent. A further check was done by introducing lateral displacements in a system that had equilibrated without them in order to determine if it would return to the same equilibrium solids fraction. In the results of this study, not shown here for the sake of brevity, it was observed that random lateral displacements did not move the system out of equilibrium.



Fig. 8 Comparison of the evolution of the ensemble-averaged bulk solids fraction at intensity $\gamma = 1.25$ with(×) and without(\Box) the application of random lateral displacements. The results with and without these displacements are statistically indistinguishable.

3.1 Evolution behavior

A phenomenological relationship for the evolution observed in the Monte Carlo simulations is described in this section. This relation proved to be quite useful in the prediction of the equilibrium packing fractions for the case studies presented in this paper. However, it must be noted that the connection between the Monte Carlo evolution and that which occurs in dynamic simulation is not clearly understood and is a topic that requires further investigation. Nonetheless, a comparison of the evolution of the bulk solids fraction computed from our simulations is made with relationships reported in the literature.

Our simulation data could be fit to a hyperbolic tangent model (solid lines in **Fig. 5**) of the form

$$\nu(n;\gamma) = \nu_{\rm o}(\gamma) + \left[\nu_{\infty}(\gamma) - \nu_{\rm o}(\gamma)\right] \tanh\left(A(\gamma)n\right) \tag{9}$$

where $\gamma_0(\gamma)$ and $\gamma_{\infty}(\gamma)$ are its initial and equilibrium values, respectively and $A(\gamma)$ is the controlling rate constant. The use of (9) is motivated in part by

the rate law $\frac{d\rho(t)}{dt} = -\beta\rho$, the solution of which suggests a difference equation of the form,

$$\rho_n - \rho_{n-1} = C e^{-\beta n} \tag{10}$$

The general solution of this difference equation is given by

$$\rho_n = B + \frac{C}{1 - e^\beta} e^{-\beta n} \tag{11}$$

By expressing the model in (9) in terms of Linz's ³⁰⁾ compaction ratio $\rho_n \equiv \frac{\nu_n - \nu_\infty}{\nu_o - \nu_\infty}$, it becomes

Table 1	. Fitting	parameters	for hyper	bolic tangent la	w
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γ	v_0	v_{∞}	$A imes 10^{-3}$
1.2	0.5699	0.6592	2.57
1.25	0.5663	0.6542	3.91
1.3	0.5651	0.6238	5.18
1.35	0.5759	0.6139	4.22
1.4	0.5666	0.5939	4.34
1.5	0.5721	0.5825	3.94

 $\rho_n = 1 - \tanh(An) \tag{12}$

The solution (11) with B = 1, $\beta = 2A$ and $C = 2(1 - e^{2A})$ is actually the first two terms of the asymptotic expansion of (12).

Parameters determined from the least-squares fit to (9) using the simulation results appear in **Table 1** for $\gamma \ge 1.2$. Recall that these parameters are the initial and final solids fractions $v_0(\gamma)$ and $v_{\infty}(\gamma)$, respectively, and the rate constant $A(\gamma)$. Observe that the initial solids fractions $v_0(\gamma)$ from the fit fall within the range 0.560 to 0.580 generated by the simulation. The graph of $v_{\infty}(\gamma)$ versus γ in **Fig. 9** shows that a reduction in the lift intensity results in the creation of a more dense system, but at the expense of an increasingly growing number of taps (see **Fig. 6**) to reach equilibrium via criterion (6). Values of $v_{\infty}(\gamma)$ from the fit closely matched that obtained from the simulation for $\gamma \ge 1.2$. Furthermore, the model dis-

Table 2. Fitting parameters for stretched exponential law

γ	v_0	v _∞	τ	β
1.2	0.564	0.658	246	0.85
1.25	0.569	0.654	196	1.29
1.3	0.568	0.623	152	1.40
1.35	0.575	0.614	174	1.17
1.4	0.564	0.593	176	1.30
1.5	0.572	0.583	133	0.60



played rather good agreement with the progression of the data with tap number n, although (as expected) less than perfect conformity was found at the onset of the densification process.

However, the hyperbolic tangent function was not observed fit the lower intensity data (at $\gamma = 1.1$ and 1.15) as well since computational limitations precluded the generation of a data set of sufficient size in the sense of being close to equilibrium. In fact, a crude backward extrapolation of the data in **Fig. 6** suggested that for lift intensity $\gamma = 1.1$ upwards of 40,000 taps may be required.

For the sake of completeness, we have also considered fits of the simulation data to other models in the literature. In particular, comparisons were done with the stretched exponential ^{28, 55}, and the inverse log law²⁷. The stretched exponential takes the form

$$\nu(n) = \nu_{\infty} - (\nu_{\infty} - \nu_{o}) e^{-(n/\tau)^{\beta}}$$
(13)

There are four parameters in this model, corresponding to the initial solids fraction v_0 , the equilibrium solids fraction v_∞ , the Monte Carlo time scale τ and the stretching exponent β^{280} . The fits to the data appear in **Table 2** from those cases in which equilibrium was attained in accordance with (6); these fits do not reveal a consistent value or a trend in the stretching exponent β . Furthermore, neither τ nor τ^{β} revealed a decrease with intensity γ , as would be expected for a time scale measure. Despite these issues, the fits matched the data for the tap intensities considered in this study, with statistical measures of goodness of fit (such as R^2 values) not substantially different than those seen in the hyperbolic tangent fits.

The inverse log model is given by

$$\nu(n) = \nu_{\infty} - \frac{\nu_{\infty} - \nu_o}{1 + B \log(1 + n/\tau)}$$
(14)

where the four parameters are the initial and equilibrium solids fractions v_0 and v_∞ , respectively, the Monte Carlo time scale τ and an amplification factor *B*. For tap intensities $\gamma \ge 1.2$, poor correlation between this model and the simulation data was found since equilibrium was attained more rapidly than could be accommodated by the form (14). In the lower tap intensity regime (i.e., $\gamma = 1.1$ and 1.15), **Table 3** shows that nearly constant values of the ratio B/τ were obtained as a function of the number of taps, with the value of this ratio being dependent on γ . The possibility that B/τ is a relevant parameter for low tap intensities is also suggested by the experimental data in **Fig. 5** of Knight et al.²⁷⁾. An exact correlation between γ in the Monte Carlo simulations and the bed's response to the sinusoidal taps, as in the experiments of Knight et al., is a matter of further research. However, rough scaling arguments (done by equating the normalized average bed expansion in the simulations with the experimental tap amplitude *a*) suggest that the lower intensities ($\gamma = 1.1$ and 1.15) correspond to accelerations $\Gamma \equiv a \omega^2/g$ greater than the experimental values, but within the same order of magnitude. A similar fit analysis of the data to (14) for $\gamma \ge 1.2$ revealed that B/τ was not constant as a function of the number of taps; for example, the ratio increased monotonically by an order of magnitude for $\gamma = 1.25$ when $600 \ge N_T \ge 3000$.

Further exploration of the significance of B/τ was carried out by fitting the low intensity data ($\gamma = 1.1$ and 1.15) to the functional form

$$\nu = \nu_{\infty} - \frac{\nu_{\infty} - \nu_{o}}{1 + Dn} \tag{15}$$

The results are given in **Table 4**, where it is observed that the values of *D* are close to B/τ obtained from the inverse log fits (**Table 3**). Furthermore, the increase of *D* with γ is in line with the expected behavior of a time scale parameter. These

Table 3. Fitting parameters for inverse logarithmic law

γ	N_T	<i>v</i> ₀	ν_{∞}	B/ $\tau \times 10^{-3}$
	4,000	0.5920	0.6723	1.44
11	6,000	0.5915	0.6714	1.51
1.1	8,000	0.5919	0.6728	1.45
	10,000	0.5914	0.6822	1.37
	4,000	0.5920	0.6723	4.11
1 15	6,000	0.5750	0.6702	3.93
1.15	8,000	0.5748	0.6748	3.84
	10,000	0.5747	0.6756	3.85

Table 4.	Fitting	parameters for	reciprocal	linear	law
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γ	N_T	V 0	v∞	$D \times 10^{-3}$
	4,000	0.5920	0.6723	1.43
1 1	6,000	0.5915	0.6714	1.50
1.1	8,000	0.5919	0.6728	1.47
	10,000	0.5925	0.6725	1.40
	4,000	0.5746	0.6684	4.11
1 15	6,000	0.5751	0.6686	4.00
1.15	8,000	0.5759	0.6693	3.84
	10,000	0.5763	0.6696	3.75

findings suggest the ratio B/τ is an important factor that captures the evolution of the data as a function of Monte Carlo time (i.e., tap number *n*). Note that (15) is simply the first order approximation to the denominator of (14) with the identification that $D \equiv B/\tau$.

4. Characterization of the Microstructure

The dependence of the configuration microstruc-





Fig. 9 Behavior of the equilibrium solids fraction v_{∞} obtained from the fit of the data to the hyperbolic tangent model ($v(n; \gamma) = v_0(\gamma) + [v_{\infty}(\gamma) - v_0(\gamma)] \tanh(A(\gamma)n))$ versus intensity γ . Smaller tap intensities yield more dense configurations.

ture was examined by computing the ensemble-averaged (i.e., equilibrium) distribution of near-neighbor contacts as well as the radial distribution function. These computations were done for a variety of lift intensities. Distribution functions were determined by averaging on configurations in which the upper 20% of the particles was removed from the data so as to minimize the influence of the top surface and to simplify (without a loss in accuracy) the numerical procedure.

Spheres were defined as being in contact if the distance between their centers is less than or equal to 1.05*d*. The number of nearest neighbors is commonly referred to as the coordination number. **Fig. 10** shows the expected result that the near-neighbor contact distributions shift to the right corresponding to an increase in mean coordination number $\langle Nc \rangle$ with bulk solids fraction ν_{∞} as determined from the fit to equation (9). A comparison of the simulated values



Fig. 10 Mean coordination number (i.e., fraction of particles with mean number of nearest contacts $\langle N_C \rangle$) for equilibrium bulk solids fraction values $\nu_{\infty} = 0.593$ (*); $\nu_{\infty} = 0.623$, (\diamond), and $\nu_{\infty} = 0.659$ (\blacklozenge). As expected, systems which are more tightly packed have, on the average, more contacts per particle.



Fig. 11 Mean coordination number $\langle N_C \rangle$ versus ν_{∞} from the simulation results (\blacktriangle) and experimental measurements (\diamondsuit) of Aste et al. [53]. This comparison with the experimental data shows good agreement.

 $\langle Nc \rangle$ as a function of v_{∞} with the experimental measurements of Aste et al.⁴⁾ is shown in **Fig. 11**, where the simulation results are denoted by solid triangles. Here, good agreement is observed with the trend of the data, as indicated by the linear regression fits appearing in the figure and a quantitative comparison of the data with the reported experimental averages.

The radial distribution function ²²⁾ is given by $\bar{g}(r) = \frac{1}{\rho N} \left\langle \sum_{i}^{N} \sum_{j < i}^{N} \delta[r - r_{ij}] \right\rangle$, where *N* is the number of particles, ρ is the bulk density (i.e., number of particles per unit volume where $v = \rho \pi d^3/6$), r_{ij} is the distance between the centers of particles *i* and *j*, and δ is the standard delta distribution. Thus, $\bar{g}(r)$ may be considered as that quantity which, when multiplied by the bulk density, yields the local density. Computationally, $\bar{g}(r)$ is approximated as an ensemble-average quantity taken at the last Monte Carlo time step (or tap).

$$\langle \bar{g}(r/d) \rangle \cong \frac{\langle N(r) \rangle}{24 \langle \nu \rangle \left(r/d \right)^2 \left(\Delta r/d \right)}$$
 (16)

where $\langle \cdot \rangle$ represents the ensemble average, N(r) is the number of sphere centers within a spherical shell of radius *r* and thickness Δr , and *v* is the bulk solids fraction. Due to limited computational facilities, more refined 'time' and ensemble averaging was not possible over the range of tap intensities considered in this study. However, several preliminary calculations indicated little difference in the radial distribution results when 'time' averaging was included.

Fig. 12 shows $\langle \overline{g} \ (r/d) \rangle$ of the initial configuration and the result of three tap intensities corresponding to decreasing solids fractions v_{∞} . As the density increases, observe that the peaks in the distribution function become more pronounced. For $v_{\infty} = 0.675$, a power-law singularity at r = d of the form
$$\bar{g}(r) \approx c_0 \left| r - r_0 \right|^{-\alpha} \tag{17}$$

was found. The least-squares fit to (17) yielded $\alpha = 0.528$, in agreement with the value reported in the molecular dynamics studies of Silbert et al. ⁴⁷⁾ and later experiments of Aste⁵⁾. The second and third peaks in the distribution appear at $r/d = \sqrt{2}$ and $\sqrt{3}$. The influence of the plane floor in the simulations is enhanced by the taps, as can be seen in the radial distribution function of **Fig. 12** at $v_{\infty} = 0.675$. At the lowest tapped solids fraction (circled in **Fig. 12**, for $v_{\infty} = 0.583$), it is observed that the two peaks at $r/d \sim 1.8$ and 2.0 provide evidence of a local structural arrangement similar to the experimental results of Aste⁵⁾. This structure does not appear in the poured



Fig. 12 Radial distribution function for a poured assembly and for various equilibrium bulk solids fractions ν_{∞} with their associated intensities γ shown. The higher ν_{∞} results reveal local crystalline structure, while systems with smaller ν_{∞} exhibit features observed in experiments.

assembly $v_0 = 0.567$ as seen in the plot at the lower right hand corner of **Fig. 12**. We remark that this local arrangement differs from that seen by Nicolas et al.³⁶, who observed hexagonal close-packed structures resulting from the application of horizontal cyclic shearing.



Fig 13 Solids fraction $\langle v \rangle$ as a function of normalized height y/d from the floor for the case $v_{\infty} = 0.654$.

It is well-known that the presence of a flat plane boundary affects the local packing structure. In our simulations, this effect is enhanced through the taps as can be seen in Fig. 13, where the solids fraction as a function of the height is shown for the case v_{∞} = 0.654. The graph was obtained by computing solids fraction within successively increasing layers starting from the floor. The oscillations are the signatures of a microstructure that is strongly affected by the presence of a planar floor. As the top of the packing is approached, there is the expected decay in the magnitude of the oscillations and eventual rapid decrease. Preliminary case studies of larger systems have demonstrated substantially the same effects. Further investigations of these phenomena are in progress and the results will be reported elsewhere.

5. Summary and Conclusions

Density relaxation is a phenomenon of great interest because of its importance in the industrial section concerned with the handling and processing of bulk solids. In this paper, a Monte Carlo study was carried out to investigate the density relaxation process arising from discrete taps applied to a granular material consisting of monodisperse hard spheres within a laterally periodic computational volume. A single tap of intensity γ is modeled by applying vertical position-dependent displacements to the particles, which are then allowed to collapse under gravity via the Metropolis algorithm, thereby generating stable configurations. The algorithm is tailored so that motions which increase the system potential energy occur very rarely. The application of random lateral displacements in conjunction with the vertical expansion produced no effect on the final outcome. In order to accelerate the process and avoid trapping at local minima, the size of the neighborhood in which a particle is allowed to move was dynamically reduced as the system density increases. For tap intensity γ , the equilibrium value of the bulk solids fraction $\langle v(n; \gamma) \rangle$ at tap *n* was computed as an ensemble average over a sufficient number of realizations to ensure a standard deviation of less than 0.001.

It was found that more dense systems were created at smaller tap intensities, but this was at the expense of an increasingly growing number of taps to reach equilibrium. The evolution of the simulated data fit well to a hyperbolic tangent model of the form $v(n; \gamma) = v_0(\gamma) + [v_\infty(\gamma) - v_0(\gamma)] \tanh(A(\gamma)n)$ for tap intensities $1.2 \le \gamma \le 1.5$. For these energetic taps, poor correlation between the inverse log model



 $u\left(n\right) = \nu_{\infty} - \frac{\nu_{\infty} - \nu_{o}}{1 + B \log\left(1 + n/\tau\right)} \text{ and the simulation}$

data was found because equilibrium was attained more rapidly than could be accommodated by this functional form. However, at smaller intensities that roughly corresponded to the magnitudes of the tap accelerations used in experiments ²⁷, the inverse log model was consistent with the data. The fit of the data to this model and to the form indicated that the ratio $D \sim B/\tau$ is a relevant parameter for low tap intensities. A fit to the stretched exponential $v(n) = v_{\infty} - (v_{\infty} - v_{0})e^{-(n/\tau)\beta}$ showed reasonably good agreement with the data, albeit neither τ nor τ^{β} exhibited an expected decrease with intensity γ compatible with a time scale parameter.

Quantification of the microstructure via the radial distribution function g(r/d) revealed local crystalline order consistent with a face-centered cubic structure. In the densest tapped configuration $v_{\infty} = 0.675$, a power-law singularity in g(r/d)near r/d = 1 was found, while at the lowest tapped solids fraction $\tau_{\infty} = 0.583$, the appearance of a double peak for 1.8 < r/d < 2.0 resembled that seen in experiments and molecular dynamics simulations in the literature. The behavior of the mean coordination number, computed from the near-neighbor distributions as a function of the equilibrium bulk solids fraction was found to be in reasonably good agreement with experimental results in the literature. The ordering influence of the floor in the simulations was pronounced, but its occurrence is in accord with experimental observations in the literature. Preliminary calculations of the solids fraction behavior from the floor demonstrated the ordering effect of a smooth base. Further investigations of this effect are underway for deeper systems with a larger number of particles under various tapping strategies.

The findings of this study with regard to the effect of tap intensity on densification support our previous conjecture ⁵⁶⁾ on the existence of a range of vibration parameters that favors an increase of solids fraction in continuously oscillated systems. Our Monte Carlo results suggest that a bulk solid will experience an increase in density for a range of tap intensities that promote a 'slow' rearrangement of particle positions, i.e., for tap intensities that do not inhibit the creation of local ordering in the microstructure. On the other hand, for larger accelerations for which the system is aggressively expanded at each tap, the bulk solids fraction does not grow as a function of the number of taps. Discrete element studies are currently underway to study these phenomena.

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The Shape of Pulverized Bituminous Vitrinite Coal Particles[†]

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Abstract

The shape of pulverized bituminous coal particles (vitrinites) was determined by optical and laser light scattering. Vitrain samples were collected from obvious tree remains located in the ceilings of two Appalachian coal mines. Wet sieving produced narrow size cuts. The particles were determined to be oblong or blocky in shape, with average length-to-width ratio of 1.7 and sphericity of 0.78. They were analogous in shape to a square ended, rectangular "house brick". The two bituminous coals and different size cuts of each coal had essentially the same shape parameters. Characteristic heating times and terminal velocities were higher by 22 and 20%, respectively compared to spherical particles.

Keywords: Coal particle shape

1. Introduction

The size and shape of coal particles influence their heat and mass transfer characteristics, behavior in fluids, erosion potential, and inhalation-related health risks¹⁻⁴⁾. Unfortunately, the exiguous information that is available on the shape of coal particles has often been inferred from indirect techniques⁵⁾. Coal is a complex organic solid. The chemical and physical composition is influenced by the organic and inorganic precursors, deposition environment, and burial history. The macerals (those components of coals identifiable under the microscope as organic and identified based upon morphology and reflectance), which emanate from diverse biomass precursors also possess characteristic sizes, shapes and friabilities and thus tend to concentrate in different size fractions⁶⁻¹¹⁾. Hence, maceral composition has the potential to affect shape parameters of size fractions. Advanced separation techniques can produce high purity maceral concentrates¹²⁾ but only in particle sizes far smaller than those found in conventional pulverized coal. In addition, extensive milling is likely to produce increasingly spherical particles.

North American coals tend to be rich in vitrinite. The average vitrinite content of the 878 samples in the Penn State Coal Sample Bank is 75% (based on an ASTM point counting technique)¹³⁾. In this work the influence of other macerals was minimized by sampling obvious coalified trees that were monomaceral (telocollinite) in composition. Digital image analysis of reflectance microscopy images (along with SEM micrographs) provided direct observation of particle shape and allowed mineral matter to be excluded from the statistical analysis.

2. Experimental

The vitrain samples were collected from Sigillaria (a type of Lycopod) tree remains in the ceilings of coal mines in the Upper Freeport (UF) and Lewiston-Stockton (LS) seams. Samples were crushed in an adjustable plate mill to reduce the topsize to nominally 2mm, then comminuted in a (Holmes 501XLS) pul-

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verizer. Particle were separated by wet sieving. The mean maximum vitrinite reflectance was determined by the ASTM procedure¹⁴⁾. For shape analysis, polished pellets were prepared using a modified ASTM method. Approximately 0.5g of vitrinite was mixed with epoxy in a small vial, centrifuged to remove air bubbles and placed in a vacuum oven to aid epoxy impregnation. After setting, the vial was removed and the sample cut in half lengthways. The sample was cast in a standard optical microscopy pellet and polished. Size and shape analyses were performed using a digital image analysis system (IMAGIST, PGT, Princeton, NJ) interfaced with a (Nikon Microphot-FXA) microscope and a workstation. Oil-immersion objective lenses of $20 \times$, $40 \times$ and $100 \times$ magnifications were used for 100×200 , 200×400 and -400mesh (U.S. Standard Sieve) size cuts. Over 500 particles were evaluated in each cut, with approximately 20-30 particles in each micrograph.

Oil-immersion objective lenses were used to increase the contrast between mineral matter and vitrinite particles to aid in excluding mineral matter from the shape analyses. Computational editing of the particle outlines removed any holes in the face of the particle silhouette (emanating from mineral matter removal during polishing or from optics contamination). Particle segmentation was used to separate particles that were so closely located as to be erroneously classified as a single particle. Epoxy features, mineral matter (identifiable from reflectance levels), scratched particles, incorrectly segmented particles, particles with greater than 5% of the perimeter off the field of view, and particles with outlines altered by mineral matter inclusions were excluded from the analysis (based on a comparison between the image captured digital silhouette view and microscopy observations). More than 500 particles were analyzed for size and shape in each size cut.

The particle size distributions were also determined by laser light scattering (Malvern Instruments). A monochromatic collimated beam of light was passed through a sample cell containing the sample (several mg) in an ethanol medium with agitation supplied by a spinning bar magnet. The scattered light was brought to focus at the detector and the particle size distribution calculated assuming spherical particles. The assumption of spherical particles is commonly applied in coal science, despite the knowledge that coal particles are not spherical. The lack of quantified shape parameters hinders a more accurate description. To enable the impact of mineral matter to be determined, one sample was demineralized by



treatment with 10% HCl overnight followed by concentrated 52% HF for 100 hours with occasional stirring. Any remaining fine clays were removed with the aid of a dispersant. Following demineralization the samples were washed thoroughly with distilled water and air-dried.

3. Results & Discussion

Maceral identification confirmed the vitrain samples collected from obvious coalified trees were monomaceral (telocollinite) in composition. The mean maximum vitrinite reflectance values were 0.97 (sd 0.04) and 0.93 (sd 0.08) for the UF and LS samples, respectively. These reflectance levels indicate the samples were high volatile bituminous A in rank. Particle diameters were measured with an optical microscope approach and via laser light scattering. Image analysis of micrographs was used to determine individual particle diameters from the average of 12 diameters separated by 15°. The elongation ratio was defined as the smallest of the ratios obtained from these diameters to its perpendicular diameter (the width and the breadth in rectangles.) The aspect ratio was defined as the reciprocal of the elongation ratio. Circularity (O) was calculated from the largest diameter of the particle (dm) and the particle area using Equation 1. The area (A) was determined from the number of (calibrated) pixels in the particle silhouette. A sphere has a circularity of unity and elongated shapes have higher values.

Circularity O = $(d_m)^2(\pi) / (4A)$ (1)

An example of the particle shapes observed from a polished surface of a pellet is presented in **Fig. 1**. The unnumbered features were excluded from the analysis based on the exclusion criteria discussed earlier. The 12 diameters are drawn manually on the particle labeled number 5 to illustrate diameter placement. The size and shape parameters of the numbered particles are listed in **Table 1** to illustrate the relationship between shape and numerical characterization of the shape. As the field of view is from a polished surface, the particles are expected to have different orientations or may expose only a portion of the particle.

As indicated in **Table 1** and **Fig. 1** the UF vitrinite had a variety of shapes. Particle size (determined by microscopy and by light scattering) and shape parameters (determined by microscopy) are shown in **Table 2** for various size cuts. The laser light scat-





Fig. 1 Silhouette Image of Polished Face the UF 200×400 Cut Embedded in Resin.

tering technique measures particle diameters using a median volume-weighted diameter (D[v,50]). The microscopy technique measures the median lengthweighted diameter (D[1,50]). The average aspect ratios were 1.66 and 1.64 for the UF and LS vitrinites, respectively. For the UF size cuts the average aspect ratio and circularity decreased slightly with decreasing particle size cut, indicating that the smaller particles were slightly less elongated. The -400 mesh (US Standard Sieve) cut had an average circularity of 2.36 (Table 2), indicating significant non-sphericity (see examples in Fig. 1 and Table 1). There was little change in the average shape parameters among the size cuts and the LS and UF samples had similar values for the same size cut. In contrast to the vitrinite particles, the highly reflecting mineral matter

Table 2. Size and Shape 1	Parameters for UF	and LS Vitrinite	Size Cuts
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 Table 1. Size and Shape Parameters for UF 200x400 Mesh Size Cut

 Shown in Fig. 1

Particle	Mean	Circularity	Elongation	Aspect
Number	Diameter, µm	0	Ratio	Ratio
1	27.3	3.21	0.37	2.70
2	102.8	2.87	0.43	2.33
3	61.9	1.74	0.77	1.30
4	58.0	7.83	0.19	5.26
5	105.2	1.83	0.62	1.61
6	61.8	1.78	0.85	1.18
7	70.6	1.52	0.90	1.11
8	69.3	1.74	0.64	1.56
9	91.3	4.90	0.28	3.57
10	57.5	2.08	0.65	1.54
11	85.5	2.94	0.50	2.00
12	89.5	2.11	0.55	1.82
13	16.1	2.83	0.43	2.33
14	87.0	1.42	0.82	1.22
15	56.8	2.07	0.64	1.56
16	169.6	4.64	0.27	3.70

particles were almost spherical, in agreement with previous observations¹⁵⁾.

There was good agreement between the lengthweighted diameters (microscopy) and the volumeweighted diameters (light scattering) for the smaller size cuts (**Table 2**). This is unexpected, as the volumetric weighted diameter is an indication that 50 % of the total volume of the particles is in particles of greater diameter, while the length-weighted diameter indicates that 50 % of the total length of the particles is in those particles of greater diameter. Thus, larger particle sizes contribute disproportionately to the volume-weighted diameter than to the length-weighted diameter. For the LS 200 × 400 cut the volume-weight

Sample	D[v,50]/μm	D[1,50]/μm	Circularity O	Elongation Ratio	Aspect Ratio
$\rm UF100{ imes}200$	131	77 (40)	2.57 (1.09)	0.57 (0.18)	1.75 (0.77)
$UF200 \times 400$	65	66 (37)	2.47 (0.96)	0.59 (0.17)	1.69 (0.69)
$UF200 \times 400 \ddagger$	63				
UF-400	26	25 (29)	2.36 (0.90)	0.65 (0.16)	1.54 (0.59)
LS100×200	102	82 (40)	2.48 (0.97)	0.60 (0.16)	1.67 (0.64)
LS200×400	61	73	2.49	0.58	1.72
LS-400	20	24 (26)	2.30 (0.81)	0.66 (0.16)	1.52 (0.54)

D[1,50] is the length weighted mean diameter. D[v,50] is the volumetric weighted average diameter. Other parameters as defined in the text. Values in parentheses are standard deviations.

‡ demineralized sample.

ed (light scattering), surface-weighted (calculated), and length-weighted (calculated) median diameters were 61, 55, and 47µm, respectively. It is not clear why the volume-weighted and length-weighted median diameters agree so well for the smaller size cuts. One possible explanation is the inclusion of discrete particles of mineral matter in the light scattering data, however demineralization did not significantly alter the volume-weighted diameter of the 200×400 UF cut (**Table 2**). The deviation from sphericity contributes to the significant difference between the calculated (47µm from light scattering) and measured (73µm from microscopy) length-weighted diameters for the LS 200×400 cut.

To establish the shape of the coal particles, it was necessary to obtain information on the third dimension. An SEM micrograph conveniently permitted an estimation of the depth of the particle. From **Fig. 2** and other micrographs (not shown), it was concluded that the depth was of the same magnitude as the width. The shape was generally "blocky" with angular transitions. Thus, as a first approximation, the particle can be represented by a square-ended rectangular brick of length and width *a* and depth b = a/1.7 as shown is in **Fig. 3**.



Fig. 2. SEM Micrograph of the UF 200×400 Cut.



Fig. 3. Shape Descriptors for a Square-Ended House Brick Shape.



Assuming that a vitrinite particle is adequately represented by a square-ended rectangular brick, then equating the diameter of a sphere (dp), of the same volume as the brick, to the length (*a*) and width (b=1/1.7)) yields equation 2.

$$Vol = \frac{a}{b^2}^3 = \frac{\pi d_p^3}{6} \text{ or } dp = 0.87a$$
 (2)

Sphericity (ϕ_s), the ratio of the surface area of a sphere to the surface area of the particle (of the same volume), yields equation 3, and substituting for d_p in equation 3

$$\phi_s = \frac{\pi d_p^3}{\left(\frac{2}{b^2} + \frac{4}{b}\right)a^2} \tag{3}$$

vields a sphericity ϕ_s of 0.78. Constant sphericity values of 0.73 for pulverized coal dusts have been reported^{16, 17)} based on microscopic and sieve analysis of 80, 65 and 50 % of the particles passing 200 mesh British Standard sieve¹⁸⁾. A sphericity of 0.38 has also being reported for fusain fibers^{16, 17)}. Unfortunately the coal classification was not reported with these data. A consistent shape factor (using surface areas as determined by liquid permeability and sieve sizes) has also been reported for various size cuts (11 fractions between 16 to 325 US mesh), although particle shape was found to be rank dependent⁵⁾. Aspect ratios of 1.39 to 1.55 have been determined for Pittsburgh seam coal dusts (less than 75µm diameter) generated within the mine and by a variety of pulverizers⁴⁾. These aspect ratios are consistent with those reported here for the smallest particle size cuts.

When coals are comminuted, the particles break first at the weakest junctures, which are the organicinorganic, maceral-maceral interfaces and along the pores¹⁹⁾. Thus, at least initially, macerals tend to retain their characteristic shape¹⁹⁾. Macerals also concentrate in different size fractions because of the different friabilities and/or heterogeneity among maceral groups⁶⁻¹¹⁾. Thus, coals are expected to have different shape parameters in different size fractions. With increasing pulverization residence time (of an hour or more), however, the shapes of the particles are altered towards more spherical or "blocky type" shapes¹⁹⁾. Also, there is evidence that different methods of pulverization produce different particle shapes^{4, 5, 20)}, although one study found little influence of pulverizer type upon shape²¹⁾. Extended comminution time has also been shown to influence particle shape²⁰⁾ for most of the devices used, the exception



was a high-energy mill. Lithotypes also have different friabilities, with the monomaceral microlithotypes of vitrinite and inertinite being the easiest to grind under Hardgrove grindability conditions, thus, increasing the concentration of trimaceral lithotypes in the coarser grinds²²⁾. Caution must therefore be exercised in comparing the results of different studies, as rank, maceral content and pulverization method influence the shape^{4, 5)}.

Having established the deviation from a sphere, the question arises: what is the impact? As stated earlier, the size and shape of coal particles influence their heat and mass transfer characteristics, behavior in fluids, erosion characteristics and inhalation-related health risks¹⁻⁴⁾. A simple heat transfer calculation will show if the impact is significant on convective heating where spheres are commonly assumed. Equation 4 shows the commonly used convective heat transfer calculation, Nu is the Nusselt Number (a dimensionless heat transfer coefficient), λ is the thermal conductivity of the gas, and T_g and T_p are the temperature of the gas and particle, respectively.

$$\frac{dQ}{dt} = \frac{Nu\lambda}{d_p} \left(T_g - T_p\right) \frac{\pi d_p^2}{\Phi_s} \tag{4}$$

The sphericity is used as a corrective term for nonspherical particles. Addition of the energy gradient term in equation 4 yields equation 5, where Cp is the specific heat of the particle and ρ_p is the particle density. Rearrangement of equation 5 generates equation 6.

$$\pi d_p^3 \rho_p C_p \frac{dT_p}{dt} = \frac{Nu\lambda}{d_p} \left(T_g - T_p \right) \pi \frac{d_p^2}{\Phi_s}$$
(5)

$$\frac{dT_p}{dt} = \frac{6Nu\lambda}{d_p^2 \Phi_s \rho_p C_p} \left(T_g - T_p\right) \tag{6}$$

Defining a characteristic heating time (τ) enables simplification and calculation of the role of sphericity in the heating time. The characteristic heating time is shown in equation 7.

$$\tau = \frac{d_p^2 \Phi_s \rho_p C_p}{6Nu\lambda} \tag{7}$$

Making the assumption that the Nusselt Number is 2 and that the sphericity $\phi = 0.78$, then τ becomes 22% greater than in the case of a sphere. A more accurate comparison would include the influence of the house brick shape on the characteristic length

component of the Nusselt Number. While this is potentially a significant decrease in effective particle heating rate it is important to note that under rapid heating conditions, occurring during pulverized coal combustion, that most bituminous coals will deform and alter shape. In earlier work these samples were exposed to rapid-heating pyrolysis in a drop-tube reactor²³⁾. A range of time-temperature histories was predicted for particles, depending on path and proximity to the hot walls, utilizing computational fluid dynamics. SEM observations showed that at center line gas temperatures around 841 K (approximately 0.06 s residence time) that rounding of sharp edges was evident in some particles and the occasional particle had formed a swollen spherical particle with an empty interior, known as a cenosphere²⁴⁾, however most particles were unchanged²³⁾. At around 1,000 K center line gas temperatures (0.15-0.17 s center line residence times for UF and LS particles, respectively) many spheres were evident with slightly larger size than the raw feed (a 10-15 μ m increase in D[v,0.5])²³⁾. By 1600 K gas temperature and 0.2-0.3 s residence time spectacular swelling (tripling in D[v,0.5] in comparison to the feed) was observed for UF with large cenospheres dominating the particle distribution²³⁾. The LS sample doubled in size on average²³⁾. Particle size influences the heating rate and release of volatiles²⁵⁾, it is demonstrated that the shape influence heating rate and is thus expected to influence volatile transport within the particle and influence thermoplastic behavior and hence char physical and chemical structure²⁶⁾.

To determine the impact of this shape factor on terminal velocity, a petroleum-based modeling material was weighed and shaped into 3 spheres and 3 appropriately sized square ended rectangular bricks. The same mass was used in each sample. The samples were placed in oil and dropped one at a time into a graduated cylinder filled with the same viscous oil. Time measurements and velocity calculations (timing occurred after terminal velocity had been reached) indicated the sphere fell slower than the orientated house brick shaped samples, 4.0 (± 0.2 s.d.) versus 4.8 (± 0.3) seconds for the sphere. Essentially, the velocity of the square ended brick shape, of the same mass, was 20% faster than the sphere. Time measurements showed random scatter implying the samples did not gain mass after exposure to oil. Thus aerodynamic calculations assuming spheres (of the same mass) will overestimate the suspension of particles in the air or coal-water slurry suspensions.

4. Conclusion

The shapes of two pulverized vitrinite samples in the bituminous rank range were found to be similar among and between the size cuts, in agreement with previous work. A slight decrease in aspect ratio and a slight increase in circularity accompanied decreasing particle size. The -400 mesh US Standard Sieve size cut for each vitrinite had the lowest aspect ratio and the lowest circularity value. The particles had a distribution of shapes but the average particle was approximately 1.7 times as long as it was broad. It was concluded that on average a square-ended rectangular block (house brick shape) of length a and depth and width of b=a/1.7 was a more realistic representation of a vitrinite particle than a sphere of the same volume. The two bituminous coals and different size cuts of each coal had essentially the same shape parameters. A sphericity value of 0.78 was determined for the pulverized bituminous vitrinites in agreement with a previously reported value of 0.73 for coals in general. Characteristic heating times and terminal velocities were higher by 22 and 20%, respectively compared to spherical particles.

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Symbols

A	particle area	$[m^2]$
a	particle width	[m]
b	particle breadth	[m]
Ср	specific heat of the particle [J]	$K^{-1}kg^{-1}$]
D[l,50]	median length-weighted diameter	[m]
D[v,50]	median volume-weighted diameter	[m]
d_m	largest particle diameter from 12 m	neasure
	ments 15° apart	[m]
LS	Lewiston Stockton seam coal sample	e [-]
Nu	Nusselt Number	[–]
$ ho$ $_p$	particle density	[kgm ⁻³]
0	circularity	[—]
Q	heat	[J]
τ	characteristic heating time	[S]
T_{g}	temperature of the gas	[K]
T_p	temperature of the particle	[K]
$U\!F$	Upper Freeport coal seam sample	[–]
vol	particle volume	$[m^3]$
π	pi	[-]



[-1]

- ϕ_{s} sphericity
- λ thermal conductivity of the gas [Wm⁻¹K⁻¹]

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Jonathan Mathews is a coal scientist. He holds an honors degree in Applied Chemistry (1991) from the Nottingham-Trent University in Britain and a doctorate in Fuel Science (1998) from the Pennsylvania State University. He is an assistant professor in the Energy & Mineral Engineering Department, College of Earth & Mineral Sciences, at the Pennsylvania State University. His research is focused on the structure of coal and structural influences upon coal behavior. His focus spans the molecular scale with molecular modeling simulation, micron scale with advanced image analysis, and larger scales with X-ray computed tomography among other techniques. Currently his focus is on sequestration of CO₂ in coal.



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Author's short biography



Dr. Patrick G. Hatcher

Patrick G. Hatcher obtained his Ph.D. in chemistry (geochemistry) from the University of Maryland in 1980 after having obtained a MS degree in chemical oceanography from the University of Miami (1974) and a BS degree in chemistry from N.C. State University (1970). He then was employed by the U.S. Geological Survey and later accepted a position at Penn State University. From his eventual position as a Professor of Fuel Science and Geosciences, Adjunct Professor of Chemistry, and Director of The Center for Environmental Chemistry and Geochemistry at Penn State, Hatcher joined the Department of Chemistry at The Ohio State University in July, 1998 and assumed the Directorship of the Ohio State Environmental Molecular Science Institute. In 2006, Hatcher accepted the Batten Endowed Chair of Physical Sciences in the Department of Chemistry and Biochemistry at Old Dominion University and is the Faculty Director of the College of Sciences Major Instrumentation Cluster (COSMIC). He is the author of more than 250 peerreviewed articles that report on the numerous studies in the area of environmental chemistry and geochemistry, specifically emphasizing the origin, structure, and chemical transformations of plant-derived biopolymers in soils, peats, coals, marine sediments, and oceanic waters. Hatcher relies on modern analytical methods that include 1-,2-, and 3-D liquids NMR as well as solids NMR and electrospray ionization with ultrahigh resolution mass spectrometry.

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An Application of Solid Particles in Fuel Cell Technology[†]

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Abstract

Solid fuel particles will become increasingly important in the future. Present energy conversion systems for solid fuels are too inefficient. New energy conversion systems for solid fuels with higher energy conversion efficiencies are possible. Fuel cell technology is a key-technology in these new conversion systems. The direct carbon fuel cell (DCFC) operates on carbon particles obtained from a variety of solid fuel feedstocks. The DCFC is the only fuel cell designed to directly oxidize carbon particles in a special anode chamber. The particles are generally graphite structure with high purity. The electrolyte used is the high temperature solid oxide, molten carbonate or hydroxide electrolyte. Since a pure stream of CO_2 is produced the stream can easily be sequestered and disposed. Pure carbon dioxide produced as a by-product would also have a market in many industries. A well defined technology roadmap identifying key research and development (R&D) issues is necessary to provide a framework for the development of these systems and to prevent entrenchment in inherently inefficient technologies. This review paper describes the direct carbon fuel cell and its system, how it works, the developmental status, the characteristics of the carbon particles needed, and the research and development issues for the technology.

Keywords: Carbon particles, Direct carbon fuel cell, High efficiency

1. Introduction

The DCFC has been under development for many years. It was researched as early as 1896¹⁾, but an intense research and development is necessary to realize its potential. William W Jacques, a US electrical engineer and chemist, described a DCFC in 1896 in US Patent 555511 for a "Method of converting potential energy of carbon into electrical energy". Jacques used coke electrodes in a molten NaOH electrolyte.

Molten carbonate fuel cell (MCFC), solid oxide (SOFC) or hydroxide electrolyte (AFC) technologies can be used as the basis for the DCFC technology. A schematic of the direct carbon fuel cell in the MCFC mode is shown in Figure 1. The molten carbonate fuel cell operates at approximately 650° C (1200°F). The high operating temperature is needed to achieve

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sufficient conductivity of the carbonate electrolyte, yet allow the use of low-cost metal cell components. A benefit associated with this high temperature is that noble metal catalysts are not required for the cell electrochemical oxidation and reduction processes. For the hydrogen reaction the half cell electrochemical reactions are

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$$H_2 + CO_3^{=} = H_20 + CO_2 + 2e$$
-

at the anode, and

 $1/2O_2 + CO_2 + 2e = CO_3^{=}$

at the cathode. The overall cell reaction is

 $H_2 + 1/2O_2 + CO_2$ (cathode). $H_2O + CO_2$ (anode)

In the case of carbon and the DCFC the reaction at the anode is generally replaced by

1/2C (s) + $CO_3^{=} = 3/2CO_2 + 2e$ -

For the case of the electrolyte being a molten carbonate salt, the carbonate ions move from the oxygen cathode to the special anode chamber where they react with the carbon fuel particulates dispersed in the molten salt and form CO_2 in high concentration. The particulate carbon dispersed in the molten salt is converted to CO_2 which emerges from the anode compartment of the cell at 100% concentration. MCFC current materials, thicknesses and processing techniques are shown in **Table 1**². The materials for the anode listed in **Table 1** are for use when the fuel is hydrogen or methane. A special anode is required

	Table 1 MCFC Materials
Anode	 Ni-Cr/Ni-Al/Ni-Al-Cr 3-6 µ m pore size 45 to 70 percent initial porosity 0.20 to .5 mm thickness 0.1 to1 m²/g
Cathode	 Lithiated NiO-MgO; 7 to15 μ m pore size; 70 to 80 percent initial porosity; 60 to 65 percent after lithiation and oxidation; 0.5 to 1 mm thickness; 0.5 m²/g
Electrolyte Support	 γ -LiAlO₂, <i>a</i> -LiAlO₂; 0.1 to12 m²/g; 0.5 to1 mm thickness
Electrolyte	 62 Li-38 K; 60 Li-40; tape cast 0.5 to1 mm thickness

for the DCFC.

The SOFCs (600-1000°C) being developed, particularly the planar types, have unique designs, are constructed of various materials, and are fabricated by different techniques. The electrochemical reactions associated with hydrogen fuel are:

 $H_2 + O^{=} = H_2O + 2e$ -

at the anode, and

$$1/2 O_2 + 2e = O^{\dagger}$$

at the cathode. The overall cell reaction is

 $H_2 + 1/2 O_2 = H_2O$

In the case of carbon and the DCFC the reaction at the anode is generally replaced by

$$1/2C(s) + O^{=} = 1/2CO_{2} + 2e$$
-

SOFC materials widely vary. The basic SOFC materials, thickness and processing techniques are shown in Table 2^{2} .

Table 2	SOFC Materials
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Anode	 Ni/ZrO₂cermet Deposit slurry, EVD fixed 12.5 × 10⁶cm/cm[°]C CTE ~150 μ m thickness 20 to 40 percent porosity
Cathode	 Doped lanthanum strontium manganite (LSM); Extrusion, sintering ~2 mm thickness 11 × 10-6cm/cm℃ CTE from room temperature to 1000℃ 30 to 40 percent porosity
Electrolyte	 Yttria stabilized ZrO₂ (YSZ) (8 mol percent Y₂O₃) EVDd 10.5 × 10⁻⁶ cm/cm[°]C CTE from room temperature to 1000[°]C 30 to 40 µm thickness
Cell Interconnect	 Doped lanthanum chromite Plasma spray 10 X 10-6cm/cm[°]C CTE ~100 μm thickness

The materials for the anode listed in **Tables 1 and 2** are for use when the fuel is hydrogen. Special anode materials selective for carbon oxidation are available and will be discussed later. In addition to hydrogen, carbon monoxide (CO) and other hydrocarbons such as methane (CH₄) can be used as fuels. It is feasible that the water gas shift reaction involving CO (CO + H₂O = H₂ + CO₂) and the steam reforming of CH₄ (CH₄ + H₂O = 3H₂ + CO) in the high temperature environment of SOFCs produce H₂ that is easily oxidized at the anode. The direct oxidation of CO in fuel cells is also well established. In the SOFC case oxidation of carbon could occurring at the surface is quite different than oxidation after vaporization of the carbon.

In the AFC mode the hydroxide ion approach which occurs at 100-500°C is believed to have several advantages - lower cost lower-temperature materials of construction, more electrochemically active carbon and greater production of CO₂, although hydroxide reacts with carbon dioxide.

For the hydrogen reaction the half cell electrochemical reactions are

 $H_2 + 2OH = 2H_2O + 2e$

at the anode, and

 $1/2O_2 + H_2O + 2e = 2OH$

at the cathode. The overall cell reaction is

 $H_2 + 1/2O_2 = H_2O$

In the case of carbon and the DCFC the reaction at the anode is generally replaced by

 $1/2C(s) + 2OH = 1/2CO_2 + H_2O + 2e$

Electrode development in circulating electrolyte AFCs (hydroxide electrolyte) has concentrated on 1) multi-layered structures with porosity characteristics optimized for flow of liquid electrolytes and gases (H₂ and air), and 2) catalyst development. Most developers use noble metal catalysts; some use nonnoble catalysts. Spinels and perovskites are being developed in an attempt to lower the cost of the electrodes. Development of low-cost manufacturing processes includes powder mixing and pressing of carbon-based electrodes, sedimentation and spraying, and hightemperature sintering. AFC electrolyte development has been restricted to KOH water solutions with



concentrations ranging from 6 to 12 normal. Still, use of less expensive NaOH has been considered. Minimal cost advantages appear to be far outweighed by performance reductions due to wetting angle and lower conductivity. However, NaOH as an electrolyte increases the lifetime of electrodes when CO₂ is present, because sodium carbonate, although less soluble than potassium carbonate, forms much smaller crystals, which do not harm the carbon pores.

2. Performance Potential of DCFC

For direct oxidation of carbon to CO₂ the maximum intrinsic thermal efficiency of conversion of the enthalpy (heating value) of the carbon to electricity is 100% at any temperature or pressure. This is because the entropy of oxidation of carbon is zero ($\Delta S = 0$). Thus, the enthalpy of oxidation equals the free energy (Δ H= Δ G). This is not the case for the hydrogen fuel cell. The maximum intrinsic thermal efficiency for hydrogen fuel cells is plotted in Fig. 2 as a function of temperature. In the case of hydrogen as a fuel the maximum intrinsic thermal efficiency decreases with increasing temperature. Pressurization of the fuel cell to 30 atmospheres further improves hydrogen fuel cell performance, but it does not equal the 100% theoretical achievable by the DCFC. It is no mystery then why the interest in the DCFC.

Fig. 3 shows the expected fuel cell efficiency performance of carbon graphite solid particles in a simple SOFC hybrid system as a function of temperature with only 75% carbon utilization³⁾. The reaction

MAXIMUMINTRINSIC THERMAL EFFICIENCY



Fig. 2 Fuel Cell maximum intrinsic thermal efficiency. DCFC thermal efficiency is 1.0 at all temperatures.





SIMPLE SOFC HYBRID SYSTEM 75% CARBON UTILIZATION CARBON SOLID TO $\rm CO_2$

Fig. 3 Projection of DCFC Thermal Efficiency in a Simple SOFC Hybrid System

occurs almost to completion as soon as the conductivity of the SOFC electrolyte, LSGM in this case, is sufficient to conduct oxygen ions to complete the direct carbon oxidation reaction.

3. DCFC Developmental Status

There are several DCFC developers - Lawrence Livermore National Laboratory (LLNL) and Contained Energy (MCFC), SRI (MCFC + SOFC), SARA (hydroxide) and CellTech (SOFC). There is some work around the world at other organizations such as Stanford University, Akron University, Virginia Polytechnic Institute and State University, University of Colorado, Technical University Delft, Brown University, Duke University, AIST, and NEDO that has occurred over the years⁴.

The LLNL and Contained Energy design utilizes an MCFC cathode, a nickel or high-fired graphite anode and porous ceramic separator. The anode reaction is carbon and carbonate ions forming CO₂ and electrons. De-ashing processes, such as those developed by UCC Energy (Sydney, Australia), the New Energy and Industrial Technology Development Organization and South African Synthetic Oil Limited could yield fuel at competitive costs (about \$2–3 per million BTU). LLNL has demonstrated the technology in small, experimental cells with areas between 3 and 60cm². LLNL has tested a five-cell, self-feeding bipolar stack using pure fine carbon. LLNL reports that in repeated tests the cells deliver up to 0.1 watt/cm² continuously and are 80% efficient at 80 milliwatt/cm^{25,6,7}.

The reported performance⁸⁾ of the SARA design is average output power in Mark III-A of 12-20 watts (over 540 hours) with peak output power (sustained for 5 to 10 seconds) 35-50 watts. The concepts have achieved 300 millivolt at 40 amperes in Mark III-A and 100 milliampere/cm² in Mark III-A 250 milliampere/cm² in Mark III-D. The efficiency was 60% measured in the non-optimized Mark III. They project the maximum efficiency of the DCFC at \sim 85-90% and the practical DCFC plant efficiency at \sim 70-75%.

The SRI design combines advances in SOFC and MCFC technology with the concept of using a circulating liquid-molten salt anode that incorporates the carbon-containing fuel. SRI is examining various molten salts, including molten carbonate, and using a YSZ electrolyte and a lanthanum strontium manganite cathode. A variety of fuels have been tested, including biomass, coal, tar, coke containing 6% sulphur, acetylene black, plastic and mixed waste. Using conventional coal without pretreatment, SRI has achieved power densities >100mW/cm²⁴).

CellTech technology⁹⁾ builds upon conventional solid oxide fuel cell materials and components (Fig. 4). Oxygen ions are extracted at the cathode and pass through the electrolyte to the anode (fuel) side where they combine with hydrogen or carbon monoxide from the fuel to form water or carbon dioxide. Meanwhile, electrons are released at the anode and travel through the load producing useful electrical energy on their way to the cathode. The cathode is made of conventional cathode materials such as lanthanum manganite doped strontium - LSM. The electrolyte is YSZ. The design is currently a cathodesupported with a tubular configuration. The anode is a p-orbital-electron metal such as tin which is molten at operating temperatures. The tin is held in place by a ceramic matrix. Tin is converted to tin oxide at the anode. In a separate reaction, the tin is "recharged" by the carbon. CellTech has integrated the reforming reaction (the reduction of tin oxide to tin) into the fuel cell, but uncoupled that reaction from the electrical production reaction (the oxidation of tin to tin oxide).



Fig. 4 CellTech DCFC Concept



It is hardly expected that the DCFC development will precede the state-of-development of its base AFC, MCFC or SOFC technologies. There state-of-readiness appears eminent, however.

4. Solid Carbon Particle Fuel Production and Quality Requirements

The problem of the application of fossil fuels for powering fuel cells is to process the hydrocarbons in fossil fuels to produce elemental hydrogen and/or solid carbon. This can be accomplished by thermal cracking (decomposition) and pyrolysis processes. According to recent reports¹⁰, the carbon formed in the plasma reactor is of a quality suitable for the molten carbonate cell type DCFC.

Graphite particles are commercially made from the sooting of methane; however, graphite is also available from coal, coal coke, petroleum coke, etc.. Sulfur, chlorine, sodium and trace metals are components of coal known to present problems to catalytic surfaces such as that of the fuel cell anode. Fouling, erosion, blockage of active catalyst sites, and chemical reaction are known problems occurring with coal ash. In addition, with coal the production of an aromatic or cyclic carbon compound rather than an active graphite solid particle is a problem inherent with the use of coal feedstock. What happens to the contaminants in coal with or without coal cleaning is an issue. Coal contains volatile components, so the DCFC system must be designed so that the coal can be introduced to the hot fuel cell without the explosive release of volatile components.

The cost of the chemical clean-up of coal particles to a low-ash, clean carbon has been estimated at \$ 60/ton¹¹⁾. Lower cost carbon particle clean-up systems obviously need to be developed. The estimated cost of oil agglomeration and advanced flotation are 17 and 12 \$ /ton of clean coal, respectively. Depending on the carbon content of the beneficiated coal, this could be in the economic range and competitive with other carbon formation processes providing the carbon content was high and the carbon reactive. For the MCFC-type DCFC, the anode chamber can be a carbonate melt similar to the MCFC electrolyte. This permits actually cleaning of impurities in the melt. For a low ash content carbon or coal this could be a batch process.

Nanoparticles of carbon if produced could be highly reactive. These hold great promise for subsequent development. LLNL^{6,7)} has examined the relationship between the nanostructure of carbons and their electrochemical reactivity in molten salts by correlating significant differences in the 3D atomic structure of carbon fuels with their electrochemical reactivities. The more disordered the carbon atoms, the more easily they yield electrons. DCFC performance depends on disorder more than on carbon purity or even aggregate surface area. Extremely fine $(10-1000 \ \mu \text{ m})$ carbon particles with a high degree of structural disorder on the 30–100nm scale work well. Fine carbon particles, when mixed with molten carbonate to form a dense paste or slurry, operate like rigid electrodes when the melt is brought into contact with an inert metallic screen or graphite current collector.

5. DCFC Systems

Thermal cracking (decomposition) and pyrolysis processes can occur in a variety of reactors. There could be a good match between the hydrogen plasma black reactor (HPBR) and the DCFC for producing electric power and/or hydrogen and maximizing the power cycle efficiency¹²⁾. The HPBR combined with the DCFC and SOFC in a combined power cycle is an example of an integrated power plant for use with the DCFC which a high power cycle efficiency. The HPBR produces hydrogen and CO for the SOFC and carbon for the DCFC in an efficient manner. In the SOFC oxygen ion is transmitted through the SOFC ceramic membrane and oxidizes the CO and H₂ to CO₂ and H₂O with the production of DC power to complement the direct oxidation of carbon in the DCFC.

LLNL has designed a DCFC system that incorporates a self-feeding cell that can be refueled pneumatically with cleaned coal. The DCFC incorporates a



Transportation and Stationary Power

Fig. 5 Thermal efficiencies of power plants Source: DOE



pyrolysis step that produces hydrogen (which can be used as fuel for a conventional fuel cell or as a chemical reactant), low-molecular-weight hydrocarbons and a nonagglomerating char that could potentially be reactive and conductive and useable in the DCFC.

One of the most efficient systems incorporate fuel cells and turbines - the fuel cell turbine hybrid. **Fig. 5** shows the efficiencies of stationary and transportation systems. Hybrids are the highest efficiency power plants yet devised. Hybrids are combinations of energy conversion devices. Many combinations of energy conversion devices are possible, but the combination of the high-temperature fuel cell with the gas turbine is a very high efficiency one^{13,14}. In the direct fuel cell turbine hybrid concept the fuel cell replaces the turbine combustor. The turbine expands the high-temperature fuel cell exhaust.

Although the DCFC is capable of 100% energy conversion and 100% fuel utilization at any temperature, this efficiency and utilization will probably not be realized. Therefore, one would want to operate at in a hybrid system to take advantage of fuel cell underutilizations, irreversibilities and inefficiencies. The high exergy exhaust from the higher temperature DCFC is quite suitable to perform useful expansion work in a gas turbine.

The plant costs of various power plants have been projected by EPRI in **Fig. 6**¹⁵⁾. In this comparison DCFC long-term compares very favorably having the lowest plant cost projection. Specific applications for DCFC systems may exist in low-cost power, combined heat and power, and peak shaving/loadmanagement applications in which DCFCs help utilities to balance supply and demand during periods of high electricity demand. For DCFC systems to be competitive, however, they must present an attractive alternative not only to today's technologies, but to technologies that will be available when DCFCs are eventually commercialized.



Fig. 6 EPRI Capital Cost Comparison

6. Research and Development Needs

The major development required is for the anode and anode chamber, for all the modes of the DCFC. The reactor strategy - batch or flow - depends on the purity of the solid graphite particles.

In the SOFC-mode case special anode materials tungsten carbide, vanadium carbide (VC), zirconia carbide, titanium carbide, nickel metal, and carbon - have been researched¹⁶⁾. Several transition metal carbides were investigated as anodes. Observed values of open circuit voltage of carbide anode SOFCs were found to be in the same order as the oxygen potentials calculated for the respective metal carbide/metal oxide equilibrium. All the carbide anodes showed better performance than graphite anode. No CO₂ was detected even at high oxygen potentials due to its reduction. The VC was able to best activate the carbon solids. Redox reactions of anodes play an important role in activating carbon. Oxidation of the anodes themselves hinders the electrochemical reactions. The CO evolution was not proportional to the current density due to consumption of oxygen for the oxidation of TiC (See Fig. 7).

US DOE-funded research has been conducted on V2O5-Pt catalysts for carbon oxidation anodes in DCFCs at the University of Akron and on carbon ionic conductors for use as electrolytes in novel DCFCs at Duke University¹⁴.

For the molten carbonate DCFC type¹⁷⁾ Selman has identified the following research needs, primarily dealing with the anode chamber:

1. Wetting characteristics of various types of carbon, in melts of variable basicity (cation composition, and OH-added) and temperature

PERFORMANCE OF DCFT ANODES



Fig. 7 Outlet CO evolution rates from VC and TiC anodes as function of current density



- 2. Spectroscopic characterization of molten carbonate in reducing medium, in contact with carbon, to establish identity of stable and semi-stable species
- 3. Molecular Dynamics calculations to establish the relative stability of carbon-carbonate-CO-CO₂con-figurations in the melt
- 4. Monte-Carlo (stochastic) modeling of assemblies consisting of cells representing carbon particles, gas bubbles (CO₂, CO), and carbonate melt. Buoyant forces, interfacial forces, and electrochemical reactions to be accounted for, cell-to-cell.

Cell and stack area and height scale up, heat removal, performance degradation as a result of electrolyte contamination, and electrolyte purification and re-injection processes are also critical issues which need to be addressed for all DCFC technologies.

Other special R&D requirements vary with the developers technology and system development schemes identified in this paper.

7. Conclusions

In theory, the DCFC holds the highest promise of any fuel cell. An intense period of research would be required to develop the anodes and anode chamber for various designs. Carbon particle reactivity, impurity level and cost will play major roles in any eventual DCFC commercialization. It can hardly be expected that the DCFC development will precede the state-of-development of its base AFC, MCFC or SOFC technologies.

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Phenomenology, Kinetics and Application of Abrasive-Reactive Wear during Comminution (Overview)[†]

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Abstract

Valuable information on the phenomenology of mechanical activation will be obtained from the accurate characterization of wearing processes that take place within mechanochemical reactors. Favoring the contamination of reactant powders with material from a reactor's debris, for a long time such processes represented one of the greatest limitations to practical mechanochemistry applications. We will focus on two related aspects of mechanochemical processing by grinding in a ball mill: (i) nanoscale wear of the treated substances and of the milling tools (balls and container wall); and (ii) deposition of a powder coating on the surface of the milling tools (self-lining phenomenon). A new technology called abrasive-reactive wear (ARW) has been developed that utilizes wear debris as an integral component of the reaction system rather than treating it as a harmful impurity. This technology is applied to the preparation of nanocomposites and to the processing of mineral raw materials and industrial byproducts. This review includes preparation experiments, material characterization, ARW kinetics and simulation. Besides developing new technologies, ARW will contribute to a better understanding of the mechanochemical or mechanical alloying process in general.

Keywords: Mechanochemistry, material of milling tools, abrasive-reactive wear, nanocomposites

1. Introduction

The mechanical activation (**MA**) of powders, usually carried out in suitably designed ball mills that are considered mechanochemical reactors (**MR**) essentially consists of the repeated mechanical loading of powders trapped between the colliding surfaces of the milling tools¹⁻⁴. The local compressive and shear events create hot spots and induce plastic deformation and fracturing of the particles⁵⁻⁷. Under such circumstances, powder particles undergo continuous comminution associated with interface renewal processes. These promote the occurrence of physicochemical transformations including microstructural refinement down to nanometer size⁸⁻¹².

TEL: +7 (383) 333-2007, FAX: +7 (383) 333-2792 E-mail address: urakaev@uiggm.nsc.ru Contamination due to the abrasion of milling tools is an inevitable problem of conventional MA in MR; the level of contamination can reach several percent and can rarely be kept below a few tenth of a percent ⁴⁾. Many authors mentioned this problem in their works on mechanochemistry. Moreover, some concrete examples of the possible participation of the milling tools' material in mechanochemical processes were reported¹³⁻²¹⁾, but these works have not been followed up on.

In¹³⁾, the Mössbauer effect was used for studying MA processes of quartz. The metal iron, which contained 2.17% of isotope ⁵⁷Fe, was introduced into quartz during the process of MA as a result of the steel milling tools of a disintegrator (pin disc mill or UDA) being worn by the particles of quartz at their relative linear speed of impact up to 270 m/s. Experiments on the mechanical activation of quartz were carried out in a vacuum and in air. It is shown that the Mössbauer effect can be used successfully for studying the mechanochemical reactions of quartz with an

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iron material of disintegrator milling tools. In¹⁴, the quantitative characteristics of the steel material wear of milling tools dependent on MA time were determined for the first time with the purpose of mechano-chemical opening of sulfide and arsenide minerals.

In¹⁵⁾, the participation of the milling tools' steel material in the process of mechanochemical sulfidizing of some oxidized copper minerals in the presence of water was shown and the sulfidizing mechanism was established for the first time. In¹⁶⁾, the influence of mill power and grinding environment on the contamination of quartz by iron during vibration grinding was studied. It was found that the Fe content in ground powders increased with increasing specific milling energy. The specific contamination expressed as the ratio of Fe content to newly created surface area depended upon the physical properties of the grinding environment. The influence of grinding conditions on the state of the iron in the products of grinder wear was investigated by Mössbauer spectroscopy and by measuring the magnetic susceptibility of the ground powders. It was shown that the iron produced from grinder wear is present in two main forms: as a magnetically ordered form identical with the basic material of the grinder and in a form of finely dispersed iron compound showing superparamagnetic behavior. Based on the results obtained, the formation of a silica-supported iron or iron oxide catalyst was presumed.

In¹⁷⁾, the wear of high-carbon low-alloy cast steel balls during the grinding of a chalcopyrite ore was evaluated under different experimental conditions. The role of oxygen in enhancing ball wear during wet grinding is emphasized. Contributions from corrosion and abrasion towards ball wear are quantified in terms of ball wear rates as a function of time, particle size and gaseous atmosphere in the mill. In¹⁸, guartz powders prepared by MA in a planetary mill in the presence of monohydric or dihydric alcohols were found to exhibit magnetic properties as the result of abrasive wear of the material of the steel milling tools. Tile magnetic susceptibility of milled quartz depends on the milling time and the amount of additions. The material was shown to undergo aging: its susceptibility and electron paramagnetic resonance spectrum vary during storage. The magnetization of quartz is interpreted in terms of Fe-containing clusters present in tile amorphized surface layer. In¹⁹⁾, the interaction of the sample with wear products from milling tools made of steel, tungsten carbide and strengthened ball bearing steel (ShKh15) is investigated by means of Mössbauer spectroscopy, X-ray diffraction and gravi-



metric measurements. It is stated that under identical conditions, ShKh15 steel is the most resistant to wear and the least prone to participate in mechanical alloying. It is shown that when choosing materials for milling bodies for the investigations of mechanical alloying, one should take into account a condition that ensures the delivery of reliable information: an increase of the mass of the sample under investigation should not exceed 10% during mechanical treatment.

Research of new nanocomposites prepared by the non-conventional mechanochemical route under the abrasive-reactive wear conditions was stimulated by the works of $^{20,21)}$.

In the work of Goya et al.²⁰⁾, who followed the phase evolution of CuFe₂O₄ during high-energy ball milling in a steel vial, it was shown that a two-phase mixture consisting of magnetite and a spinel solid solution (Cu_xFe_{3-x}O₄) yields the final product of the mechanical treatment of Cu-ferrite. This indicates that the high-energy milling of the oxide generates a complex series of solid-state transformations, including mechanochemical decomposition and reduction. In view of the fact that the milling is done in air, the appearance of reduced phases in an oxide matrix is a surprising experimental result. Although several mechanisms have been proposed for the reduction processes occurring during high-energy milling, to the best of our knowledge, no conclusive explanation for mechanically induced redox reactions has been given yet. Identification of the factors representing the main driving force for mechanically induced redox processes in complex oxides, the elucidation of the microscopic mechanism(s), and the determination of rate-determining steps of reduction therefore represent a major challenge for research in mechanochemistry and require further efforts.

In²¹⁾, the product of ball milling magnetite and amorphous silica (40-mole % Fe₃O₄ in SiO₂) for an extended period of time (800 h) in a closed vial was investigated by Mössbauer spectroscopy, X-ray diffraction and infrared spectroscopy. It was found that the milling induces an extensive reduction of Fe (III). The material constitutes a mixture of ultrafine Fe-rich spinel particles (magnetite/maghemite) and amorphous Fe (II)-containing silicate with a magnetic transition temperature of approximately 25K. The amorphous phase has a rather high Fe content and is distinctly different from the initial amorphous silica.

On the other hand, for example, the chemical activity of ammonium thiocyanate or the high hardness of boron resulted in wear to the steel material of the milling tools of the MR, the particles of abraded iron



entered into mechanochemical reactions with the treated mix of reagents²²⁻²⁵⁾, and the quartz and other mineral particles were modified by abrasion from iron compounds¹³⁻²¹⁾.

From these scattered reports it is evident that regular research of the participation of a material of milling tools in the course of mechanochemical reactions was not carried out. A novel strategy for their exploitation as an effective synthetic route will be described which will permit the preparation of fine materials for high-tech purposes²⁶⁾. The choice of focusing on abrasive-reactive materials is motivated by the possibility of synthesizing them via both gradual⁴⁾ and combustive⁵⁾ mechanochemical reactions starting from elemental powders. The prospect of their realization does not cause doubts. In a method offered by us of obtaining nanocomposite powders on a copper, graphite and diamond basis, only copper fittings will be used. As against the traditional realization of mechanochemical reactions in mixes of powders with the sizes of initial particles ~50 microns^{4,5,27,28}, the synthesis, for example, of nanocrystalline final products proceeds for hundreds of hours of MA²⁷, and owing to participation of the nanosized material resulting from the abrasive wear of milling tools, a significant reduction of this time could be expected. Recently begun intensive research of mechanochemical reactions with the participation of a material of milling tools not only confirmed this assumption, but also revealed many other advantages and prospects of their realization²⁹⁾.

Sometimes it is possible to select the material of the milling tools in such a way that the wear debris becomes a beneficial component of the intended product. We plan to carry this possibility to the extreme: We will develop a new technique called abrasive-reactive wear (ARW) that uses the material of the milling tools as a reactant that becomes a major component of the product, not just a tolerable impurity. This innovative new approach has not been considered by any other laboratory. It opens the door to applications of the ARW phenomenon to obtain nanocomposite powders and for carrying out the synthesis of chemical compounds, functional materials, and for processing mineral and man-made raw materials. It will be shown here how the wearing of milling tools could instead provide an alternative synthetic route to materials of technological interest ^{26,29} such as the Cu-diamond composites that possess a high thermal conductivity³⁰⁾.

We must note that throughout the world, there is currently no direction of research analogue to that pursued by us. From the viewpoint of its application for the preparation of new functional materials, the work will be innovative and useful. The probable scopes of the ARW method stated in the paper lead us to believe that it can find specific application in various areas of modern technical mineralogy and tribology.

2. Experimental

2.1 Planetary mills with steel fittings and MA

The relative velocity W of collisions between milling tools is given by the equation^{2,6,31-36)}

 $W = 2 \pi \omega_1 l_2 \left[(k+1)^2 + m^2 - 2m(k-1)\cos\varphi + (m+1)^2 \right]^{0.5}; \ W_n = W \sin\varphi; \ W_t = W \cos\varphi$ (1)

where $\cos \varphi = -(1+k)/m$ determines the angle of ball rebound from walls. The geometric factor $m = l_1/l_2$, where l_1 and l_2 are the radii of the carrier and drum, respectively; the kinematic factor $k = \omega_2/\omega_1$, where ω_2 and ω_1 are the number of revolutions of the drum and the opposite number of carrier revolutions, respectively. An analysis of the interaction of milling tools must be performed taking into account both the normal component W_n and the tangential component W_t of the W^{33} . W_n determines the conditions of the interaction of particles in the layer. W_t determines the conditions of abrasive wear and mechanochemical processes on the frictional contact between milling tools and treated particles.

For the mechanical treatment (the process time τ was varied over the range 5-240 min), we used:

- A three-drum planetary mill from "NPO Mekhanobr", the characteristics of the mill were^{33,34}:
- m = 2.3 ($l_1 = 11.5$ cm and $l_2 = 5.0$ cm); k = -1.7 ($\omega_2 = 20$ s⁻¹ and $\omega_1 = 11.7$ s⁻¹); $W \approx 1700$ cm/s, $W_n \approx 500$ cm/s, $W_t \approx 1600$ cm/s; the drum volume V = 450 cm³; and the working part of the surface of the drum $\Pi_d = \pi l_2(2h+l_2) \approx 250$ cm², where h = 5.5 cm is the drum height. The ball radius was R = 0.5 cm, their density $\rho = 7.8$ g/cm³, number N, and the totaled surface area $\Pi_b = 4 \pi R^2 N$.
- An AGO 2 water-cooled two-drum planetary mill with the characteristics^{25,35,36}: m = 1.7 ($l_1 = 5.3$ cm and $l_2 = 3.1$ cm); k = -2.4 ($\omega_2 = 29 \text{ s}^{-1}$ and $\omega_1 = 12 \text{ s}^{-1}$); $W \approx 1100$ cm/s, $W_n \approx 900$ cm/s, $W_t \approx 630$ cm/s; V =140 cm³, $\Pi_d \approx 150$ cm² (h = 4.6 cm); R = 0.2 cm. To provide more efficient processing, we used all four possible orientations of the mill axis: vertical, horizontal and $\pm 15^\circ$ to the latter in each case.
- An EI -2×150 two-drum planetary mill characterized by^{2,26)} m = 1.8 ($l_2 = 2.9$ cm), k = -1 ($\omega_2 = \omega_1 = 14$ s⁻¹), $\cos \varphi = 0$ and $W = W_n \approx 850$ cm/s, V

=150 cm³, $\Pi_d \approx 130 \text{ cm}^2$ (h = 5.6 cm); R = 0.2 cm.

The powdered mixtures had previously been ground and homogenized for 15-30 min in a Fritsch Pulverisette mill fitted with steel (a mortar of diameter 9.5 cm + 1 ball of diameter 5.2cm) or agate (9.2 cm and 7.1cm, respectively)^{37,38)} elements. We selected preparation of nanocomposites under various conditions of MA of the A (material of milling tools) -B (abrasive) and A-B-C (reagent) systems (e.g. iron-quartz; iron-diamond, iron-quartz-sulfur, ironquartz-graphite, copper-diamond-graphite, etc.) in a MR as an example of ARW, cf.³⁹⁾. The ratio between the weight of the treated substances $(M = M_A + M_B)$ +Mc) and the mass of the ball load (Mb) was varied. Let ρ_A , ρ_B , and ρ_c be the densities. The uniform selflining of milling tools (balls and inside drum walls) by a batch mixture layer occurs during MA^{2,40,41)}. The calculated lining thickness is^{12,34,39}

$$\delta = (\rho_B \rho_C M_A + \rho_A \rho_C M_B + \rho_A \rho_B M_C) / \rho_A \rho_B \rho_C (\Pi_d + \Pi_b) (1 - p)$$
(2)
$$\delta_C = M_C / \rho_C (\Pi_d + \Pi_b + \Pi_{A+B})$$
(3)

Here, the porosity of the lining *p* is taken to equal that of a close packing of differently sized spherical particles ($p \approx 1 - \pi/4$). In a number of cases, *C* – substance (e.g. graphite or sulfur), as the most plastic and pliable components, covers all metallic (*A*) and abrasive (*B*) surfaces with a continuous layer with a thickness calculated by Eq. (3), where the areas *A* and *B* particles are $\Pi_{A+B}^{39,42}$.

2.2 Product and process characterization

The initial mean particle size (R_0) was determined by optical microscopy (NU-2E) on parts of the starting homogenized specimens for MA, and was in the range 0.01-0.025cm. MA products were studied by the standard XRD, DTA, Mössbauer (MC1104EM), Raman (Dilor/OMARS), infrared (Satellite FTIR) and electron microscopy (JSM-6380 and LEO-1550) methods. MA amorphous samples were also isothermally annealed (2 h) in a flow of argon ($\sim 1 \text{ cm}^3/\text{s}$) in alundum crucibles with graphite plugs and titanium sponge placed upstream of the crucibles in the heated area of the quartz tube to remove the possible oxygen impurity from argon using a new heating stage for high-temperature (up to 1600° C) investigations⁴³. The degree of grinding was determined by the thermal desorption of argon with additional disaggregation^{15,34)}. Possible iron forms in some specimens (e.g. in quartz particles) were determined by acid etching of the material according to³³⁾. Washed samples were studied by routine analysis methods. ARW kinetics was studied by two methods: weight, with accurate



measurement of drum weight and ball loading before and after experiments not less than 0.01 g; and volumetric in the case of diamond-containing MA products, on reaction of samples with an acid.

3. Results and Discussions

3.1 ARW processes caused by the MA of quartz

One of the purposes of this work was to study the influence of the material of milling tools on the MA of quartz in MRs with steel fittings. We selected these objects of study because MA quartz and mixtures based on it exhibit ferromagnetic properties and are distinguished by good sorption ability toward organic substances, the synthesized sorbents were used to collect petroleum spill over water, high water purification, etc.^{44,45)}. A ball mill from "NPO Mekhanobr" was used, the ratio between the weight of ball loading M_b to that of quartz M was set equal to 4 at $M_b + M = 480$ + 120 = 600 g. The number of balls N = 120, and the totaled surface area $\Pi_b = \approx 370 \text{cm}^2$. According to Eq. (1), abrasion conditions should be given preference over impact conditions for this mill. In several control tests (Fig. 1), we also used an AGO-2 mill and fused quartz (from the standpoint of interpretation of XRD data, amorphous materials are the most suitable abrasive components). It follows from³³⁾ that ~90% of iron is present in guartz in an acid-soluble (metallic and magnetic) form.

The total wear of steel mill fittings can amount to ~5% (~7 g), and the dependence of the amount of worn iron on the time of processing is not linear (**Fig. 2**). The deviation from linearity is caused by the self-lining of milling tools to a degree that increases as the specific surface area of the material under



Fig. 1 X-ray pattern of fused quartz (3 g) processed for 12 min in an AGO-2 mill (number of balls N = 400). The size of worn particles for a material of milling tool ~10 nm^{33,34}.



Fig. 2 ARW kinetics under MA of quartz in "Mekhanobr" mill by expression $K \times \tau^n = 1.8 \times \tau^{0.23}$ is described in⁴⁶).

processing grows^{33,46)}. This partially protects milling tools from wear.

Temperature and pressure pulses^{2,3,7)} favor the occurrence of chemical reactions involving the material of milling tools, substance being processed, and medium^{33,34)}. As the reaction between Fe and SiO₂ is forbidden, we consider the possibility of steel oxidation by air; the drums of our mill did not have vacuum gaskets, and processing occurred under air access conditions, as distinguished from control tests with the AGO-2. As a result of abrasive and oxidative wear, Fe and FeO are formed as nanoscale particles and should be adsorbed on much larger quartz particles.



On the other hand, part of the surface layer of quartz particles subjected to MA becomes amorphous (**Fig. 3**). The mechanism of the transition to the amorphous state and the thickness of the amorphous layer have long been the subject of discussions^{1,33,34)}. The question of the form in which iron is contained in activated quartz particles is the most interesting one. For this reason, along with modeling, we used the most informative methods for quartz studying, namely Mössbauer and infrared spectroscopy.

MA samples washed to remove the elemental iron only contain quartz particles with a very insignificant iron content in an acid-insoluble form (up to ~0.6% or ~0.75 g based on iron). It follows that acid-insoluble³³ iron silicates formed during processing approximately in an amount of 2 g can only occur on the surface of quartz particles. The estimated mean thickness of this layer is ~1 nm³⁴.

The Mössbauer spectra, **Fig. 4** (see also infrared, **Fig. 5**), of iron atoms in iron oxides are characteristic sextets resulting from the magnetic splitting of nucleus levels.

Our samples give additional lines, which are evidence of changes in the character of bonds between iron atoms and their environment. A quadrupole doublet, whose hyperfine coupling parameters show that iron occupies two nonequivalent sites in the quartz lattice, describes the internal part of the spectrum. For the first doublet, the isomeric shift and quadrupole splitting parameters show that iron Fe^{3+} ions have an octahedral oxygen environment characteristic of iron oxides in the super paramagnetic state.



Fig. 3 Electron micrograph of the quartz particles after MA: general view (left); separate particle (right).





Fig. 4 Mössbauer spectra of MA quartz particles processed 30 (left) and 90 (right) minutes.



Fig. 5 Infrared spectroscopy of the MA quartz.

The hyperfine coupling parameters of the second doublet can be attributed to Fe^{2+} ions in the high-spin state. The population of these two sites by iron ions depends on the duration of MA, and the presence of such iron forms in quartz can only be explained by the formation of iron silicates. The infrared spectra of the initial quartz samples and MA samples for 15 min indirectly substantiate the formation of iron silicates. There were no differences between the Si – O – Si and O – Si – O bands in the spectra of different samples. However, a band at ~833cm⁻¹ appeared in the MA sample; this band was assigned to the Si – O – Fe bond in³³⁾.

At high temperatures³⁴⁾, the formation of iron metasilicate (FeO + $SiO_2 = FeSiO_3$) in the FeO - SiO_2 system is more favorable thermodynamically and

kinetically than the formation of iron orthosilicate $(2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4)$, because the reaction occurs in the presence of excess quartz. As a separate phase of iron silicates is not observed, they can only occur in the amorphous layer on activated quartz particles. The empirical mean thickness of the layer of iron silicates on the surface of quartz particles if iron silicates are distributed uniformly is ~2 nm³³.

3.2 ARW in abrasive – graphite/sulfur systems

Extending the ARW method is of particular interest as regards the use of carbon^{26,35)}, in particular graphite³⁷⁾, and sulfur³⁸⁾, which have unique physicochemical and mechanical properties^{29,36,47)}. Carbon and sulfur in ARW can open up a new line in making nanocomposite materials on a carbide^{4,19,24,25,31)} or



sulfide^{1,5,8,9,14,15,27,28,39} basis. This method can also be successfully used in the utilization of dust formed in decarbonization and desulfurization of the coke-oven gas formed in the coke and by-product industries³⁷. The accumulation of sulfur at oil refineries and plants processing natural gas also makes its utilization a matter of current interest.

Cementite (Fe₃C) is commonly obtained by the MA of mixtures of iron and carbon powders, with subsequent thermal or arc-plasma processing of the MA products^{48,49)}. Sulfides are, as a rule, obtained from elements on MA and heating^{5,8,9,27,28)}. However, the morphology and the homogeneity of the target products are not always of the required level. It depends on a number of factors and, in particular, on the area and state of the surface of the starting reagents. The use of MR eliminates these drawbacks. At present, iron sulfides, especially those of nanosize^{8,9,27,28)}, are applied in power cells with a high energy density, in photoelectrolysis and solar power engineering, and in the synthesis of superconducting, diagnostic and luminescent materials and chalcogenide glasses.

The results of the simulation of mechanochemical reactions involving sulfur⁴²⁾ show that the most important process for the synthesis of sulfides, e.g., ZnS^{50} , is the plastic flow of sulfur. The heat pulse in the shock displacement of molten sulfur is determined by the thickness of layers on the surface of Zn particles lined with softer sulfur. The thinner this layer, the higher the temperature and the faster the amorphization of sulfur (polymerization with a transition to the glassy state). However, the occurrence of this process has not been confirmed experimentally. Therefore, to substantiate the theory⁴²⁾, it was necessary to choose a system for MA that would contain an inert amorphous component alongside crystalline sulfur. Ordinary glass and fused silica are suitable for this purpose. Confirmation of the mechanochemical polymerization of sulfur is also the goal of this study. The MA was performed in an AGO-2 mill (N = 400, $\Pi_b \approx 200 \text{cm}^2$). Graphite or sulfur were introduced in amounts of 0.3-1.6 g into a crushed amorphous (slide glass or fused silica) or crystalline (quartz) abrasive taken in an amount of 3.0 g. The annealing temperatures chosen were considerably lower than the temperature of cementite formation³⁶⁾, i.e. were equal to $660 \pm 5^{\circ}$ C and $960 \pm 10^{\circ}$ C.

The XRD patterns of the system constituted by fused quartz and graphite after MA is shown in **Fig. 6a**. It indicates an amorphization of graphite and wear of steel milling tools, see **Fig. 1**.

In the course of MA of the system with α –SiO₂, quartz reflections are preserved, but with significant broadening and decrease in intensity compared with the initial homogenized sample. Wear of steel grinding tools also occurs (see a fragment of the spectrum



Fig. 6 XRD patterns of the system constituted by quartz (3g) and graphite (1.5g).
(a) Fused quartz, MA duration (τ) 90 min;
(b) α - Quartz, MA duration 90 min;

(c) Annealing of MA sample (a) for 2 h in argon at $960^\circ\!\!\mathrm{C}$.

in **Fig. 6b** at $2\Theta = 44.68^{\circ}$).

In both low- (660 $^{\circ}$ C) and high-temperature (960 $^{\circ}$ C, Fig. 6c) annealing, cementite crystallizes (PDF 75-910) from the amorphous phase. However, the degree of cementite crystallization from the amorphous phase for samples annealed at 660°C is lower than that for the samples annealed at 960°C. The presence of residual nanoscale iron particles in the samples (Fig. 1) is confirmed by the following: the peak of cementite at $2\Theta = 44.72^{\circ}$ overlaps the base reflection of α – Fe, but not its reflection at $2\Theta = 82.4^{\circ}2-82.5^{\circ}$. In annealing, a partial crystallization of graphite also occurs (halo at $2\Theta = 26^{\circ}$ in Fig. 6). Similar results were obtained for the system with quartz. It can be stated that the nanocomposite $Fe - Fe_3C - C - SiO_2$ is formed in the course of the MA of quartz-graphite systems.

Experiments on the MA of sulfur crystals (weighed portion 2 g) only were carried out under identical conditions. The XRD data for samples of MA sulfur (MA duration of up to 180 min) show that no structural transformations in sulfur take place [38]. All the reflections are preserved without any appreciable change in their shape and relative intensity (PDF 83-2285), except for the absence of a halo associated with the presence of amorphous particles of fused quartz or glass. The situation changes (**Fig. 7a**) when sulfur is treated in the presence of inert glass particles.



Fig. 7 XRD patterns of systems with sulfur.
(a) Glass (3g) and sulfur (0.4 g), τ = 135min;
(b) Fused quartz (3g) and sulfur (1.6g), τ = 135min.



Fundamental changes occur in the MA of samples based on fused quartz: Pyrite is formed (FeS₂, PDF 71-2219; **Fig. 7b**). The hardness of quartz particles is considerably higher than that of steel, and its softenning point substantially exceeds that of glass. In this case, amorphization of sulfur (absence of reflections of excess surfur in **Fig. 7b**) and its chemical reaction with iron nanoparticles (which have already appeared in a significant amount as a result of the ARW of steel accessories) to form pyrite FeS₂ occur simultaneously. The formation of just FeS₂ is due to the excess of sulfur in the MA samples.

Using the method^{4,27)} and the XRD data, we also calculated the sizes of crystal blocks and the extents of distortion in the structure of the resulting pyrite (and Fe particles). The parameters of fine crystal structure were calculated from the half widths of the diffraction peaks (220) and (440), which are commonly associated with FeS₂⁴⁷⁾. To determine the instrumental broadening, we used the profile of lines of crystalline FeS₂. The resulting size of blocks in FeS₂ was about 24 nm (~10 nm for iron particles), and the extent of distortion 1%. Similar results were obtained in²⁷⁾, but after more than 110 h of MA of a 1:2 mixture of powders of Fe (starting particle size ~0.05cm) and S.

We determined the ARW kinetics (**Fig. 8**) and the following absolute (g) and relative (%) values of wear of the material of the steel milling tools, i.e. drum (*D*) and balls (*B*), for the systems under study³⁶.

- (i) Fused SiO₂ (3g) and C (1.5g), τ =90min, D (0.63g or 0.077%), B (0.52g or 0.5%), ARW = 1.15g.
- (ii) α -quartz (3g) and C (1.5g), τ =60min, D (0.23g or 0.027%), B (0.25g or 0.26%), ARW = 0.48g.



Fig. 8 ARW kinetics under MA in an AGO-2 mill of systems: (1) fused quartz-graphite, $0.26 \times \tau^{0.33}$; (2) quartz-graphite, $0.091 \times \tau^{0.37}$; (3) fused quartz-sulfur, $0.005 \times \tau$.



- (iii) Fused SiO₂ (3g) and S (1.6g), 135 min, D (0.21g or 0.028%), B (0.47g or 0.49%), ARW = 0.68 g.
- (iv) Glass (3g) and S (1.6g), 135min, D (0.03g or 0.004%) and B (0.043g or 0.05%), ARW = 0.073g.

We note that the experiment gives higher ARW characteristics for fused silica compared with quartz.

Let us assume that the nanoscale particles formed upon ARW are completely consumed for formation of the phase Fe₃C or FeS₂ by the reaction 3Fe + C =Fe₃C or Fe + 2S = FeS₂. Then we would have the following composition of MA products: Fe₃C (1.23g), C (1.42g), and fused quartz (3g); Fe₃C (0.51g), C (1.46 g), and quartz (3g); and FeS₂ (1.46g), S (0.82g), and fused quartz (3g).

3.3 ARW processes caused by the MA of diamond

From the point of view of enhancing the possibilities of the ARW method, the use of diamond is of special interest owing to its unique mechanical and abrasive properties³⁵⁾ and ability to interact with transitional metals and alloys, i.e., a combination of properties of both abrasives and reagents. It should also be noted that mechanochemical synthesis could in the future provide a more efficient utilization of both natural and synthetic diamonds as the result of introducing the low-grade raw material into the technological process. This section is devoted to the study of the influence of the MA of diamond on the synthesis of cohenite (Fe,Ni)₃C, which is a very rare but well-described⁵¹⁾ mineral. It exists in two forms (Pbnm, PDF 23-1113; Pnma, PDF 35-772). Generally, this mineral has a man-made or extraterrestrial origin³⁵⁾. Its synthetic analogue in the *P*_{bnm} structure is cement-



Fig. 9 ARW kinetics under MA of systems: (1) copper-diamond-graphite (MA in an EI – 2×150mill), 0.23×τ^{0.64}; (2) diamond charge 2.85 g (MA in an AGO-2), 0.0135×τ; (3) 1.75g (MA in an AGO-2), 0.0097×τ.

ite (Fe₃C).

The diamond used in the experiments was obtained in the (Fe,Ni) – C system on a multianvil highpressure split-sphere apparatus at 6 GPa and 1500°C ^{52,53)}. Polycrystalline diamond aggregates left as byproducts in prolonged experiments⁵³⁾ with the growth of coarse diamond monocrystals are used. The obtained powder, with a particle size of ~0.011cm, was treated with a heated mixture of nitric and hydrochloric acids to remove impurities. MA of the diamond was conducted in an AGO-2 mill with N = 400 for M = 2.85g and N = 150 for M = 1.75g.

We determined the ARW kinetics, see **Fig. 9** (straight lines 2, 3) and **Fig. 10a**, and the next values of wear of the material of milling tools, i.e. drum (*D*) and balls (*B*), for the systems under study³⁵:



Fig. 10 XRD patterns illustrating the phase composition: (a) Dynamics of the abrasive wear of the steel milling tools during the diamond MA (M = 1.75 g); (b, c) after the diamond MA (1.75g) for 2 h with subsequent annealing for 2 h in the Ar atmosphere at 660 and 960°C, respectively.





Fig. 11 ARW kinetics under MA in an AGO-2 mill: (1) tenorite, $0.53 \times \tau^{0.17}$; (2) galena, $0.0070 \times \tau$.



Fig. 12 ARW under MA of ilmenite in "Mekhanobr" mill: 1(C), $0.038 \times \tau^{0.73}$; 2(B), $0.083 \times \tau$; 3(A), $0.078 \times \tau$.

MA of diamond (2.85g) for 2 h: *D* 0.42g (0.051%), *B* 1.20g (1.22%), and ARW(total wear) = 1.62g; MA of diamond (1.75g) for 2 h: *D* 0.53g (0.064%), *B* 0.63g (1.65%), and ARW(total wear) = 1.16g.

Fig. 3a shows a change in the XRD data for the fused quartz-graphite system after the MA. Doublet reflections of diamond at $2\Theta = 43.94^{\circ}$ and 75.30° (see PDF 75-623) persist during its MA, but their intensity significantly decreases relative to those of the initial sample. The steel milling tools are also worn (**Fig. 10a**). As can be seen from the XRD patterns of samples of the MA diamond after annealing (**Figs. 10 b**, **c**), cementite (see PDF 75-910) is crystallized from the amorphous phase during both the low- and high-temperature annealing. The cementite reflection at $2\Theta = 43.85^{\circ}$ overlaps the basic reflection of diamond. The inadequacy of the intensity of this line and pres-

ence of the second diamond doublet reflection at 2Θ = 75.30° indicate the presence of residual diamond crystals in the annealed samples. Hence, the MA of diamond can produce the Fe – Fe3C – diamond composite.

If we admit that the particles produced by the ARW are entirely expended in the generation of the amorphous cementite phase, we would have the following composition of the MA products:

After the MA of diamond: cementite 1.24g and diamond 1.667g (for a diamond sample of 1.75g);

cementite 1.74 g and diamond 2.734 g (for a diamond sample of M = 2.85 g).

3.3.1 ARW in copper-diamond-graphite system

The MA of copper-diamond-graphite mix was carried out in an EI -2×150 milling⁴⁶⁾. Initial weight of the drum $M_d = 953.65$ g, ball charge $M_b = 109.056$ g (R = 0.2 cm, N = 400). The following powdered sample was subjected to MA (MA time τ varied up to $\tau =$ 60min): diamond (1.3g)-copper (1.3g)- graphite (1.3 g). After the experiment, the weight of the drum was $M_d^* = 952.76$ g, the difference being $M_d - M_d^* = 0.89$ g. The weight of the ball charge was $M_b^* = 106.78$ g the difference being $M_b - M_b^* = 2.27$ g. The total wear of the steel material of the EI -2×150 milling tools appeared equal $m^* = 0.89 + 2.27 = 3.166$ g, i.e. close to the weight of the initial charge. The ARW kinetics for this system is presented by curve 1 in **Fig. 9**.

XRD data show that the MA product represents a composite powder containing besides initial components (Cu, diamond, C) of the mix (graphite becomes amorphous and reacts with iron, forming cementite Fe₃C^{35,36)}), some nanoparticles of Fe and Fe₃C of ARW. Annealing this product in an argon atmosphere at 600°C and 900°C does not result in the formation of new phases, but rather only the ordering of lattices of mix components. As expected, annealing the MA product during DTA on air up to 1030°C results in the burning-out of carbon and the formation of an appropriate mix of copper and iron oxides.

A specific example of a property of technological relevance that characterizes materials prepared by techniques studied in the present paper is the heat conductivity. Linked to this, the problem of heat removal is very important for the semiconductor industry. For this reason, the improvement of thermal properties of materials used for manufacturing microelectronic components becomes crucial^{30,54}. The "ADS" company offered nanocomposite materials on a Cu and diamond basis that have a higher heat conductivity in comparison with traditionally used





Fig. 13 Process of production (Picture 1a) and description of Cu-C sample (Picture 1b).





Fig. 14 X-ray phase analysis of the product of mechanical activation of diamond (weight 3g) for 210 min in an $EI - 2 \times 150$ mill with Cu fittings.



Fig. 16 Results of processing the XRD data on Cu reflections by the Williamson-Hall method.

materials on a Cu or Al basis. Moreover, particles of diamond in copper-diamond composites show a high degree of stability to graphitization under sintering at temperatures up to 1150-1250K, and thus this composite material can be used for the creation of contacts and high-current electric contacts in the low-voltage equipment⁵⁵⁾.

In order to prepare such nanocomposites, the method based on ARW by MA in MRs (with cupric milling tools) using particles of substandard diamonds appears interesting and very able to replace various labor- and power-consuming processes, see **Fig. 13-17** and details in²⁶.

After the MA of diamond and diamond-graphite mixture (1:1), the XRD data virtually did not differ under identical measurement conditions (**Fig. 14**): the MA of both samples does not produce carbon and copper compounds, see also **Fig. 17**. Analysis of MA samples in atmosphere by the DTA method (thermo-gravimetry - TGA, heating rate 10°C/min) yielded important information (**Fig. 15**). The TGA data can



Fig. 15 TGA of the diamond (1.5g) – graphite (1.5g) system in the atmosphere (210 min, EI – 2×150 mill).



Fig. 17 Raman spectrum of the MA copper – diamond – graphite sample. The line of 1334 cm⁻¹ corresponds to diamond.

be used to decipher constituents of composites. For example, based on the TGA, the composite in sample 2 contains 24% carbon (7.3% amorphous carbon and 16.7% diamond). Hence, the Cu content should be 76%, which is very close to the weight analysis data. In order to determine characteristics of the state of copper in the MA powder samples, we processed the XRD data using the Williamson-Hall plot (**Fig. 15**): copper-diamond system (D₁≈26nm, ε_1 =0.43%); copper-diamond-graphite system (D₂≈30nm, ε_2 =0.39%). Based on the high-resolution SEM data, the relatively large agglomerates of particles have the cauliflowerlike internal structure with block dimension similar to certain dimensions of Cu crystallites.

3.4 ARW in abrasive-mineral systems

Recently, a high increase has been observed for the research processing of geological materials in MRs⁵⁶⁻⁵⁸⁾. Of specific interest for extending the potential of the ARW method is also the processing of mineral and technological raw materials^{29,33,37,47,59,60)}.

MA of quartz mixes with tenorite (CuO) or galena (PbS) was carried out with the purpose of their reductive processing by iron of the milling tools to obtain copper- or lead-containing composites^{33,59}. Tenorite or galena was introduced in amounts of 1.5 g into a crushed fused silica abrasive in an amount of 3.0g. MA time τ in an AGO-2 mill (N = 400) varied from 15 to 210 min. ARW at 60 min in the investigated systems amounted to about 1 g (Fig. 11). MA of ilmenite (FeTiO₃) concentrate and its mixes with coke were carried out with the purpose of concentrate reduction to obtain iron and coke, rutile and/or anatase⁵⁸⁾. Conditions of MA in a "Mekhanobr" mill were the following: (A) relation $M_b/M = 2$ at $M_b + M$ = 166.67 + 83.33 = 250g; (B) $M_b/M = 4$, $M_b + M =$ 200+50 = 250g; (C) $M_b/(M+M_k) = 4$ at $M_b + M + M_k =$ 200 + 42.5 + 7.5 = 250g, where M_k - weight of coke. MA time varied from 15 to 90 min. ARW curves are shown in Fig. 12.

The initial tenorite was obtained by the thermal



Fig. 18 XRD patterns of the system constituted by fused silica (3g) and tenorite (1.5g). (a) Initial tenorite (cf. PDF 48-1548 and 80-1917); (b) MA duration 60 min; and (c) MA duration 60 min, annealing for 2 h in argon at 700°C (PDF 4-836 for copper).



decomposition of malachite at ~ 250° C over the course of 7 h. XRD spectra of this black powder are shown in Fig. 18a. The XRD spectrum of the starting sample, based on galena, is shown in Fig. 19a. It indicates the presence of not only galena, but also some admixtures (mainly quartz) commonly contained in this mineral. Preliminary experiments demonstrated that the MA involving tenorite and galena shows both similarity and significant differences. In both of the systems, ARW occurs to the steel milling tools, which is more pronounced in the system with galena. Even a short-term (5-15 min) MA of the system with tenorite (Figs. 11, 18) results in a self-lining of the milling tools with the material being processed. Tenorite starts to change color to green after 1 h of MA, and this color, as well as the self-lining, is preserved and becomes more intense in the course of MA. By contrast, the self-lining phenomenon is completely absent in the system with galena (Figs. 11, 19), and, after a short time of MA, a black homogeneous "oily"



Fig. 19 XRD patterns of the system constituted by fused silica (3g) and galenite (1.5g). (a) Initial mixture (PDF 1-880); (b) MA duration 60 min (PDF 4-686 and 6-696); (c) MA duration 210 min.



powder of a composite material is formed.

The results obtained in studying the products of MA of the systems under study by XRD and isothermal annealing methods indicate the occurrence of various processes. These are the abrasive wear of steel milling tools, amorphization, and reduction of copper from tenorite and lead from galena. There are no crystalline phases of other products (iron oxides and sulfides) of reduction reactions, e.g. CuO + Fe = Cu + FeO ($\Delta_r G^\circ = -28.0$ kcal/mol).

Fig. 18b indicates that an X-ray-amorphous product is formed in the system with tenorite and iron wear occurs (peak at $44^{\circ}-45^{\circ}$). The degree of amorphization increases as the processing duration becomes longer, even the Fe peak is broadened. Metallic copper is the only product formed during annealing of this sample at ~700°C : reflections of all other products that can be formed in the exchange reaction, namely iron oxides, are completely absent (Fig. 18c).

Fig. 19b illustrates a similar phenomenon of abrasive wear of Fe and reduction of galena by this iron, which occurs in this case directly during the course of MA. It should be noted here that there are no reflections of other possible products of the reduction-exchange reaction, namely iron sulfides. If the MA duration is raised to 120 min, the spectrum remains virtually unchanged: only the reflections of the α – SiO₂ admixture in natural galena disappear (because of amorphization). Annealing of these products does not change the situation either: only the relative intensities change insignificantly and the corresponding reflections become considerably narrower. If the MA duration is increased further, abrasive wear of Fe starts to prevail over all other processes (**Fig. 19c**).

The data obtained confirm that the self-lining of milling tools prevents their abrasive wear and, consequently, hinders the reduction reaction of tenorite with the material of milling tools in the course of MA. By contrast, the complete absence of self-lining of milling tools in the system with galena results in a fast breakdown of galena by iron formed in the abrasive wearing of milling tools.

It is difficult to give an unambiguous interpretation of the fact that those reflections of iron oxides or sulfides disappear after the reductive breakdown of tenorite or galena without thoroughly studying the MA of quartz with the material of steel milling tools³³⁾. The results of ³³⁾ suggest that the surface of quartz particles can be modified not only by amorphous iron silicates (after annealing of MA tenorite samples), but also by iron sulfides after the MA of galena together with fused quartz particles. In the case of galena, a nanosize surface layer on quartz particles must be formed of a certain amorphous compound of the system $Fe_xS_y - SiO_2$. An even more complex compound of green color, which is formed upon the MA of tenorite and which contains nanosize particles produced by abrasive wear of the steel accessories (**Fig. 18b**), is the amorphous compound $Cu_xFe_yO_z - SiO_2$ on the surface of quartz particles.

The following aspect is associated with dimensional effects. In the case of the conventional MA reduction of, e.g. copper sulfides^{1,28)} with metallic Fe powders with an initial particle size of about 0.05 cm, the duration of MA is tens of hours. In the new ARW method of breakdown of, e.g. galena⁵⁹⁾, suggested here, the size of initial particles formed during the abrasive wear of Fe is close to 10 nm (Fig. 1), which is several orders of magnitude shorter than that in the conventional mechanochemical exchange reaction. Therefore, the rate of the breakdown reaction involving the material of steel milling tools is also higher and, consequently, the time of the MA breakdown of minerals becomes shorter. The XRD data were used to calculate by the known method^{4,27,61)} the structure of crystalline blocks in metal particles obtained in the course of MA in the system with galena. The parameters of the fine crystal structure were calculated from the half width of diffraction peaks (Figs. 19b, c) for an MA duration of 60, 210, and 120 min (XRD spectrum is not shown). To determine the instrumental broadening of the lines, we used the profiles of the corresponding reflections after the annealing of these samples. The resulting size of Pbblocks was (nm): 83 (MA, 60 min), 61 (MA, 120 min), and 46 (MA, 210 min); the corresponding data for particles formed during the wear of Fe were 24, 19, and 12 nm.

Thus, we obtained metal-oxide/sulfide nanocomposite powders based on the quartz matrix in the course of the MA of minerals mixed with an abrasive in an AGO-2 mill with steel accessories.

4. Kinetics and Simulation of ARW

Determination of the ARW kinetic laws of MR milling tools in the MA process of various substances and systems with an abrasive component is of current interest and comes out to the foreground. ARW kinetics was studied by two methods: weight, with an accuracy of measurement of the drum and ball loading weights before and after experiments of not less than 0.01g; volumetric (on hydrogen for diamond-



containing MA products), in reaction of samples with HCl. Data on ARW kinetics in the MA process of the following kinds of mineral raw materials into nano-composite powders were obtained⁴⁶.

Fig. 2 - quartz (preparation of a magnetic composite^{18,33,34,44,45)}). MA time varied from 5 to 90 minutes. The size of wear at 5 min, ARW in grams, came to 1.43, and at 90 min ARW = 5.14g. The self-lining phenomenon of the surfaces of milling tools by MA quartz is observed.

Fig. 8 - mixes of quartz and fused quartz with graphite or sulfur (preparation of cementite- or pyrite-bearing composites^{36,38}). MA of the system with graphite results in a self-lining of the milling tools. By contrast, the self-lining phenomenon is completely absent in the system with sulfur.

Fig. 9 - diamond (to obtain cohenite³⁵⁾) and a powder mix of diamond, graphite, and copper (to obtain high-heat-conducting composite materials^{26,30)}). During diamond MA, a self-lining of the milling tools is barely visible. During the mix MA, the self-lining takes place.

Fig. 11 - mixes of fused quartz with tenorite or galena (preparation of copper- or lead-bearing composites^{1,14,15,33,59}). MA of the system with tenorite results in a self-lining of the milling tools. By contrast, the self-lining phenomenon is completely absent in the system with galena.

Fig. 12 - ilmenite concentrate of the arm filters of titanium-magnesium manufacture and mixes of concentrate with coke (for reduction of concentrate to obtain iron, rutile and anatase⁶⁰). The appreciable self-lining of milling tools' surfaces by MA materials was only observed in case (C).

The linear law of ARW growth with MA time τ in the absence of a self-lining phenomenon is established and the ARW power law in the presence of the self-lining with an exponent less then unity. Mathematical processing of measured ARW(τ) values in various mills and MA systems gives the following empirical dependence: ARW (g) = $K \times \tau^n$, where K is a rate constant of ARW, and n is an exponent⁴⁶. We see that both a rate constant (K, from 0.0050g/min for MA system sulfur-fused quartz up to 1.8g/min^{0.23} for quartz MA) and an exponent (n, from 0.17 for MA tenorite up to 1 for systems in which the self-lining does not take place) vary in sufficiently wide numerical intervals. It is evident from an example of the MA of diamond and ilmenite that K depends on the MA conditions (n = 1). For diamond K = 0.0135g/min at M = 2.85g and number of balls N = 400, K = 0.0097g/min at M = 1.75g and N = 150. For ilmenite K =

0.0078g/min at $M/M_b = 0.5$, and K = 0.0083g/min at $M/M_b = 0.25$.

Under identical MA conditions, the *K* and *n* values essentially depend not only on the specificity of chemical reactions but also on a phase state of an abrasive. For tenorite K = 0.53g/min and n = 0.17, for galena K = 0.007g/min and n = 1. For a mix of graphite with quartz K = 0.091g/min and n = 0.37, for a mix of graphite with fused quartz K = 0.26 g/minⁿ and n = 0.33. For a mix of sulfur with fused quartz K = 0.005g/minⁿ and n = 1.

As regards the problem of ARW simulation, in our opinion, it necessary to discuss the approaches to this problem recently proposed in^{48,62}. In these works, the authors considered the athermic (diffusion⁴⁸⁾ and deformation⁶²⁾) mechanisms of the formation of cementite (Fe₃C) upon MA of an iron and carbon powder mixture. Note that the role of local heating due to the impact-friction interactions in the course of MA² was ignored completely. This contradicts the practice of mankind³⁶⁾ throughout the ages, which has been aimed either at decreasing the heating of materials upon their mechanical treatment or at using a released heat, including the primitive ways of making fire. The modeling of the MA process associated with the development of short pressure or temperature pulses or the so-called t-P-T conditions^{2,3,7)} is based on the rigorous thermodynamic basis. In our opinion, this basis can be complemented by invoking diffusion and deformation processes, but cannot under any circumstances can be replaced by them. Details of ARW simulation with the account of the *t*-*P*-*T* conditions both on contact with the treated particles and on contact with the milling tools are given in^{12,34-36,42,61}

5. Conclusion

The study performed demonstrated that the steel material of milling tools can be involved in a direct breakdown of minerals and synthesis of nanocomposites under utilization of the abrasive properties of diamond and different boron and quartz modifications. The chemical interaction between the material of milling tools and the substance being processed was simulated numerically for the example of quartz processing in a planetary ball mill. It was shown that quartz processing resulted in the synthesis of iron silicates from silica and iron oxides. Nanoscale iron and iron oxide particles were formed as a result of the abrasive-reactive wear of steel mill fittings by quartz particles. The estimated thickness of the layer


of silicates on the surface of quartz particles was ~2 nm. The mechanical activation of mixtures of quartz (or diamond) and reagents (copper, graphite, sulfur, tenorite and galena) yielded nanocomposites in a time one to two orders of magnitude shorter than that in the case of the mechanical activation of mixtures of iron powders with the reagents. We have substantiated a new field of low-grade diamond utilization, namely an abrasive-reactive synthesis based on the material of the milling tools of mechanochemical reactors. A scrap of any metal and ceramic product can be used as milling tools, which makes it possible to considerably extend the potential of the abrasivereactive wear method and the range of treated compounds. The kinetics and mechanism of abrasivereactive wear of steel milling tools in the planetary mills were investigated experimentally and modeled numerically under defined conditions of mechanical activation.

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Aggregate Structure Evolution for Size-Dependent Aggregation by Means of Monte Carlo Simulations[†]

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Abstract

Aggregation during crystallization and precipitation processes often leads to complex-shaped particle aggregates. As an alternative to low-dimensional deterministic population balance models, where assumptions on the particle shape must be made, stochastic or so-called Monte Carlo methods can be employed. In previous work a hierarchical characterization of aggregates has been proposed (Briesen, AIChE J., 52, 2436-2446, 2006), which allows the use of different levels of detail for modelling the different rate processes as primary particle growth or particle aggregation. With that hierarchical characterization, the detailed geometry of aggregates becomes accessible for rate process modelling and product characterization. Here, this framework is extended to investigate size-dependent collision rates and aggregation efficiencies. The results show that the aggregate structures can be modelled by the interplay of shear rate and the growth rate at the particle necks in a mechanistic way. Future work will address the comparison with experimental data and alternative model formulations.

Keywords: Stochastic modelling, Population balance, Crystallization, Precipitation

Introduction

Aggregation during crystallization and precipitation processes often leads to complex-shaped particle aggregates. Even though the primary particle shape and aggregate structure affect downstream processing properties such as filterability, flowability or mechanical stability, the detailed shape is rarely considered. The actual shape is often so complex that a detailed modelling which accounts for the explicit shape is infeasible due to the associated computational effort. To avoid this effort, one-dimensional population balance formulations may be used (e.g.¹⁾). There, the particles are typically characterized by one single characteristic size. However, the aggregates and their behaviour can hardly be described by only one characteristic length. If the dimensionality is extended, size and shape descriptors can be used as inner coordinates. But even then, a rigorous characterization of complex-shaped aggregates is limited. Additionally, the consistent formulation of rate expressions for multivariate formulations of the population balance equation becomes very tedious.

As an alternative to deterministic population balance models, stochastic or so-called Monte Carlo methods have gained increasing popularity for the simulation of particulate processes²⁻⁶⁾. There, the evolution of a set of representative, discrete particles is tracked. The interaction of the particles is realized by means of probabilistically selected events. Monte Carlo methods feature three principal advantages: Simplicity of implementation, capability of dealing with high-dimensional problems and ease of representing complex behaviour. Monte Carlo methods are highly promising as the dimensional restrictions of deterministic population balance modelling are a major obstacle to the mechanistic modelling of particulate processes. Despite these principal advantages,

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Monte Carlo methods are not yet commonly employed because of their usually high computational requirements. Nevertheless, the use of Monte Carlo methods seems to be a logical consequence especially in the light of unprecedented and ever increasing computational power.

Stochastic methods have frequently been used to investigate the behaviour of fractal aggregates. Based on the pioneering work by Witten and Sander⁷ as well as Meakin⁸, many studies along these lines have appeared in the literature in which the mechanisms are categorized in diffusion-limited, reaction-limited or ballistic cluster aggregation. All these mechanisms lead to different fractal dimensions that provide information on the openness of the aggregates. However, this fractal structure only becomes evident if a very large number of primary particles per aggregate is considered. Here, the number of primary particles per aggregate is too low to characterize the aggregates by a fractal dimension only. Therefore, the detailed structure of the aggregates must be reflected in the characterization to permit appropriate modelling.

The implementation of Monte Carlo schemes for solving population dynamics problems is straightforward and far less restricted in the dimensionality of particle characterization. However, their accuracy is of course limited by the number of particles considered in the discrete set. As the particle number has to be large to achieve a satisfactory accuracy, computation of the single steps in the Monte Carlo algorithm has to be as efficient as possible. Although the geometric operations involved to perform an aggregation event for complex-shaped particles are possible in principle, the consideration of a large set of these particles makes this fully detailed approach prohibitive.

Instead, ways of reducing the complexity of the systems characterization need to be found. In previous work⁹, the author has presented a hierarchical particle characterization which uses different levels of detail for representing the different particle phenomena. For aggregation, a substitution system of seven point masses is constructed which preserves the main geometry of the particles. The main features of this reduced characterization will be discussed briefly in the next section. With this type of characterization, it was possible to qualitatively model complex aggregate structures with only a moderate demand on computer power. As the focus of that contribution was on the hierarchical characterization, many assumptions have been introduced which lead

to an unrealistically simple problem description. The present contribution extends the previous approach towards a more realistic modelling of the rate processes accounting for size and structure-dependent behaviour. To rigorously consider size dependency, the aggregation rate for each combination of particles in the Monte Carlo set would need to be computed. To avoid this large effort, the particle set is grouped into several classes for which identical collision behaviour is assumed. In the Monte Carlo scheme, initially two classes are probabilistically selected. A collision is executed for two particles randomly selected from the respective classes. Whether the collision is successful in forming a new aggregate is determined explicitly as a function of the system parameters (physical properties of the solid and the fluid, shear rate, linear growth rate). To determine the success of a certain collision, a dimensionless group suggested by Hounslow et al.¹⁰⁾ is used, which has proven to be very successful in correlating their data.

Methodology

Hierarchical characterization

In this section, the main features and the construction of substitute systems for aggregation are introduced briefly. A hierarchical particle characterization allows selection of a complexity level which is just appropriate for a certain rate phenomenon. A reduced characterization can be used to perform aggregation, whereas the fully detailed characterization is still available. Thus, the detailed characterization can always be used to derive alternative reduced representations which are more suitable for rate events other than aggregation or also for a more detailed aggregation model. The discussion of the reduced characterization is separated into the characterization of the primary and the aggregate particles. For each of these systems, a fully detailed and a reduced characterization are introduced. Each of the primary particles is characterized by three dimensions. This allows arbitrary cuboids to be represented. Additionally, each primary particle within an aggregate structure is associated with a 4×4 matrix that specifies the relative position of each of the primary particles within the aggregates. The geometrical complexity of this characterization, however, is too high to permit evaluation of aggregation events in a reasonable computation time. To reduce this complexity, substitution systems comprising a set of point masses are introduced. In the substitution system, each primary or aggregate particle *i* is represented by seven point

masses. For the primary particles, the construction of the set of point masses is trivial. If symmetry is exploited and conditions to guarantee the preservation of the moments of inertia with respect to the coordinate axes are imposed, the point mass system can be determined explicitly. The construction of a reduced representation by means of seven point masses for an arbitrary aggregate structure is more demanding. First, a principal component analysis (PCA) is performed for the set of point masses comprising all point masses of the primary particles. This operation yields the main orientation of the aggregate. The actual position and mass value for the point masses is constructed by preserving the moments of inertia with respect to the principal component directions. Additionally, the position of the point masses must reflect the extensions of the original aggregate. Fig. **1** shows the full and the reduced representation by means of point masses of a primary and an aggregate particle. In this work, only the position of the mass points is relevant. This position is represented by a matrix in which the rows correspond to the coordinates of the mass points in a coordinate system which has its origin in the centre of mass and whose axes are given by the principal components directions:

$$X_{i,agg,subst} = \begin{pmatrix} L_{i,1} & 0 & 0 & L_{i,4} & 0 & 0 \\ 0 & L_{i,2} & 0 & 0 & L_{i,5} & 0 \\ 0 & 0 & L_{i,3} & 0 & 0 & L_{i,6} \end{pmatrix}.$$
 (1)

Note that this reduced system, instead of the full characterization, is used to perform the actual aggregation event. The detailed information is nevertheless still available and can be used to assess the simulation results. Further details of the particle characterization and its construction can be found in



Fig. 1 Full and substitute characterization for an aggregated and a primary particle.



previous work⁹.

During the simulation, the aggregates are sorted into size classes to study size-dependent behaviour. This is similar to a sectional method when discretizing a deterministic population balance equation^{11,12}. The size of the aggregate is determined only on the basis of the substitute system. Consider a pseudo-ellipsoid spanned by the axes $L_{i,1}$ to $L_{i,6}$. As all the axes have a different length, the volume of the pseudoellipsoid comprises 8 different sections. The size of an aggregate is considered to be the diameter of a sphere with the equivalent volume to the pseudoellipsoid:

 $d_{i,agg,subst} = \sqrt[3]{(|L_{i,1}| + |L_{i,4}|) \cdot (|L_{i,2}| + |L_{i,5}|) \cdot (|L_{i,3}| + |L_{i,6}|)}.$ (2)

Note that contrary to standard approaches, it is not the actual aggregate volume, comprised by the total volume of the primary particles, that is employed. The structural properties of the aggregate can thus be considered in the evaluation of the collision rate (i.e. open structures with the same actual volume have a larger collision diameter). The number of size classes is fixed at 20 for all the simulations presented below. Subsequent intervals are enlarged by a factor of 1.07, respectively. The interval with the largest size values is chosen such that the aggregation efficiency is zero for any value in that interval. The effective aggregation rate for two aggregates which belong to the size classes *i* and *j* defined by the interval $(d_i, d_{i+1}]$ and $(d_j, d_{j+1}]$, respectively, is given below (see equation (9)).

Monte Carlo scheme

The following steps constitute the basic Monte Carlo scheme:

- 1. Initialize system.
- 2. Determine the time between two aggregation events.
- 3. Select two particles to be aggregated. Particles may be primary or aggregate particles.
- 4. Perform aggregation event with the selected particles.
- 5. Check termination criterion. If 'false', go back to step 2.

Step1:

The system is initialized by specifying an initial number of primary particles. The initial particles are chosen to be cubes with a specified side length. Additionally, the initial solids volume fraction in the suspension is chosen.

Step 2:

The inter-event time strongly depends on the cur-

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rent state of the system; namely, the size distribution of the current set of particles. To determine the interevent time, all possible effective aggregation rates between particles of two size classes need to be evaluated. The effective aggregation rate constant β_{ij} between particles from size class *i* and *j* is a product of the collision frequency C_{ij} and the collision efficiency Ψ_{ij} :

$$\beta_{i,j} = \Psi_{i,j} \cdot C_{i,j}.$$
(1)

For the collision rate, the classical expression for aggregation in a laminar shear flow as proposed by Smoluchowski¹³⁾ is used:

$$C_{i,j} = \frac{1}{6} \dot{\gamma} \left(d_i + d_j \right)^3,$$
(2)

where $\dot{\gamma}$ is the shear rate and d_i is the representative size of size class *i*. The aggregation efficiency is evaluated following the contribution by Hounslow et al.¹⁰. They concluded from micromechanical considerations that a collision is only effective if the aggregate has enough time to grow a stable neck. The most influential parameters are therefore the growth rate at the neck and the shear rate trying to disrupt the aggregate. They introduced a dimensionless group *M* which was effective in correlating their simulation and experimental results:

$$M = \frac{\sigma^* G^2}{\mu d^2 \dot{\gamma}^3},\tag{3}$$

where σ^* is the material-dependent apparent yield stress and *G* is the linear growth rate. The kinematic viscosity is given by μ , and *d* is the diameter of a sphere from a mono-disperse system. Plotting the efficiency determined from their previous simulation studies showed that the effects of supersaturation,



Fig. 2 Collision efficiency as a function of the dimensionless group M.

shear rate and particle diameter could be perfectly correlated with the single dimensionless group *M*. Hounslow et al.¹⁹⁾ only give a graphical representation of that correlation. To obtain a functional representation $\Psi = f_{eff}(M)$, a sigmoid-type function, which is based on the graphical data and shows very good agreement, is used here. The relation used is plotted in **Fig. 2**.

One major assumption made in the derivation of this dimensionless group is that the system is considered to be mono-disperse. For the diameter d, Hounslow et al.¹⁰ used a mean particle size of the whole distribution. Here, the explicit size dependence shall be considered. As the analytical derivation can only be performed for mono-disperse spheres, a pragmatic approach is chosen to at least capture the qualitative dependence for a size-dependent dimensionless group:

$$M\left(d_{i},d_{j}\right) = \frac{\sigma^{*}G^{2}}{\mu\frac{\left(d_{i}^{2}+d_{j}^{2}\right)}{2}\dot{\gamma}^{3}},\tag{4}$$

Accordingly, the aggregation efficiency is also evaluated in a size-dependent way for each pair of possible sizes. The aggregation kernel for a particular combination of sizes d_i and d_j is then given by

$$\beta(d_1, d_2) = \frac{1}{6} f_{eff} \left(M(d_1, d_2) \right) \cdot \dot{\gamma} \cdot \left(d_1 + d_2 \right)^3.$$
 (5)

As mentioned above, the particles are grouped into size classes. Hence, representative values for these classes need to be determined because equation (6) only provides the aggregation rate for two distinct sizes. Accordingly, an averaging of the rates over each size class interval is performed:

$$\beta_{i,j} = \frac{\int_{d_j}^{d_{j+1}} \int_{d_i}^{d_{i+1}} \beta(d_1, d_2) \, \mathrm{d}d_1 \mathrm{d}d_2}{(d_{j+1} - d_j) \cdot (d_{i+1} - d_i)}.$$
(6)

A graphical representation of the aggregation rate kernel is given in **Fig. 3** for a particular set of parameters. If the particles are very small their collision efficiency will be 1. Accordingly, the effective aggregation rate increases with increasing particle size because it increases the cross-sectional area and consequently the probability of a collision. For a further increase of the particle size, the effective rate decreases because of the strongly decreasing collision efficiency for large particles. The actual rate of effective collisions between two particles of the size classes *i* and *j* can then be evaluated by

$$r_{i,j} = \beta_{i,j} \cdot N_i \cdot N_j,\tag{7}$$

where N_i and N_j represent the volumetric number



Fig. 3 Size-dependent efficient aggregation rate kernel. Size is given as the volume equivalent sphere diameter of the substitute ellipsoid. For better readability, the plot shows the rate kernel evaluated at the centre of each size interval. In the simulation, the discrete values on the intervals are used.

densities of the respective size classes. The aggregation kernel $\beta_{i,j}$ depends only on the particles' size classes. Thus, the term defined by equation (7) can be pre-processed before the actual Monte Carlo run.

From the rates of effective collisions, an average time between two aggregation events can be determined by

$$\Delta t = \frac{1}{\sum_{i}^{n_i} \sum_{j}^{n_j} r_{i,j} V},\tag{8}$$

where *V* is the current volume domain of the Monte Carlo scheme.

Step 3:

The selection of a combination of size classes from which particles should be aggregated is governed by the effective collision rates for the respective size class pairs. Obviously, preference should be given to a combination with a high collision rate instead of a combination with a very low rate. For easier notation, consider the collision rates $r_{i,j}$ to be arranged in a vector \hat{r} with the indices given by $k = (i-1) \cdot n_j + j$:

$$\hat{r}_{(i-1)\cdot n_j+j} = r_{i,j}.$$
(9)

The index k_{sel} for the selected pair of size classes (i_{sel} , j_{sel}) is determined from the condition

$$\sum_{k=1}^{k=k_{sel}} \hat{r}_k < RND \leqslant \sum_{k=1}^{k=k_{sel}+1} \hat{r}_k,$$
(10)

where *RND* is a random number on the interval [0,1]. Step 4:

From each of the selected particle size classes, one particle is randomly sampled. The following discussion of step 4 will always refer to these two particles denoted by indices 1 and 2. The aggregation of the



particles is realized with a procedure similar to that proposed earlier⁹⁾. There, two mass points of the substitution system are randomly selected to coincide. Also, they are oriented such that they share a common axis. As selection of the mass points is completely arbitrary, the structural properties of the two aggregates are not properly reflected. Although a fully rigorous model would exceed the scope of this contribution, a strategy is developed which at least qualitatively reflects the expected structural evolution behaviour. To achieve this, each combination of mass points from the selected particles is associated with a probability of being part of the axis along which the new aggregate is formed. As the aforementioned size classes only reflect a spherical diameter, this averaged size is not suitable for representing the structural properties. Responsible for the collision rate and the collision efficiency is the cross-sectional area which is exposed to the shear flow. After collision, the aggregate tumbles in the shear flow. The orientation of maximum normal force must generally be expected to be different from the orientation at collision. Therefore, different representative values are used for the collision diameter $d_{i,coll}$ and the efficiency diameter $d_{i,eff}$. For two selected mass points e and f out of the possible 6 outer mass points represented in equation (1), the effective collision rate can be evaluated:

$$\beta_{e,f} = \frac{1}{6} f_{eff} \left(M \left(d_{1,eff,e}, d_{2,eff,f} \right) \right) \cdot \dot{\gamma} \cdot \left(d_{1,coll,e} + d_{2,coll,f} \right)^3.$$
(11)

The collision diameter is chosen as the circle diameter which has the same cross-sectional area as a pseudo-ellipse. The pseudo-ellipse is spanned by the four axes which do not fall on the same coordinate axis as the selected substitution mass. As the general formulation hinders readability, only the collision diameter for e = 1 is given:

$$d_{j,coll,e=1} = \sqrt{(L_{j,2} - L_{j,5}) \cdot (L_{j,3} - L_{j,6})}.$$
 (12)

For other values of *e*, the collision diameter is computed analogously. The rationale behind this is that if the particles are orientated in a way that the cross-sectional area of the pseudo-ellipse is exposed to the flow, the particles are likely to collide with the remaining axis.

For the efficiency diameter, the doubled value of the axis of the attaching mass point is chosen:

$$d_{j,eff,e} = 2 \cdot L_{j,e}.$$
(13)

The idea behind this choice is to prefer the formation of compact aggregates as the particle size reaches



a value where the collision efficiency drops from 1. The formation of aggregates at the mass point with a small axis should yield more compact aggregates.

Note that these assumptions only allow a qualitative analysis of the structural behaviour. For a quantitative representation, more rigorous examinations of the local micro-mechanical behaviour are needed. Also, it must be fundamentally investigated whether the micro-hydrodynamics of complex-shaped aggregates can be represented by equivalent sphere diameters in the first place. The presented choice nevertheless already allows a first *mechanistic* estimation of the qualitative behaviour.

Case Study

A closed aggregating system with constant shear and growth rate is investigated as a case study. Different shear rates and growth rates are studied with the presented algorithmic framework to assess particle size and structure. Note that the growth rate will only be used to reflect the growth of the neck of attaching particles. The particles themselves are not considered to grow. The variation of shear rate affects both the collision frequency and the collision efficiency, whereas the growth rate only affects the aggregation efficiency. The values used in the present study are shown in Table 1. The case numbers are used to identify certain combinations of shear and growth rate when reporting the results. For the simulations a nominal, initial particle number of 10000 is chosen. The side length of the initial cubes is $15 \,\mu$ m. The initial solids volume fraction is set to 3.3E-5. For the apparent yield stress, the value suggested by Hounslow et al.¹⁰⁾ for calcium oxalate monohydrate is chosen: σ^* = 150 GPa. The viscosity μ is set to 1E-3 Pa s. To obtain comparable results, a final average number of primary particles per aggregate is specified as the termination criterion for the simulation. In other words, the simulation is stopped when the average number of primary particles is 10. This means that the total simulation time may vary strongly. On the

Table 1 Parameters for the 9 cases simulated in this study

		Growth rate, $G\left[\frac{m}{s}\right]$					
		$1 \cdot 10^{-10}$	$1.5 \cdot 10^{-10}$	$2 \cdot 10^{-10}$			
shear rate, $\dot{\gamma} \begin{bmatrix} 1 \\ - \end{bmatrix}$	20	case 1	case 2	case 3			
	22	case 4	case 5	case 6			
	24	case 7	case 8	case 9			



Fig. 4 Number concentration as a function of time for the different cases 1-9.

other hand, the structural properties of the resulting particles ensemble can be compared on a common basis.

Results

Fig. 4 shows the total number concentration as a function of time for the 9 investigated cases. The number concentration decreases faster for increasing shear (case sequence: $1 \rightarrow 4 \rightarrow 7$, $2 \rightarrow 5 \rightarrow 8$, $3 \rightarrow 6 \rightarrow 9$) and growth rate (case sequence: $1 \rightarrow 2 \rightarrow 3$, $4 \rightarrow 5 \rightarrow 6$, 7 \rightarrow 8 \rightarrow 9). Except for the cases 4 and 7, all simulations reach the termination criterion where on average an aggregate comprises 10 primary particles. Cases 4 and 7 reach a state where the effective aggregation rates are zero for all particle combinations before fulfilment of the termination criterion. In other words, the shear rate is already too large to allow the formation of larger aggregates. As the time step between two successful aggregation events increases dramatically in the final phase of these cases, the time axis is cut off at 15000 s, whereas the final time for cases 4 and 7 is in the order of 10^{12} s.

As a qualifier for the morphology of the particles, the compactness of the particle is introduced. The compactness ω here is defined as the ratio of the actual aggregate volume V_{agg} and the volume of the cuboid spanned by the substitute system:

$$\omega = \frac{V_{agg}}{(L_{i,1} - L_{i,4}) \cdot (L_{i,2} - L_{i,5}) \cdot (L_{i,3} - L_{i,6})}.$$
 (14)

For the primary particle, the compactness is 1 and decreases quickly to smaller values as the primary particle number in the aggregate increases. **Fig. 5** shows a histogram to assess the final state of the particle ensemble. The aggregates are grouped according to their number of primary particles and their

compactness. The low growth rate in case 1 hindered the appearance of larger aggregates. To reach the final average number of 10 primary particles per aggregate, all initial particles disappeared and formed aggregates with a narrow variation in size and compactness. In case 7, the shear rate was even too large to reach the final state. Similar to case 1, a narrow distribution of particle sizes and compactness is obtained. For the large growth rates, the aggregation efficiency remains large even for large aggregates. As the collision rate for the larger aggregates increases, many initial primary particles remain un-aggregated. As the growth rate of the neck is no longer the limiting factor, large particles with up to 35 primary particles per aggregate are observed. As the shear rate increases from case 3 to 9, the aggregates are only formed up to smaller sizes compared with case 3.

Note that the segmentation shown in **Fig. 5** is not used in the simulations. In a deterministic population balance framework, such a representation would probably also have been chosen to investigate size and structure evolution. In the case of the deterministic population balance approach, equations would



have been needed to model the aggregation and its effect on structural changes. However, the information needed to mechanistically formulate this equation (i.e. the explicit structure of the aggregates) would not be available. In the present approach, the structure is a result of the simulation and no structural assumptions must be made. The full morphological information is available at all times.

Fig. 6 shows randomly selected particles for cases 1, 3, 6 and 9 at the final simulation time. As already observed from the histogram plots in **Fig. 5**, the particles are much smaller and more uniform for the small growth rates. For larger growth rates (cases 3 and 9), the final system comprises non-aggregated particles as well as large structures. For increasing shear rates, the particle size tends to be smaller.

The largest aggregates observed in cases 1-9 are given in **Fig. 7**. Obviously, the maximum observed size increases with increasing growth rate and decreases with increasing shear rate. From case 3 in **Fig. 6** and **Fig. 7**, it can already be anticipated that the resulting structures are more open. For the final particle state, the aggregation is not yet limited by



Fig. 5 Two-dimensional histogram representation of the final particle ensemble. Each bar shows the frequency of occurrence of aggregates in a certain interval of compactness and primary particles per aggregate.





Fig. 6 Selected, representative particle morphologies for the cases 1, 3, 7 and 9. The aggregates were sampled randomly from the active set.

the collision efficiency. All particles thus stick together regardless of their orientation. As the collision efficiency decreases, only compact aggregates are allowed to be formed. This is clearly observed for cases 1 and 3. Also, the particles for case 9 seem to be more compact. However, as the visual interpretation also depends on the orientation of the particles, the results may be misleading. To quantify the structural differences, the compactness is used. **Fig. 8** shows the averaged compactness for all aggregates with exactly 15 primary particles. Only the comparison for the same number of primary particles is meaningful.



Fig. 7 Aggregates with the largest number of primary particles at the end of the simulation for the cases 1-9.



Fig. 8 Average compactness for aggregates with 15 primary particles per aggregate. To ensure a certain statistical relevance, data is only shown if at least 100 aggregates were available for averaging.

An averaging over the complete particle set would e.g. strongly pronounce the many un-aggregated initial particles with a compactness value of 1. To obtain a statistically relevant averaging, only the states are reported where at least 100 aggregates consisting of 15 primary particles were present. As the abscissa, the average number of primary particles per aggregate of the whole system is used. As discussed above, the simulation is stopped when the average number of primary particles per aggregates reaches 10. In cases 1, 4 and 7, the shear rate is already too large to allow the formation of any aggregate with 15 primary particles. In all other cases, it takes a while until enough aggregates with 15 primary particles have been formed. The plots reveal that the compactness of the particles increases with increasing shear rate (case sequences: $2 \rightarrow 5 \rightarrow 8, 3 \rightarrow 6 \rightarrow 9$). If particles reach the same size (number of primary particles) in different shear environments, higher shear rates promote the formation of compact structures. Similarly, an increasing growth rate (case sequences: $2 \rightarrow 3, 5$ \rightarrow 6, 8 \rightarrow 9) leads to more open structures as the particles tend to stick to each other regardless of their relative orientation.

Conclusion

The presented Monte Carlo framework facilitates the investigation of the structural and size evolution of particle aggregates. In contrast to alternative approaches, no predefined assumptions on the aggregate shape and structure need to be made. However, the actual aggregation event has to be considered in very high detail. Because the fully detailed geometric information is available for modelling the aggregation event, this poses new challenges on mechanistic modelling. The current assumptions can still be considered very restrictive in terms of predictive power. Simplifications have mainly been chosen for computational reasons. However, even with this simplified approach, a mechanistic modelling of the expected behaviour can be realized. Note that the contribution of this work is not the phenomenological results discussed in the previous section. They actually represent the desired and expected behaviour. Instead of reproducing this behaviour with a descriptive model, the present paper aims at providing a method to address these changes in a mechanistic way. The presented technique is a step towards predictive modelling of the intrinsic kinetics of aggregation, and allows the simulation of highly complex aggregate shapes. Using the current simplifications, the simula-



tion of fully complex shapes of particle aggregates is possible with state-of-the-art desktop computers. The computation time was in the order of 4 h for each run. With more detailed mechanistic models for the aggregation event, as they are planned in future work, one might use a multiprocessor machine. These mechanistic models will then be validated with experimental results and compared with alternative modelling approaches.

Nomenclature

- C collision frequency
- *d*_{*i*,sgg,subst} apparent size of particle i derived from the substitute system
- G growth rate
- *L*_{*ij*} axis j of the substitute system of particle i
- M dimensionless number characterising the aggregation efficiency
- N_i number concentration for the size class i
- *r* effective aggregation rate
- Δt inter-event time
- V_{agg} aggregate total volume (sum of primary particle volumes)
- V control volume of the Monte Carlo scheme
- $X_{i,agg,subst}$ data matrix for the substitution system
- β effective aggregation rate kernel
- Ψ aggregation efficiency
- $\hat{\gamma}$ shear rate
- σ^* apparent yield stress
- μ kinematic viscosity
- ω compactness

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Author's short biography



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Dr.-Ing. Heiko Briesen is a senior engineer at the Chair of Process Systems Engineering at the RWTH Aachen University. He graduated in 1998 in chemical engineering from the University of Karlsruhe. After he received his PhD in 2002 from the RWTH Aachen University, he remained at the Chair of Process Systems Engineering (Prof. Dr.-Ing. W. Marquardt) to build up a research group focusing on industrial crystallization. In 2007, Dr. Briesen joined the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg, where he is the head of a junior research group and population dynamics. One of his main research interests is the modelling of crystallization/precipitation processes with complex particle characterization.



Ultrafine Aerosol Emission from the Free Fall of TiO₂ and SiO₂ Nanopowders[†]

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Abstract

Due to the increasing production and development of nanoparticles, it has become necessary to control the exposure to ultrafine particles when handling nanopowders. The use of dustiness tests makes it possible to compare the ability of a given powder to re-suspend particles, and to determine the effect of the different external (powder handling method) or internal parameters (powder properties). A dustiness test associated with an electrical low-pressure impactor (ELPI) device is proposed to study the free fall of nanopowders. Titanium dioxide (TiO2) and fumed silica (SiO2) are the studied nanopowders. The free falling of nanopowders in the test chamber generates bimodal aerosols corresponding to the re-suspension of the micrometric agglomerates that constitute the nanopowders and to the breakage and/or erosion of these agglomerates leading to ultrafine aggregates. The presence of ultrafine aggregates was checked by scanning electron microscopy (SEM). When the height of fall and the dropped mass of the powders are increased, the aerosol concentration increases. Aerosols are mostly generated by the impact of nanopowders on the floor of the experimental chamber. Fumed silica is dustier than titanium dioxide, and its agglomerates break more easily.

Keywords: Nanopowder, Aerosol, Free-Falling powder, ELPI, Dustiness

1. Introduction

Nanoparticles, also called ultrafine particles, are defined as particles smaller than 100 nm. Their high surface-to-volume ratio gives them interesting properties: magnetic, mechanical, electrical, optical, thermodynamical and thermal properties that are different from those of the source materials¹⁾. They thus constitute an enhanced development, due to the wide range of applications in electronics, biomedicine, pharmaceutics, cosmetics, catalysts and materials²⁾. This increasing interest in nanomaterials has led to some questions about the possible adverse effects on human health²⁻⁴⁾. Previous works have studied the toxicity of ultrafine particles. Their conclusions can

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- Ultrafine particles induce much higher lung inflammation than an equal mass of larger respirable particles of the same material⁵⁾.
- Lung damages due to agglomerates and aggregates of nanoparticles (henceforth called nanostructured particles) is more severe than that caused by particles lacking a nanostructure, even when they have the same size⁴.
- Ultrafine particles can pass into the bloodstream⁶.
- Pulmonary inflammation due to low-solubility nanostructured particles is fairly independent of particle compositions and sizes. On the contrary, it correlates closely with surface area concentration³⁾.
- Particle shape should be taken into account when studying the hazards; anisotropic particles such as fibres or nanotubes enhance pulmonary damage⁴⁾.
- Surface chemistry can modify particle toxicity; for instance, the inflammation response caused by quartz can be strongly reduced by modifying the



surface of the particles (e.g. with aluminium lactate)⁷⁾.

All those studies point out that it is necessary to determine the exposure levels during manufacturing, handling and clean-up operations with nanopowders. Not only nanoparticles, but nanostructured particles as well as aerosolised liquid suspensions containing nanoparticles should be taken into account. Several parameters such as particle shape, size and surface area of the nanostructured particles are properties which should be determined.

Two different approaches can be followed. The first one concerns measurement of the exposure levels at work sites in order to obtain representative values of real industrial levels. However, it is difficult in that case to identify the parameters inducing ultrafine dust generation, as well as their influence. A good summary of this kind of approach can be found in Aitken *et al*².

The other approach concerns dustiness tests applied to nanostructured powders. Dustiness is defined as the trend of a given material to generate dust. In such tests, a powder is subjected to different constraints such as free falling, fluidisation or stirring in a rotating drum⁸⁾. Although the values obtained are less representative than measurements at work sites, the identification of key parameters affecting dust emission becomes easier.

To our knowledge, the only previous studies using dustiness tests for nanomaterials were implemented with single-walled carbon nanotubes $(SWCN)^{9, 10}$ and fumed silica¹¹⁾. Tests with SWCN were carried out in a test tube agitated by a vortex shaker. The emitted aerosol size distribution was measured by two scanning mobility particle sizers, SMPS¹²⁾, and an aerodynamic particle sizer, APS¹³⁾. The aerosol concentration was found to be quite low and ultrafine particles were not significantly detected, except when applying strong agitation. These results were checked against field measurements where the overall airborne concentration of nanotubes was estimated to be quite low (lower than $53\mu g/m^3$).

Tests with fumed silica were carried out in a rotating drum⁸⁾ and in a dropping test (Dust View¹¹⁾, from Palas society). Size distributions were not measured in that work. For the rotating drum test, a dustiness index was defined as the mass ratio of the emitted ultrafine aerosol (sucked and collected by a filter) to the initial nanostructured powder. For the dropping test, the characteristic values used were the maximum light extinction of a laser beam placed next to the settling dust stream, as well as the light extinction 30 seconds after the fall of the powder.

The aim of the present work is to design an experimental set-up which enables the study of ultrafine dust generation by free-falling nanostructured powders. The results of the test provide the size distribution and the mass concentration of the aerosol. This experiment will therefore make it possible to check the presence (or absence) of ultrafine particles suspended in air due to free-falling powders, and to study the effect of parameters such as the drop height or the dropped mass of powder on both size distribution and concentration. Such an experiment can provide a tool to quantify and to compare the ability of several nanostructured powders to generate ultrafine aerosols for a given situation (free falling). It can also help to correlate the properties of the particles to their behaviour.

2. Experimental Methods

2.1 Experimental set-up

The experimental set-up shown in **Fig. 1** is inspired by the MRI test [14]. Powder fall was performed in a stainless steel chamber with internal dimensions $180 \times 50 \times 80$ cm. The front and lateral



Fig. 1 Free-falling nanostructured powders device for aerosol emission measurement: (a) silo; (b) supporting stem; (c) inlet HEPA filter; (d) outlet HEPA filter; (e) sampling point; (f) latex gloves; (g) vacuum cleaner inlet.



sides of the chamber are partially of glass to enhance visualization. The powder is stocked in a silo (a) which can be adjusted in height inside the chamber along a supporting stem (b). The silo comprises a storage vessel that tapers into a beaker of 125cm³. The beaker is connected to a rotating system so that two positions are possible: filling and emptying. A pneumatic vibrator is added to the system in order to help both operations.

Six aerosol extraction positions (e) connected to an electrical low-pressure impactor (ELPI) are placed on both sides at 50, 100 and 150 cm from the bottom of the chamber. Both air inlet (c) and outlet (d) holes were placed at the left and the right side of the chamber, respectively. Two high-efficiency particulate air (HEPA) filters are used in order to clean the air entering and exiting the chamber. Cleaning is carried out by a vacuum cleaner (g) handled by means of two latex gloves (f) placed on both sides.

Three sets of experiments were carried out. The first one concerned video recording of the powder fall. Recording was carried out with a Photron FAST-CAM-APX camera. The resolution, the frame rate and the shutter speed were fixed at 1024×1024 pixels, 1000 fps and 1/2000 s, respectively. Since the front door of the chamber was not entirely transparent, video recording was accomplished by elevating the impact surface. Hence, the maximum height of fall in the video-recorded experiments was 130cm, and not 160cm as in the other experiments presented in the next sections.

The second set of experiments consisted of measuring the aerosol concentration and size distribution after a powder fall. The aerosol concentration and size distribution were measured by an electrical lowpressure impactor (ELPI). The ELPI device enables the particles contained in the aerosol to be separated according to their size, and to determine the particle concentration corresponding to each class. The principle of the ELPI measurements is explained in the next section.

These experiments were started by placing the nanostructured powder in the silo, closing the front door and switching on the air extraction through the HEPA outlet filter. The HEPA filter placed at the air inlet allowed the particle concentration (coming from the atmosphere) in the chamber to be decreased. At the same time, the ELPI was switched on to equilibrate the temperature in the chamber. After a stabilisation time of at least 20-30 minutes, the air extraction was switched off and the clean air evolution was recorded during 15-20 minutes. The beaker was then turned upside down and the powder fell in the chamber.

The dropped mass of powder can be changed by partially filling the beaker below the silo. In that case, the mass of powder was weighed before placing it in the beaker. Another possibility was to totally fill the beaker. In that case, the method of filling was more reproducible, but the dropped mass of powder was not directly measured before each experiment. It was obtained for each powder by carrying out preliminary experiments, recovering the dropped powder in a plastic bag and weighing the bag.

Finally, a third set of experiments were carried out in order to validate the presence of ultrafine aggregates in the emitted aerosol by scanning electron microscopy (SEM) visualisation of the particles collected on the ELPI stages. These SEM visualisations need specific experiments. They were performed for a given height of fall, fixed at 160 cm, and a given height of sampling: 50 cm.

2.2 Principle of the ELPI measurements

The ELPI¹⁵⁻²²⁾ is a device able to measure aerosol concentration as well as size distribution of the aerosol in the range between 30 nm and 10μ m at a given location. The principle of the instrument has been well explained elsewhere¹⁵⁻¹⁸⁾, so that the main elements needed for this work will only be touched upon here.

A schematical view of the ELPI device is shown in **Fig. 2**. The aerosol is sucked by a vacuum pump. It





goes first through a corona charger (a), where particles are charged positively depending on their mobility diameter. The mobility diameter (d_b) is defined as the diameter of the sphere having the same mobility, i.e. the same velocity-to-driving force ratio as the particle. Since, according to the Stokes-Einstein equation, the particle diffusion coefficient is proportional to the particle mobility²³⁾, the mobility diameter is the most representative diameter when describing Brownian motion.

The cascade impactor (b) is located downstream of the corona charger. It classifies the particles according to their aerodynamic diameter. The aerodynamic diameter (d_a) is defined as the diameter of the sphere with a unit density of 1000kg/m³ having the same settling velocity as the particle. This diameter is the key particle property for characterising respiratory deposition²³.

When the particles are collected on an ELPI stage, they generate an electrical current that is measured by the electrometers. Teflon insulators are placed between the ELPI stages in order to isolate the stages electrically.

As the particle charge depends on the mobility diameter and the particle deposition on the ELPI stages depends on the aerodynamic diameter, the conversion between both diameters is essential. If the particles are spherical, the diameters are related through equation 1, where $\rho_{\rm P}$ is the particle density, $\rho_0 = 1000 \text{kg/m}^3$ and Cc is the slip (or Cunningham) correction factor²³. The aerodynamic diameters and their corresponding mobility diameters were calculated in Table 1 for the two different particle densities used in this work. If the particle density is 1000 kg/m³, then the aerodynamic diameter and the mobility diame

ameter have the same values.

$$\rho_p d_b^2 C_C(d_b) = \rho_0 d_a^2 C_C(d_a) \tag{1}$$

Measurement data can be treated by ELPI software^{17, 19)}, which converts raw current data into aerosol concentration and size distribution. The only required parameters are the particle density and the calibration data. Both the charger and the cascade impactor calibrations are performed by the manufacturer¹⁶⁾. Cascade impactor calibration provides the cut-off aerodynamic diameters of the ELPI stages. Charger calibration provides the charger efficiency (E_{ch}) as a function of the mobility diameter. The charger efficiency represents the current carried by charged particles of a given size leaving the charger, divided by the particle number concentration in the aerosol.

For each stage, ELPI software calculates the average aerodynamic diameter given by the geometric mean of the cut-off diameters of a given stage and the previous one. Then the mobility diameter is calculated by Eq.(1). The charger efficiency is then calculated according to its calibration data. Finally, the particle number concentration is given by the ratio between the current I' and the charger efficiency E_{ch} :

$$N = \frac{I'}{E_{ch}} \tag{2}$$

I' is not the measured current I, but a corrected current¹⁷⁾ that takes into account the fine particle losses in upper ELPI stages^{20, 21)}. The rebound of the particles impacting against an ELPI stage is minimised by greasing the ELPI substrates with Vaseline.

ELPI stage	$d_a (\rho_0 = 1000 \text{ kg/m}^3)$	$d_b (\rho_p = 2300 \text{ kg/m}^3)$	$d_b (\rho_p = 3100 \text{ kg/m}^3)$
1	38.3 nm	17.6 nm	13.2 nm
2	70.9 nm	34.1 nm	25.8 nm
3	119 nm	60.5 nm	46.6 nm
4	199 nm	108 nm	85.3 nm
5	312 nm	180 nm	146 nm
6	477 nm	289 nm	239 nm
7	753 nm	471 nm	396 nm
8	1.21 μm	777 nm	660 nm
9	1.93 µm	1.25 μm	1.07 µm
10	$3.05\mu\mathrm{m}$	2.01 µm	1.70 µm
11	5.11 μm	3.37 μm	2.90 µm
12	8.05 μm	5.31 μm	4.57 μm

Table 1 Mean aerodynamic diameters of ELPI stages, and their equivalent mobility diameters



2.3 Tested nanostructured powders

Two types of nanostructured powders were selected for testing the device: titanium dioxide, TiO₂ (G5, produced by Millenium Inorganic Chemicals) and fumed silica, SiO2 (Aerosil 200, produced by Degussa). Although both powders are formed by microscopic agglomerates of nanoparticles, their structures are quite different, as can be seen on the SEM photographs (Fig. 3). TiO₂ agglomerates (Fig. 3.a) have a compact (raspberry-like) structure; whereas SiO₂ agglomerates (Fig. 3.b) resemble a foam with a high air content.

The main physical properties of both powders were measured and reported in Table 2. Agglomerate size measurements were performed by laser diffraction (Mastersizer 2000, Malvern Instruments). The difference between mass and number median diameters can be explained by the fact that for one given large particle, several fine particles are needed to obtain its weight. Primary particle sizes are provided by the manufacturers and are in agreement with our transmission electron microscopy (TEM) visualisations (same range of sizes). Particle densities were measured by helium picnometry, whereas tapped densities were obtained using a Hosokawa Micron Powder Characteristics Tester. Finally, the bulk density was calculated from the dropped mass of powder measured when the beaker was completely filled (the beaker volume is 125cm³).

3. Results

3.1 Video recording of the powder fall

In order to analyse the two sources of the aerosols: dust generation from the particles falling and dust generation after impaction on the chamber floor, the free-fall process was visualised by video camera recording. The same volume of dropping powder and same height of fall (130cm) were used for both powders TiO2 and SiO2. Several pictures were taken



Fig. 3a Titanium dioxide (TiO2).

Fig. 3 SEM photographs of the nanostructured powders.

	TiO ₂	SiO ₂
Primary particle size (provided by the manufacturer, checked by TEM)	5-12 nm	12 nm
Agglomerate mass median diameter (measured by laser diffraction)	1.3 μm	10 µm
Agglomerate number median diameter (measured by laser diffrac- tion)	0.80 µm	5.2 μm
Particle density (measured by helium picnometry)	3100 kg/m^3	2300 kg/m^3
Tapped density (measured by a Hosokawa Micron Powder Character- istics Tester)	620 kg/m^3	58 kg/m^3
Bulk density (calculated as described in the text)	370 kg/m^3	44 kg/m^3
BET surface area	320 m ² /g	190 m²/g
Crystalline structure (given by the manufacturer)	Anatase	Amorphous

Table 2 Specific properties of the nanostructured	l powders used in the free-fall test
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during the fall: they show that for both powders, the column of the falling powder is neither regular in shape nor in particle concentration. Moreover, when the first particles reach the floor of the chamber, others are still leaving the beaker in the upper part of the chamber. The mean time of the fall, considered as the time during which there was some powder falling from the silo, was found to be less than 2 s for TiO₂ and around 9 s for SiO₂.

For TiO₂, the particle cluster impacts on the sur-

face of the chamber floor and generates smaller agglomerates. Oblique jets are observed when the powder impacts on a layer of particles previously fallen. These jets can lead to particle re-suspension. **Fig. 4** is a view of the impact of TiO₂ powder, showing the rising jets.

For SiO₂ powder, the impact shown in **Fig. 5** is different: the small agglomerates seem to bounce on the surface and horizontal air/particle clouds are generated parallel to the surface.



Fig. 4a Camera visualisation

Fig. 4b Schematic representation of the fall

Fig. 4 TiO_2 nanopowder fall.



Fig. 5a Camera visualisation

Fig. 5b Schematic representation of the fall

Fig. 5 SiO_2 nanopowder fall.



Finally, in both cases, particles are re-suspended after the impact and rise along the walls of the chamber. Consequently, the measurements performed on the aerosol with the ELPI instrument correspond to the added contributions of the dust generated from the fall and the dust generated from impact.

3.2 Time evolution of the aerosol

The experimental conditions of the quantitative tests performed in the dustiness experimental set-up are reported in **Table 3**.

Although ELPI raw currents are measured in a continuous way, the results are averaged over at least 5 consecutive seconds¹⁸⁾ because of the different residence times of the particles in the cascade impactor. This time (5 seconds) compared with the time of fall (2 s for TiO₂ and 9 s for SiO₂) shows that the aerosol generation during the free fall and the aerosol generation due to impact cannot be distinguished by ELPI measurements.

Fig.s 6.a and 6.b show the time evolution of the

raw currents measured on ELPI stages during the free fall of TiO₂ and SiO₂ nanopowders, respectively, the first one corresponding to experiment E2.5 and the second one to E1.5. For both powders, when sampling near the impact surface, the aerosol concentration increases rapidly and then decreases faster than an exponential law. This is due to both settling and convection by the air vortex generated by the powder fall²⁴.

After some 10-15 minutes, aerosol concentration (which is proportional to the measured currents) decreases following an exponential law. This is typical of stirred settling²³.

For SiO₂ (**Fig. 6.b**), the fluctuations are much more significant, giving way to two independent peaks. When the second peak is reached, the aerosol concentration decreases in an exponential way. This decrease is faster than for TiO₂, since SiO₂ particles settle faster than the TiO₂ ones because of their larger aerodynamic diameter (see next section).

In the following sections, the results (size distribu-

Experiment number	Powder	Height of fall	Height of sam- pling	Dropped mass		Temperature	Humidity
E1	SiO ₂	160 cm	50 cm	$5.5 \pm 0.2 \mathrm{g}$	E1.1	23.6°C	52.2%
					E1.2	22.8°C	60.8%
					E1.3	23.1°C	56.3%
					E1.4	25.1°C	49.1%
					E1.5	24.5°C	48.4%
E3	SiO ₂	120 cm	50 cm	$5.5 \pm 0.2 \mathrm{g}$	E3.1	26.1°C	56.6%
					E3.2	23.4°C	65.2%
E4	SiO ₂	80 cm	50 cm	$5.5 \pm 0.2 \mathrm{g}$	E4.1	26.0°C	58.7%
E5	SiO_2	50 cm	50 cm	$5.5 \pm 0.2 \mathrm{g}$	E5.1	22.0°C	52.3%
					E5.2	23.7°C	53.4 %
					E5.3	22.8°C	60.0%
E2	TiO ₂	160 cm	50 cm	$45.9 \pm 0.9 \mathrm{g}$	E2.1	19.3°C	40.3%
					E2.2	22.5°C	39.1%
					E2.3	20.5°C	40.9%
					E2.4	23.1°C	37.9%
					E2.5	20.5°C	48.0%
E6	TiO ₂	120 cm	50 cm	$45.9 \pm 0.9 \mathrm{g}$	E6.1	23.7°C	55.8%
E7	TiO ₂	80 cm	50 cm	$45.9 \pm 0.9 \mathrm{g}$	E7.1	24.2°C	47.1%
E8	TiO ₂	50 cm	50 cm	$45.9 \pm 0.9 \mathrm{g}$	E8.1	22.7°C	47.3%
E9	TiO ₂	160 cm	100 cm	$45.9 \pm 0.9 \mathrm{g}$	E9.1	24.8°C	58.8%
E10	TiO ₂	160 cm	150 cm	$45.9 \pm 0.9 \mathrm{g}$	E10.1	20.6°C	57.8%
E11	TiO ₂	160 cm	50 cm	5.5 g	E11.1	23.2°C	61.1%
			<u> </u>	5.5 g	E11.2	25.0°C	50.7%
E12	TiO ₂	120 cm	50 cm	5.5 g	E12.1	23.6°C	57.3%
E13	TiO ₂	80 cm	50 cm	5.5 g	E13.1	24.0°C	54.0%

Table 3 Operating conditions of the experiments performed in the free-falling powder chamber





Fig. 6a Experiment E2.5.

Fig. 6b Experiment E1.5.



tion and particle concentration) were obtained by considering the maximum of the first peak of the current curve. In order to reduce the drift effect, the currents obtained just before the peak were subtracted from the measured currents.

Aerosol concentration at higher sampling positions (100cm and 150cm) increases more slowly, and begins to decrease following an exponential law. This behaviour can be explained by the fact that the main part of the aerosol is generated during the impact against the solid surface, and then diffuses (by Brownian and especially by hydrodynamic diffusion) to higher positions. Once the aerosol concentration is uniform in the chamber, only settling becomes important. This can be verified in **Fig. 7**, which shows the particle concentration at different sampling positions for different times. At t=0 (which corresponds to the first peak), the aerosol is much more concentrated near the impact surface (since most of the aerosol is generated during the impact). Aerosol concentration near the surface decreases rapidly, whereas concentration at higher sampling positions increases.



Fig. 7 Time evolution of the aerosol mass concentration at different sampling positions (t=0 corresponding to current maximum). Experiments E2, E9 and E10.



Fig. 8b TiO_2 (experiments E2, E6 to E8).

Fig. 8 Number size distribution of the generated aerosols at different heights of fall

At t=10 min, aerosol concentration is uniform in the chamber. At t=15 min, aerosol concentration begins to decrease homogeneously in the entire chamber.

3.3 Characterisation of the emitted aerosol 3.3.1 Size distribution

Fig. 8 shows the size distribution of the aerosols obtained in experiments E1 to E8, corresponding to different heights of fall at the same sampling position. **Fig. 9** shows the size distribution of the aerosols in experiments E2, E9 and E10, corresponding to different sampling heights for a same height of fall. Error

bars represent the confidence interval for a confidence level of 95%. In all cases, the size distributions show two maxima, one corresponding to ultrafine particles, the other one to micrometric particles. The maximum corresponding to micrometric particles is located on the 12^{th} ELPI stage for SiO₂ and on the 8^{th} stage for TiO₂. They correspond to aerodynamic diameters of 8.05μ m and 1.21μ m, respectively. If particle sizes are expressed as mobility diameters, they are equal to 4.57μ m for SiO₂ and 0.660μ m for TiO₂. They are in good agreement with the number median diameters of the initial powders, measured by light





Fig. 9 Number size distribution of the generated aerosols at different sampling heights, for TiO₂ nanopowder (experiments E2, E9 and E10).

scattering, which are equal to 5.2μ m for SiO₂ and 0.800μ m for TiO₂. Hence, these maxima correspond to the re-suspension of the particles just in the same state as they are in the powder.

The ultrafine maximum is located in the 1^{st} or the 2^{nd} ELPI stages, showing the presence of primary particles or at least ultrafine aggregates in the aerosol. This fact has been checked by visualisation of the particles collected on the ELPI stages by a scanning electron microscope (SEM), Section 3.3.2.

In order to analyse the reproducibility of the measurements, experiments E1 and E2 were repeated 5 times and reproducibility was defined as the average of the ratio between the standard deviation and the averages of the particle number concentration for each stage (Eq. (3)).

Reproducibility =
$$(1/12) \cdot \sum_{i=1}^{12} (\sigma_i / \overline{x}_i)$$
 (3)

The calculated reproducibility values are 0.47 for E1 and 0.62 for E2. The maximum corresponding to micrometric particles is reproducible for both powders $(\sigma/\bar{x})_{12}=0.16$ for E1, $(\sigma/\bar{x})_8=0.076$ for E2. However, the maximum corresponding to ultrafine particles is variable, especially for TiO₂: $(\sigma/\bar{x})_1=1.5$, whereas it is equal to 0.63 for SiO₂. This could indicate that the ultrafine aggregate generation by breakage and/or erosion of the micrometric agglomerates could be somewhat dependent on the operating conditions such as temperature or humidity which were not controlled during the experiments.

3.3.2 SEM visualisation

The presence of ultrafine aggregates in the air after the powder fall was checked by removing particles down the ELPI stages and analysing the collected particles with a scanning electron microscope (SEM). **Fig.s 10.a** to **10.c** show two ultrafine aggregates of SiO₂ and one of TiO₂ found on the 1st, the 2nd and the 3rd stage of the ELPI device, respectively.

In all cases, two main remarks can be made. The first one is that ultrafine aggregates are actually present in the aerosol, as observed from the ELPI measurements. This result shows that the peak corresponding to ultrafine particles in the size distributions given by the ELPI measurement in the chamber is representative of this population and is not due to measurement fluctuations. The second one is that aggregates and agglomerates are not spherical. This is especially the case with silica, whose aggregates seem to have a fractal structure in several cases as in **Fig. 10.a**.

3.4 Influence of the height of fall

As shown in **Fig. 8**, neither the shape of the size distribution nor the position of the maxima is modified by the height of fall. However, increasing the height of fall increases the micrometric agglomerates concentration. On the other hand, the effect of the height of fall on the ultrafine aggregates concentration is not clear due to the problems of reproducibility of the experiments. This problem is stronger when the height of fall is small (50cm, experiments E5 and E8). In this case, the peak in the raw current



Fig. 10a SiO₂, 1st stage (×120000)



Fig. 10b SiO₂, 2nd stage (×150000)



Fig. 10c TiO₂, 3rd stage (×300000)

Fig. 10 SEM visualisation of ultrafine aggregates collected on the ELPI stages.

is small and the drift of the instrument becomes too important. This leads to a larger imprecision for experiments E5 and E8 than for the others.

Fig. 11.a shows the influence of the falling height

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on the mass concentration of the TiO₂- and the SiO₂generated aerosols. For the same volume of dropped powder, the dependence of mass concentration upon the falling height seems to be well described by a straight line for SiO₂, whereas for TiO₂, this dependence correlates with the square of this height. It is generally supposed in the literature²⁵⁻²⁹⁾ that the resuspension of micrometric particles depends upon a power of the falling height, h^{*a*}, where α varies from 0.4²⁹⁾ to 2.05²⁶⁾. Moreover, the value of α could depend on the type of the powder. Hence, our results for both powders seem to agree with previous works on micrometric powders.

3.5 Influence of the dropped mass

One should not be tempted to directly compare the concentration of the SiO₂ aerosol in experiments E1, E3 to E5 with that of the TiO₂ aerosol in experiments E2, E6 to E8. One could induce that TiO₂ is much dustier than SiO₂. In fact, the mass of TiO₂ that falls in those experiments is 8 times higher than that of SiO₂. It seems more judicious to compare the aerosol concentrations normalised by the mass of the fall. Results are shown in **Fig. 11.b**. Although normalised mass concentrations of TiO₂ are within the confidence interval of the SiO₂ values for a confidence level of 95%, these values are always smaller than those for SiO₂. We can therefore deduce that SiO₂ is a little dustier than TiO₂.

Another way to compare the two powders is to use the same mass of falling powder in the beaker of the experiment (and not the same volume). **Fig.s 11.a** and **11.b** represent the mass concentrations for experiments E11, E12 and E13, for which the dropped mass of TiO₂ was equal to the dropped mass of SiO₂ used in E1, E3 to E5 experiments. We can see that for the same dropped mass, the SiO₂ aerosol mass concentrations are about 5 times higher than those of TiO₂ aerosols. This consolidates the affirmation that the tested SiO₂ nanopowder is dustier than the tested TiO₂ one.

Fig. 11.b shows that increasing the dropped mass increases the normalised mass concentration. When the dropped mass is reduced, the proportion of powder impacting on a layer of previously dropped particles is reduced. Since this is the main mechanism of particle release, the quantity of re-suspended particles is lower, even when normalising the mass by the dropping mass. This observation agrees with Heitbrink *et al*'s work²⁸.







Fig. 11b Normalised values (aerosol mass concentration to the mass of the falling powder ratio).

Fig. 11 Influence of the height of fall and the dropped mass on the mass concentration of the generated aerosols.

4. Discussion

The average number of particles falling each time (n_{fall}) can be estimated from the mass of the falling powder (m_{fall}), the particle density (ρ_p) and the diameter (d_p):

$$n_{fall} = \frac{m_{fall}}{\rho_p \cdot (\pi/6) \cdot d_p^3} \tag{4}$$

By normalising the particle number concentration on the 1^{st} ELPI stage by n_{fall} , a value of 10^{8} part/cm³ in the aerosol per dropped particle was obtained for

SiO₂, whereas it is 10^{11} for TiO₂ (experiments E1 and E2, respectively). Although it is a rough estimation, it is a good indication of the fact that SiO₂ agglomerates break more easily than the TiO₂ ones. The reason seems to be the much more open structure of the SiO₂ agglomerates (see Fig. 2).

The void fraction, ε , of TiO₂ agglomerates can be estimated from the agglomerate density ρ_{agg} (measured by helium picnometry, **Table 2**) and the primary particle density ρ_{PP} , calculated from the crystallographic parameters³⁰⁾. It is found to be equal to



0.20.

$$\varepsilon = 1 - \left(\rho_{agg}/\rho_{pp}\right) \tag{5}$$

Since fumed silica is amorphous, the void fraction must be estimated using another method. It can be calculated from their fractal dimension, D_f , Eq.(7)³¹⁾. The average fractal dimension for SiO₂ agglomerates can be measured by laser scattering³¹⁾ with Mastersizer 2000, and it has been found to be roughly equal to 2.1; this method, however, cannot be performed with TiO₂ since TiO₂ agglomerates are too small, and very large scattering wave vectors, not available in the Mastersizer 2000, are needed³²⁾.

The solid-fraction-to-void-fraction ratio for SiO₂ can be calculated by Eq.(6). It is found to be $4 \cdot 10^3$ for SiO₂. This ratio is 1 000 times higher for TiO₂.

$$\frac{1-\varepsilon}{\varepsilon} \cong (d_{agg}/d_{pp})^{D_f - 3} \tag{6}$$

If the interparticle forces are attributed to van der Waals interactions³³⁾, then they are roughly equal for both SiO₂ and TiO₂.

$$F = \frac{A \cdot d_{pp}}{24 \cdot z^2} \tag{7}$$

Finally, the primary particle size for TiO₂ is smaller than for SiO₂ (see **Table 2**). Rumpf's theory³⁴) establishes that the tensile strength of an agglomerate (σ_1) depends upon its void fraction (ε), the interparticle force (*F*) and the primary particle size (d_{pp}):

$$\sigma_t = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{F}{d_{pp}^2} \tag{8}$$

Applying Rumpf's theory, we find that the tensile strength for TiO_2 agglomerates is at least 1000 times higher than for the SiO_2 ones. This could explain why SiO_2 agglomerates break more easily than the TiO_2 ones. However, attention should be paid to the fact that the hydrodynamic stresses are not necessarily the same.

In the future, the powder fall will be simulated by an Eulerian-Lagrangian approach, in order to study the mechanism of the particle release.

Nomenclature

Α	Hamaker constant	[J]
Cc	slip correction factor	[-]
\mathbf{d}_{a}	aerodynamic diameter	[m]
d_{agg}	agglomerate diameter	[m]
$\mathbf{d}_{\mathbf{b}}$	mobility diameter	[m]
\mathbf{d}_{p}	particle diameter	[m]
\mathbf{d}_{pp}	primary particle diameter	[m]
$E_{\rm ch}$	charger efficiency	[A/m3]

F	interparticle force	[N]
h	falling height	[m]
Ι	measured current	[A]
ľ	corrected current	[A]
m_{fall}	mass of powder falling	[kg]
Ν	particle number concentration in the air	•
		[particles/m ³]
\mathbf{n}_{fall}	number of particles falling	[-]
$\mathbf{\bar{x}}_{i}$	average of the particle number conce	ntration corre-
	sponding to the ith ELPI stage	[particles/m ³]
Z	interparticle distance	[m]
3	void fraction of an agglomerate	[-]
ρ_0	unit density: 1000 kg/m ³	
$ ho_{ m agg}$	agglomerate density	$[kg/m^3]$
$ ho_{ m p}$	particle density	$[kg/m^3]$
$ ho_{ m pp}$	primary particle density	$[kg/m^3]$
σ i	standard deviation of the particle count	t concentration
	on the ith ELPI stage	[particles/m ³]

 σ_{t} tensile strength of an agglomerate [N/m²]

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DEM-CFD Simulations of Fluidized Beds with Application in Mixing Dynamics[†]

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Abstract

Discrete element models of fluidized beds allow the accurate reproduction of many aspects of the flow of the fluid and solid phases on both microscopic and macroscopic scales. In the present paper, we first discuss some of the basics of the DEM-CFD model, along with an illustration of areas where it proved successful. Then, a discrete element computational code is used to analyse in detail the key mechanisms governing the mixing of solids in fluidized beds. Air fluidization of a mixture of glass ballotini and steel shots is simulated, and the steady-state concentration profiles are successfully validated with experimental data. By changing the density of the heavier component, the effect of the gas velocity in combination with the density ratio is investigated in terms of an equilibrium degree of mixing and a characteristic time to reach this condition. The maximum mixing achievable is found to depend strongly on the difference of density. For mixtures with a density ratio close to 3, full mixing is practically impossible due to the presence of a non-mixable region, rich in the heavy component, at the bottom of the bed.

Keywords: Fluidized Beds, Mixing, Segregation, Discrete Element Modelling, DEM-CFD

1. Introduction

Fluidized particle bed processing is a particularly efficient technology due to the high quality of fluidsolid contacting, low fluid pressure drop and prevention of dead zones or fluid channelling. It is used in a variety of industries such as oil, petrochemicals, minerals, pharmaceuticals and food processing. Accurate models which provide detailed information on the key phenomena occurring in the bed are necessary to properly design and operate fluidized beds at the desired conditions.

Computational models have proved effective in reproducing most of the features on both microscopic and macroscopic scales of complex units involving multiphase flows¹⁾. This is particularly true for first principles models, which typically are not directly ap-

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The flow of particulate solid-fluid mixtures in fluidized beds is characterized by a wide multi-scale nature in both time and, especially, space. There are quick and local phenomena such as the microscopic deformation of the particles during collisions as well as the development of the fluid boundary layer around particles, or events occurring at intermediate time and space scales such as bubble formation and growth, up to generally slow processes such as the mixing of solids, which typically involve the whole macroscopic scale of the system.

In the literature, computational models of solid-fluid systems have been developed aiming to represent one or more of the mentioned scales. They can be broadly subdivided into three categories: two-fluid, direct numerical simulations and discrete element models.

In an effort to capture the bubbling characteristics of fluidized beds by similarity to the boiling of fluids, two-fluid models (TFM) have been developed²⁾. They are based upon the assumption that the fluid and

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the particles as a whole can both be assimilated to fluids which dynamically interpenetrate, exchanging momentum as well as heat and mass. The continuity and momentum balance equations can be derived by locally averaging the equations governing the fluid and particles' motion on a scale much smaller than the macroscopic scale of the system but still larger than the particle diameter³⁾. The key point underlying these so-called Eulerian-Eulerian models is the way in which solid-solid and solid-fluid interaction are taken into account. The former is by far the most complex, as Newtonian behaviour requires the definition of a solid-phase pressure and viscosity and, usually, does not adequately represent the actual rheology of granular materials. Significant results in terms of bubbling bed hydrodynamics have been achieved by describing the solid-phase properties based on the Kinetic Theory of Granular Flows (KTGF)⁴⁾. Many of them have been summarized in a book of Gidaspow¹⁾. However, aspects such as multicomponent fluidization and highly polydisperse systems or fluidized beds of cohesive solids can be analysed by TFM only with extreme difficulty.

At the highest level of detail, the microscopic fluid motion (Direct Numerical Simulation or DNS) around each particle can be solved by means of numerical methods on very fine computational grids. Then, using the calculated stress tensor acting on each particle's surface to evaluate the drag force, Newton's second law for each particle in the system can be integrated to find the granular phase dynamics. This approach can be classified as really based on first principles, and is therefore considered as a reference for the other models. The huge computational intensity of such a method for large systems involving billions of particles and evolving slowly is evident. This explains why no simulations of representative fluidized beds have been reported in the literature, although fluid-solid flows involving 1204 particles in motion⁵⁾ and the sedimentation of 10000 spheres in a liquid have been already analysed⁶⁾. A similar degree of resolution can be achieved using an even smaller scale approach such as that of lattice-Boltzmann simulations⁷, a technique recently utilized to evaluate the drag force on clusters of spheres^{8,9}.

The discrete element approach represents a promising combination of the two approaches discussed above. It arises from coupling the Discrete Element Method¹⁰⁾ for the solid-phase hydrodynamics with a solution of the locally averaged Navier-Stokes equations for the fluid-phase flow field, similar to two-fluid models. The approach adopted for the solid phase is



Lagrangian, and the scale of analysis of the fluid and solid flow field is different. This allows a considerable advantage in that assumptions on the solid-phase rheology is unnecessary, as particles move due to wellcharacterized forces. However, the fluid drag acting on the particles has to be evaluated by a function of the instantaneous particle velocity, of the local fluid velocity and, most critical, of the local voidage around the particle considered. After the pioneering work of Tsuji and co-workers¹¹⁾, significant improvement and developments were introduced by Hoomans et al.¹²⁾, who used a hard-sphere collision model, and Xu and Yu¹³⁾, who introduced enhancements in the fluidparticle interaction terms. Since then, a considerable number of authors demonstrated the highly promising potentiality of the model, as recently reviewed by Deen et al.¹⁴⁾ and Zhu et al.¹⁵⁾.

In the present paper, we explore the capabilities of the DEM-CFD approach in the study of the key mechanisms governing mixing and segregation in fluidized beds of two solids differing in density. A brief summary of the DEM-CFD model implemented in our code will be presented first. Then, simulations will be used to represent the behaviour of a mixture of glass and steel particles fluidized by air, validating the results in terms of steady-state concentration profiles with experimental data. Finally, the influence of the gas velocity and density ratio of the mixture on the equilibrium and dynamic degree of mixing will be investigated.

2. The DEM-CFD Approach

2.1 Areas of application of DEM-CFD simulations

As compared to other modelling approaches derived on a larger scale, the DEM-CFD technique allows the relaxation of simplifying assumptions related to the particle-phase stress tensor. Collisions are treated on a mechanical basis and this leads to more realistic reproduction of the actual behaviour of the solids. One example of the power of this method is that there is no need to control values of the voidage in the computational cells. In fact, in TFM simulations, it is possible that unrealistic voidage values occur because they are calculated as continuous variables, so special constraining techniques have to be used to prevent excessively low values^{16, 17)}. In contrast, in DEM this condition is virtually impossible.

Another interesting feature of DEM models is the ability to provide results on the particle scale, thereby allowing careful analyses of the transient- and steady-

state momentum exchange between the solids. This capability makes it appropriate for applications in the study of surface erosion for immersed objects such as, e.g. heat exchanging tube bundles¹⁸⁾. The ability to track individual particles in the system also means that solids in which each particle is different from the others can be conveniently analysed. The instantaneous distribution of the components in fluidized beds of mixtures of solids can be obtained, allowing the characterization of typical mixing and segregation patterns (see, e.g. Refs.^{19, 20, 21)}). In the light of these promising results, the analysis of elutriation problems in fluidized beds of polydisperse solids as well as the characterization of the fluidization quality enhancement due to the addition of fines appear attractive fields for potential applications of the DEM technique.

Apart from purely hydrodynamic aspects, due to its relevance in industrial applications, heat exchange phenomena between fluidized beds and immersed objects or external walls has long attracted the interest of the research community, beginning with the pi-



oneering work of Mickley and Fairbanks²²⁾. However, despite the efforts, a real comprehensive insight into the phenomena and the ability to predict the overall heat transfer coefficient are still lacking. Further insight into the microscopic heat transfer mechanisms between bubbling beds and immersed objects is likely to be gained in the near future thanks to discrete element simulations, as proved by the encouraging results found by few workers^{23, 24)}.

Useful results are also expected to be found in purely fundamental studies on gas- and liquid-fluidization. It is well known that gas-fluidized beds of fine and light solids exhibit a distinction between the minimum fluidization and minimum bubbling conditions²⁵⁾. This has long been observed and studied, and a number of possible interpretations for it have been proposed (see, e.g. Refs.^{26, 27)}). The key point is whether stable and homogeneously expanded beds are actually fluid dynamically stable or whether it is the onset of cohesion, known to be inversely dependent upon the particle size, that is responsible for the homogeneous fluidization.

Table 1 Equations used in the DEM-CFD model

Solid phase	
$ma = mg + V_p \nabla p + f_d + \sum_{j=1}^{nc} f_{c,j}$	(T1)
$I\alpha = \sum_{j=1}^{nc} R \times f_{c,j}$	(T2)
$f_{cn} = \frac{4}{2} E^* \sqrt{R^* \delta_n} \delta_n$	(T3)

$$f_{\perp} = \frac{16}{G^*} \sqrt{R^* \delta} \delta. \tag{T4}$$

$$f_{d} = \frac{1}{2} \rho_{f} \left(\varepsilon u_{r} \right)^{2} \pi \frac{D_{p}^{2}}{4} C_{D} \cdot \varepsilon^{-\chi}; \qquad \chi = 3.7 - 0.65 \cdot e^{-0.5 \left(1.5 - \log 10 \left(\text{Re} \right) \right)^{2}}$$
(T5)

$$C_{D} = \left(0.63 + \frac{4.8}{\sqrt{\text{Re}}}\right)^{2}; \quad \text{Re} = \frac{\rho_{f}(\varepsilon u_{r})D_{p}}{\mu_{f}}$$
(T6)

Fluid phase

$$\frac{\partial \rho_j \varepsilon}{\partial t} + \nabla \cdot \rho_j \varepsilon \mathbf{u} = 0 \tag{T7}$$

$$\frac{\partial \rho_f \mathcal{E}u}{\partial t} + \nabla \cdot \rho_f \mathcal{E}uu = -\mathcal{E}\nabla p + \nabla \cdot \psi + f'_D + \rho_f \mathcal{E}g$$
(T8)

Two-way coupling

$$f'_{D} = \frac{\sum_{i=1}^{np} f_{d,i}}{\Omega} \tag{T9}$$



Among the disadvantages of DEM-CFD simulations, the computational intensity certainly occupies one of the first positions. With the CPU speed and memory resources available today (and in the near future), simulations of large-scale industrial units are not feasible. Probably, pilot-scale fluidized beds already exceed the capability of DEM-CFD-based models. However, distributed parallel computing on grids will certainly be beneficial in this regard.

2.2 The DEM-CFD model implemented

A Fortran90 code implementing the DEM-CFD strategy was developed in the last years²⁸⁾ and details of the model are briefly summarized here. A fully 3D DEM framework, including the possibility to insert internal walls, coupled to a 2D standard CFD algorithm for the flow of a compressible or incompressible fluid through the particulate phase are implemented. A summary of the equations used is reported in **Table 1**.

Within the DEM context, the translational and rotational motion of each individual particle is calculated by integrating the Newton-Euler differential equations (Eqs. (T1-T2)). The total force is obtained by summation of the gravitational force, the action of the fluid accounted for through a pressure-gradient-related term and a drag force contribution Eq. (T5)²⁹⁾ and, finally, the sum of the forces exerted by each of the bodies in contact with the particle considered, evaluated by a soft-sphere approach as in Eqs. $(T3-T4)^{30}$. As is common practice, additional contributions such as added mass, Basset's history, lift forces and so on are neglected here under the assumptions that for gas fluidization, the case under examination in the present work, they are very small compared to the other terms.

For the fluid-phase flow field, the spatially averaged continuity and momentum balance equations for multiphase fluid-solid systems are considered, following the approach proposed by Anderson and Jackson²⁾. Since the solid phase is dealt with via DEM, only the fluid-phase part of the original study is considered, using the coupling strategy as in Eq. (T9) and discussed elsewhere³¹⁾.

As far as post-processing of the results is concerned, mixing and segregation patterns in both steady-state and transient conditions are analysed in terms of a *mixing index*, as introduced by Lacey³²⁾ and defined as:

$$MI = \frac{\sigma_S^2 - \sigma^2}{\sigma_S^2 - \sigma_M^2} \tag{1}$$

where σ^2 indicates the variance of the concentration

distribution in the system at the time instant considered. The subscripts S and M denote perfectly segregated and mixed conditions, respectively, whose variances can be calculated by analytical expressions. The variance σ^2 of the system is estimated by decomposing the system into rectangular areas that are small compared to the macroscopic size of the system (one-tenth of the system width by roughly one twenty-fifth of the bed height in the present study), calculating the volumetric concentration of one component (flotsam in the present study) in each area and finally evaluating the average concentration and its variance in the distribution. The procedure used allows calculation of the instantaneous mixing index even in the presence of bubbles, as each small area adapts its height to include a fixed number of particles, thus virtually eliminating void zones.

3. Mixing of Solids in Fluidized Beds

In multi-component fluidized beds, the degree of mixing of the components is a complex function of the particle properties and operating parameters. In order to make use of DEM-CFD simulations to improve knowledge and understanding on mixing/segregation phenomena, a system composed of 15000 monosized spheres representing a two-component mixture of glass ballotini and steel shots was simulated. To distinguish between the two components, we follow the notation introduced by Rowe et al.³³, denoting the former as *flotsam (f)* and the latter as *jetsam (j)*.

A preliminary verification of the capabilities of DEM-CFD simulations to capture the essential features of the mixing in fluidized beds of two solids is carried out by comparing some experimental measurements with model predictions.

In order to avoid excessively large CPU times due to a fully 3D description of the system, in simulations the system is confined to a pseudo-3D geometry, i.e. spherical particles are allowed to move in a domain whose thickness equals the particle diameter, so that a limited number of particles are sufficient to represent the behaviour of the real system. However, the constraint for particles to move only along a plane determines a generally higher voidage than in real experiments, so that even key variables such as the minimum fluidization velocities can be significantly different. This prevents the possibility of directly comparing the phenomena occurring at the same absolute values of the superficial velocity, suggesting that proper scaling of variables is necessary. For this



purpose, and considering that the mixing patterns in a system can be expected to be observable at velocities higher than u_{mfj} for that system, the ratio of the actual velocity to this reference value $u^* = u / u_{mfj}$ appears a suitably scaled variable.

3.1 Comparison with experimental data

Experiments were performed³⁴⁾ on a mixture of glass ballotini and steel shots of comparable Sauter mean diameters ($D_f = 450 \ \mu m$ and $D_j = 433 \ \mu m$) in a 10-cm diameter column with a packed bed aspect ratio of 1.7. The axial profile of component concentration was determined by instantaneously cutting off the fluidizing gas feed, withdrawal of solids from the top of the column in horizontal layers 1.5-cm thick and subsequent measurement of the flotsam volumetric fraction in each layer.

Simulations were carried out considering a system similar to the one used in experiments, whose details are listed in **Table 2**. An initial packed bed condition was generated by letting particles fall randomly until complete settlement. As expected, due to the pseudo-3D geometry, the average voidage obtained ($\varepsilon_0 =$ 0.447) is noticeably different than that measured experimentally ($\varepsilon_0 = 0.403$). The minimum fluidization velocities of the jetsam component, calculated by using the pressure drop relationship proposed by Di Felice²⁹⁾, corresponding to these two voidage values are 68 cm s⁻¹ and 45 cm s⁻¹, respectively, and will be used as references for the calculation of the dimensionless velocities u^* .

Table 2 System data and parameters used in the simulations								
Column size	$4.0 \times 15 \times 0.0433 \text{ cm}^3$							
Number of cells	$30 \times 100 \times 1$							
Number of particles	15000							
Particle diameter	433 μm							
Flotsam density	2480 kg m ⁻³							
Jetsam density	7600 kg m ⁻³							
Young's modulus	0.1 GPa							
Poisson's ratio	0.25							
Friction coefficient	0.3							
Restitution coefficient	0.9							
Flotsam volumetric fraction	0.5							
Fluid density	1.2 kg m^{-3}							
Fluid viscosity	$1.8 \cdot 10^{-5}$ kg (m s) ⁻¹							
Time step	$2 \cdot 10^{-6}$ s							

Simulation results and experimental data were compared at various gas superficial velocities, starting from an initial flotsam-on-jetsam segregated configuration and extracting the component distribution after steady-state conditions are attained. **Fig. 1** shows the axial concentration profiles corresponding to dimensionless velocities around 1.17 and 1.31 ob-



Fig. 1 Experimental (left) and simulated (right) flotsam volumetric concentration along the dimensionless bed height. The top row corresponds to low velocity and the bottom row to high velocity, as indicated. Simulation conditions are reported in **Table 2**.

tained after about 30 s for the experiments and 25 s for the simulations. Note that significant differences exist in the actual velocities necessary to obtain similar u^* , e.g. 52 cm s⁻¹ in experiments and 80 cm s⁻¹ in simulations for the former value. Despite this, the agreement between the simulations and experimental observations may be considered as good. At the lower velocity, the model is able to capture the small amount of jetsam uniformly distributed in the flotsam $(0.95 < x_f < 1$ in the upper region of the bed). At the higher velocity, the experimental system is vigorously fluidized, exhibiting a small jetsam-rich region at the bottom of the bed and a roughly uniform upper zone, although the flotsam fraction tends to increase slightly moving towards the top of the bed. The simulated bed shows a concentration profile that follows the same trend, though with a slightly worse agreement than the low-velocity case.

In order to check the influence of the initial configuration adopted on the steady-state degree of mixing, it is useful to compare the time evolution of the system starting from a fully segregated or fully mixed bed. However, although concentration profiles provide detailed information on the mixing and segregation patterns, they prove inconvenient to carry out analyses in transient conditions. For this purpose, an overall measure of the mixing state such as the mixing index defined in Eq. (1) appears more appropriate.

In **Fig. 2**, the time evolution of the instantaneous mixing index is reported, as obtained by post-processing DEM-CFD results, for velocities of 80 cm s⁻¹ ($u^* = 1.18$) and 90 cm s⁻¹ ($u^* = 1.32$) and starting from the two extreme configurations. It is shown that for



Fig. 2 Evolution of the degree of mixing from initially mixed ($MI \approx 1$) and segregated ($MI \approx 0$) configuration at the two dimensionless velocities indicated. Simulation conditions are reported in **Table 2**.



both values of the superficial velocity, a similar ultimate value of the mixing index is found irrespective of the initial *MI*. Similar indications were obtained following an analogous procedure by Feng et al.³⁵⁾, by DEM simulations and experiments. They found that the degree of mixing of two solids differing only in size eventually reaches a value of dynamical equilibrium, irrespective of the initial condition, but depending on the gas velocity. It is therefore expected that a unique equilibrium state exists at a given velocity for mixtures of solids differing in both density and size.

The presence of an equilibrium state allows measurements and simulated results obtained at different times, typically of the order of minutes for experiments and tens of seconds for simulations, to be compared as in **Fig. 1**, as long as transient phenomena have vanished. The overall agreement confirms that despite the unavoidable simplifying assumptions, the model is able to reproduce the key mechanisms by which mixing or segregation occurs in multi-component fluidized beds.

3.2 Mixing dynamics: effect of the gas velocity and the density ratio

To investigate the hydrodynamic effects on solids mixing, simulations were carried out changing the gas velocity from values above $u_{mf,i}$ up to $u^* = 1.47$ (**Fig. 3**), the latter corresponding to a condition where particles reach the top of the simulated domain. It can be observed that around a dimensionless velocity of about 1.25, the equilibrium state of the bed changes from predominantly segregated at low velocities to well mixed at higher values, i.e. when particles undergo vigorous bubbling.



Fig. 3 Time evolution of the mixing index at the indicated gas dimensionless velocities. Simulation conditions are reported in Table 2.



A clearer picture is obtained by looking at the instantaneous particles' positions, flotsam composition colour map and axial profile along the dimensionless height, as reported in **Fig. 4** for gas velocities of 85 and 100 cm s⁻¹, corresponding to $u^* = 1.25$ and $u^* = 1.47$, respectively. **Figs. 4a** and **4b** are snapshots of the state of the system after 25 seconds of simulation, showing the flotsam particles in grey and the jetsam



Fig. 4 Simulation snapshots (a,b) showing flotsam (orange) and jetsam (black) particles, flotsam volumetric fraction colour map (c,d) and flotsam fraction profile along a dimensionless bed height (e,f), at t = 25 s. Plots in the left column: u* = 1.25; plots in the right column: u* = 1.47.



in black. The colour maps (**Figs. 4c,d**) show the subdivision of the particle bed into small areas containing approximately the same number of particles (60 in this case) and, on a colour scale, the flotsam concentration in each area. It is worth noting how bubbles are dealt with through higher cells. The same arrangement is utilized to calculate the variance of the distribution and, thus, the mixing index. Using the same subdivision and averaging the concentrations layer by layer, a volumetric fraction profile along the bed height (**Figs. 4e,f**) is obtained.

With respect to the steady-state information contained in **Fig. 3** ($MI^* = 0.62$ at $u^* = 1.25$ and $MI^* =$ 0.89 at $u^* = 1.47$), this set of plots provides a more complete view on the state of the system. In particular, in the lowermost part of the bed, a region rich in jetsam is found for both velocities, despite the fact that the higher velocity is well above the jetsam minimum fluidization velocity. The presence of these zones determines a large deviation of the concentration profile from the value exhibited in the rest of the bed (**Figs. 4e,f**). Consequently, the large variance of the concentration distribution leads to values of the mixing index that can hardly approach unity, especially at $u^* = 1.25$.

The glass-steel particle mixture showed that even at a velocity considerably higher than u_{mfj} , full mixing can be extremely difficult to accomplish. This could be attributed to the high density ratio of the mixture (about 3.1) that is known to drive the system towards segregation. It therefore appears interesting to analyse the effect of the density difference in combination with that of the velocity on the equilibrium degree of mixing. For this purpose, a comprehensive set of simulations was carried out considering mixtures of particles with the same properties as those reported in **Table 2** except for the density of the jetsam component, which was allowed to vary. In particular, considering a reference density of the glass ballotini, jetsam-on-flotsam density ratios ranging from 1 (degenerate case) to 3 were set by increasing the density of the other component. The corresponding minimum fluidization velocity of the jetsam, calculated at the packed bed voidage, increases accordingly from about 27 cm s⁻¹ to about 66 cm s⁻¹. **Table 3** reports the values of the dimensionless velocities for all cases analysed and serves as a reference for the results listed in **Tables 4** and **5**.

Analysis of the results allowed recognition, as a common feature, of a time evolution of the mixing index closely resembling profiles typical of an exponential dependence towards an asymptotic value. The two parameters of this type of curve are the steady-state mixing index *MI*^{*} and the characteristic time τ . Thus, the simulated evolutions of the degree of mixing of the system, starting from a fully segregated configuration, were post-processed to extract these two parameters. The steady-state mixing index resulted from time averaging the values on the plateau, whereas a non-linear fit procedure was applied in each case to determine the characteristic times.

The results for *MI*^{*} are collected in **Table 4**, from which, despite the coarse discretization of the velocity range, it can be seen that the highest values of the mixing index are achieved at velocities that increase with the density ratio. This trend can also be observed in terms of dimensionless velocity u^* . For example, a mixing index of 0.83 is found at $u^* = 1.22$ for a mixture with $\rho_j/\rho_f = 1.8$ whereas, to achieve a similar index for a mixture with the maximum density ratio considered, a velocity u^* higher than 1.44 is necessary.

ρ _j / ρ _f	$u_{mf,j}$	$u [\mathrm{cm} \mathrm{s}^{-1}]$												
	[cm s ⁻¹]	40	45	50	55	60	65	70	75	80	85	90	95	100
1.0	27.5	1.45	1.64	1.82		2.18		2.55						
1.2	32.2	1.24	1.40	1.55		1.86		2.17						
1.4	36.6	1.09	1.23	1.37	1.50	1.64	1.78	1.91						
1.6	40.9	0.98	1.10	1.22	1.34	1.47	1.59	1.71						
1.8	45.0			1.11	1.22	1.33	1.44	1.56	1.67	1.78	1.89			
2.0	49.0			1.02	1.12	1.22	1.33	1.43	1.53	1.63	1.73	1.84		
2.2	52.8					1.14	1.23	1.33	1.42	1.52	1.61	1.70		
2.5	58.3						1.11	1.20	1.29	1.37	1.46	1.54	1.63	1.72
2.8	63.7							1.10	1.18	1.26	1.33	1.41	1.49	1.57
3.0	66.1								1.13	1.21	1.29	1.36	1.44	1.51

Table 3 Dimensionless velocities for the combinations of density ratios and actual velocity investigated


Table 4 Steady-state mixing index values obtained for various density ratios and gas velocities

0./0.	Umf,j						1	<i>u</i> [cm s ⁻¹]]					
p_1 / p_f	[cm s ⁻¹]	40	45	50	55	60	65	70	75	80	85	90	95	100
1.0	27.5	0.99	0.99	0.99		0.99		0.99						
1.2	32.2	0.99	0.99	0.99		0.99		0.99						
1.4	36.6	0.54	0.90	0.93	0.97	0.99	0.99	0.99						
1.6	40.9		0.27	0.71	0.91	0.94	0.96	0.96						
1.8	45.0			0.23	0.83	0.88	0.92	0.94	0.96	0.96	0.97			
2.0	49.0			0.10	0.52	0.83	0.86	0.92	0.93	0.94	0.97	0.96		
2.2	52.8					0.43	0.79	0.84	0.90	0.90	0.93	0.93		
2.5	58.3						0.14	0.56	0.75	0.85	0.87	0.89	0.93	0.95
2.8	63.7							0.13	0.47	0.74	0.80	0.85	0.87	0.91
3.0	66.1								0.14	0.33	0.52	0.78	0.82	0.82

Table 5Characteristic mixing times in seconds. Bold values resulted from a fit with a determination factor $R^2 < 0.95$

	$u_{\mathit{mf},j}$						1	<i>u</i> [cm s ⁻¹]]					
p_j / p_j	[cm s ⁻¹]	40	45	50	55	60	65	70	75	80	85	90	95	100
1.0	27.5	1.16	0.82	0.67		0.62		0.51						
1.2	32.2	6.55	1.44	1.27		0.61		0.55						
1.4	36.6	14.4	3.76	1.67	1.17	1.11	0.83	0.52						
1.6	40.9	7.52	3.06	3.17	2.12	1.72	0.81	0.95						
1.8	45.0			4.89	5.92	2.33	1.81	1.18	0.92	0.73	0.72			
2.0	49.0			11.0	13.6	7.72	3.04	1.81	1.18	0.90	0.81	0.74		
2.2	52.8					7.38	4.95	3.14	2.61	1.35	1.26	0.87		
2.5	58.3						2.87	7.60	3.86	2.09	1.61	1.51	1.16	0.86
2.8	63.7							6.13	6.95	4.00	3.97	1.99	1.48	1.51
3.0	66.1								3.60	5.18	3.97	2.96	3.03	2.37

The characteristic times resulting from the fitting procedure are reported in **Table 5**. It shall be remarked that, different from MI*, the characteristic time depends on the initial condition. As already mentioned, simulations were carried out starting from an initially segregated configuration, so that τ assumes the meaning of characteristic *mixing* time. For most of the systems considered, monotonically decreasing mixing times are found as the velocity is increased. In particular, it is interesting to note how, for a given mixture, characteristic times may change by more than one order of magnitude, moving from slightly to well above u_{mfj} . This is particularly evident for density ratios close to unity. However, some values appear in contrast to the expected decreasing trend, especially at the lower velocities. Most of these correspond to cases for which a determination factor R^2 lower than 0.95 results from the fit, indicating that these systems follow an evolution not well represented by the simplified model assumed, and interpretation of the results needs to be done with caution.

It appears evident that a normalization of the val-

ues reported in **Table 5** would help to understand the mixing phenomena and better characterize the dependence on the velocity. However, in contrast to what has been done for the velocity, individuation of a reference value is not trivial. Further work addressing this aspect is in progress.

6. Conclusions

After introducing discrete element models of fluidized beds and discussing their properties, a DEMbased code was extensively utilized to investigate the role of gas velocity and density ratio on the solids mixing in fluidized beds of two components of different density. The mixtures considered, characterized by density ratios spanning 1 to 3, were fluidized at velocities higher than the minimum fluidization velocity of the jetsam and up to about twice this value. The results, in terms of steady-state mixing index and characteristic time, showed that full mixing can be unachievable for high density ratios, due to the presence of a jetsam-rich region at the bottom of the



bed. From a dynamic point of view, it was shown that, depending on the gas velocity, the time necessary to move from full segregation to the equilibrium state can vary by more than one order of magnitude.

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Notation

- a acceleration, m s⁻²
- CD drag coefficient, dimensionless
- D diameter, m
- E^* equivalent Young's modulus, Pa
- f modulus of force, N
- f force, N
- f_d cumulative drag force per unit volume, N m⁻³
- g gravitational acceleration, m s $^{-2}$
- G^* equivalent shear modulus, Pa
- *h* vertical coordinate, m
- H particle bed height, m
- I particle moment of inertia, kg m²
- *MI* Lacey mixing index, dimensionless
- MI* steady-state Lacey mixing index, dimensionless
- *m* mass, kg
- *nc* number of contacting particles, dimensionless
- *np* number of particles in the control volume, dimensionless
- *p* fluid pressure, Pa
- R radius, m
- *R* vector pointing from particle centre to contact point, m
- R^* equivalent radius, m
- Re Reynolds number, dimensionless
- t time, s
- u modulus of the fluid velocity, m s⁻¹
- u fluid velocity, m s⁻¹
- u_r fluid relative to particle velocity, m s⁻¹
- v particle velocity, m s⁻¹
- *V* volume, m³
- w horizontal coordinate, m
- *x* volumetric concentration, dimensionless

Greek letters

- α angular acceleration, rad s⁻²
- δ displacement, m
- ε voidage, dimensionless
- μ_f fluid viscosity, Pa s
- *v* Poisson's ratio, dimensionless

- ρ particle density, kg m⁻³
- ρ_f fluid density, kg m⁻³
- σ^2 variance of the concentration distribution, dimensionless
- ψ deviatoric stress tensor, Pa
- τ characteristic time, s
- χ exponent in Eq. (T5), dimensionless
- Ω control volume size, m³

Subscripts

- 0 initial
- c contact
- d drag
- D cumulative drag
- *f, j* flotsam, jetsam
- *mf* minimum fluidization
- *n*, *t* normal, tangential *p* particle
- *S,M* segregated, mixed

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Author's short biography



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Comparative Study of Two Processes to Improve the Bioavailability of an Active Pharmaceutical Ingredient: Kneading and Supercritical Technology[†]

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Abstract

Two processes have been developed for the enhancement of bioavailability of a poorly-soluble active substance, Eflucimibe by associating it with γ -CD (γ -cyclodextrin).

In the first process (process a), Eflucimibe was added to an aqueous slurry of CD, in a kneading device. The evolution of the transformation was followed by DSC, FTIR, Eflucimibe dissolution kinetics, as well as semi-solid state change of the mixture. An optimization of the process was performed and a prevision of the scaling-up was made using dimensionless numbers. This process is simple and robust. It can be compatible at the industrial scale with a good economy and appropriate control.

In the second process (process b), Eflucimibe and CD are co-crystallized using an anti-solvent process, dimethylsulfoxide being the solvent and supercritical carbon dioxide being the anti-solvent. Then, the co-crystallized powder is held in a static mode under supercritical conditions for several hours. A final stripping step, is used to extract the residual solvent. The coupling of the first two steps brings about a significant synergistic effect to improve the dissolution rate of the drug.

Both processes resulted in a strong acceleration of the in vitro dissolution rate of the drug. Finally, in an in vivo test, these two processes appeared to be very effective, process (a) and (b) giving respectively an 8-fold and 11-fold increase in bioavailability.

Keywords: Eflucimibe, Cyclodextrin, Kneading, Supercritical CO2, Scale-up, Bioavailability

Introduction

An important parameter in pharmaceutical formulations is the bioavailability of the active substance. Many new Active Pharmaceutical Ingredients (API) are very poorly water soluble. Their absorption by the human organism is therefore extremely low and difficult to control. In case of very low solubility, one of the first rule of the formulation process is to increase this bioavailability by enhancement of the dissolution rate and apparent solubility. A way to reach this goal is to associate these low-solubility active molecules with cyclodextrins (CDs) by forming inclusion complexes.

Although many articles describe the interactions between active molecules and CD only few papers deal with the processes used for such complexes production. Four classes of processes can be distinguished: liquid (co-precipitation, co-evaporation, spray-drying, freeze-drying, neutralisation), using supercritical CO₂, semi-solid (kneading), and solid (sealed-heating, high energy co-grinding). Anyhow, the success of a drug delivery technology and of the process used to produce it, are highly dependent on whether it can be scaled-up, is reproducible and allows for cost-effective manufacturing. This paper is focused on the comparison of two of them: kneading (a) and supercritical fluid processing (b), in the case of the complexation of Eflucimibe with γ -cyclodextrins (γ -CDs).

A first description of the kneading process has been presented by Gil¹⁾ and Hutin²⁾. The use of supercritical carbon dioxide (SC-CO₂) for particle generation of pharmaceuticals and for improving their

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Fig. 1 Structure of Eflucimibe.

Table 1	Biopharmaceutics	Classification	System
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	High Solubility	Low Solubility		
High Permeability	Class I	Class II		
Low Permeability	Class III	Class IV		

bioavailability is well documented³⁾.

These processes (a) and (b) will be described in the case of Eflucimibe, a highly potent acyl-coenzyme A O-acyltransferase (ACAT) inhibitor with the molecular formula $C_{29}H_{43}NO_2S$ (**Fig. 1**), treating hypercholesterolemia. Its structure and extreme hydrophobicity confers to this molecule a very poor solubility in water.

In terms of solubility and permeability, according to the Biopharmaceutics Classification System BCS ⁴⁾, it can be considered as a Class IV compound (**Table 1**), with low solubility in aqueous media and low permeability through the intestinal mucosa. The result is a high variability in blood level when formulated in lactose capsules¹⁾ and a poor bioavailability.

 γ -CD is a cyclic octasaccharide (**Fig. 2**) obtained by enzymatic degradation of starch, consisting of 8 D-Glucose units, and presenting an hydrophilic external wall and an hydrophobic internal cavity that can receive organic molecules.

This configuration allows to perform the dissolu-



Fig. 2 Structure of γ cyclodextrin.

tion of the drug substance in aqueous solutions and to liberate it by dissociation of the complex, followed by the absorption of the drug in the circulatory system (**Fig. 3**)

Eflucimibe was provided by Pierre Fabre Laboratories (Castres, France). *y* -CD was purchased from Wacker-Chemie GmbH (München, Germany).

1. The Kneading Process

The kneading process can be considered as a mechanochemical process carried out in the presence of a small amount of solvent (water or other) that acts as lubricant for the molecular diffusion. This catalyst behaviour of the solid sate process, results in a smooth transformation of the reactants into the final products avoiding the contamination of the active ingredient by secondary transformation not suitable in the production of pharmaceutical products⁵.

We applied this process to the complexation of Eflucimibe with γ -CD.



Fig. 3 Mechanism of the API (Active Pharmaceutical Ingredient) liberation from its complex with cyclodextrin.



Experimental set-up and process

Kneading equipment

The kneading equipment was a 316 L stainless steel Aoustin[®] kneader with dual Z blades (**Fig. 4**). Those dual blades take up an important relative volume and the space between the wall of the kneader and the side of the blades is very small, initiating large shearing effects. Two scales of this apparatus were used : MX1 with a nominal capacity of 1.5 L and MX2 with a nominal capacity of 3 L.

Kneading process

The blade speed of the kneader was fixed at 50 rpm. γ -CD was introduced in the kneader bowl kept at 305 K (optimized temperature²⁰); Purified water (1 ml.min⁻¹) is added to a mixture of Eflucimibe/CD at a (1:2) molar ratio and the blend is kneaded thoroughly while following simultaneously the tempera-



Several approaches are available for controlling



Fig. 4 Kneading equipment.



Fig. 5 Torque and temperature versus time during complexation of Eflucimibe and cyclodextrin.



Fig. 6 Characterisation of kneading process evolution.



the process at one scale and for scaling-up to another scale. The experimental design approach can be a powerful tool to model processes. Three input variables that are water extent, blade speed and temperature have already been selected. Two output variables are also selected : dessolution rate of the product and the extent of inclusion determined by DSC. The principle is to determine for each output variables a model involving each input variables and their interactions. By comparison of the models it is possible to optimise the different input variables to obtain a compromise between them and achieve the desired results of the output variables. The effect of the following process parameters on the extent of inclusion and solubility enhancement (Fig. 7) has been investigated by means of an experimental design analysed at MX1 scale which allows the definition of an optimised experiment with those operating conditions.

DSC and thermoanalytical procedure for the determination of the percentage of transformed Eflucimibe (Y)

Thermal analysis by DSC was carried out using a Perkin Elmer DSC 7 apparatus. Samples of 3 mg were introduced into sealed aluminium pans.

DSC scans were performed in triplicate under nitrogen, at a heating rate of 5 K.min⁻¹ in the temperature range of 303 K to 378 K. Heats of fusion were automatically determined by the software following calibration with Indium (28.4 J.g⁻¹), using integration of the areas under the DSC endothermic peaks of melting. A thermoanalytical procedure can be applied to quantify the interaction yield⁶). F is the fraction by weight of Eflucimibe in the starting mixture and N,



Fig. 7 Eflucimibe dissolution kinetics.

the fraction by weight of Eflucimibe in the initial state after the kneading step. The percentage of transformed Eflucimibe after interaction, Y, is calculated according to equation (1)

$$Y = 100 - 100 \left(\frac{N}{F}\right) \tag{1}$$

where N is calculated according to DSC results and equation (2)

$$N = \frac{\Delta H_{eflucimibe\ melting\ after\ kneading\ step}}{\Delta H_{pure\ eflucimibe\ melting}}$$
(2)

FTIR spectroscopy and spectroscopic procedure to follow Eflucimibe interaction

The infrared spectra were recorded on a Nicolet FTIR spectrometer. The analysed component was dispersed in KBr medium in solid state before acquisition.

The Eflucimibe interaction with CD led to a decrease of Eflucimibe band intensity. In order to quantify this modification, the Beer-Lambert law was applied by the determination of Log I₀/I with I₀ corresponding to the absorbance at 1572 cm⁻¹ (spectral region where Eflucimibe and CD do not present spectral band) and I corresponding to absorbance at 1537 cm⁻¹ (spectral region where only Eflucimibe presents spectral band).

Determination of Eflucimibe solubilisation kinetics

The Eflucimibe solubilisation kinetics were determined with samples corresponding to 50 mg of Eflucimibe. These samples were added to 100 ml of the solubilisation medium corresponding to an aqueous solution containing 5 % (w/V) of sodium lauryl sulfate. The samples were continously stirred while remaining in a water bath at 310 K (normalized temperature for pharmaceutical test). At various time intervals, samples were withdrawn and filtered through $0.45 \,\mu$ m membrane. The amount of Eflucimibe dissolved was determined by HPLC using UV detection at 220 nm. Acetonitrile and purified water at 82 : 18 V/V was run at 1ml.min⁻¹ flow rate through a reverse phase C8 column.

Use of dimensionless numbers to study the scaling-up

The principle of the methodology is to solve the relationship on one scale and then to use it to calculate the power required on another scale to obtain a same finished product quality.



We applied the Buckingham theorem⁷; the main physical variables are found to be:

The power number :	$Np = \frac{\Delta P}{\rho . N^3 R^5}$
The Reynolds number :	$\operatorname{Re} = \frac{\rho.NR^2}{\eta}$
The Froude number :	$\operatorname{Fr} = \frac{RN^2}{g}$
The fill ratio of the kneader :	H/R
The blade size :	(R)/L
Where g is the gravitational of	constant, R, L re

Where g is the gravitational constant, R, L respectively the blade, length and radius, N the blade rotational speed, h the height of powder, ρ the bulk density of the powder, η the viscosity and ΔP the net blade power consumption that is to say total power less power required to stir the dry powder.

Hence, the physical phenomena before complexation can be described by a relationship as follows (equation 3) :

Np = f(Re, Fr, H/R, (R)/L). (3)

Results and discussion

The process is fast and evolves as shown on **Fig. 6** The complexation induced a dramatic increase of

Eflucimibe dissolution rate (**Fig. 7**)

An optimization of the process was performed and a prevision of the scaling-up was made using dimensionless numbers.

As the viscosity is unknown, it was replaced by the mean torque before complexation and the dimensionless Re becomes a pseudo-Reynolds ψRe^{8} .

The relationship between the power number and the other dimensionless group is established by **Fig. 8** and equation 4:

Np = k (
$$\psi$$
 Re.Fr.(H/R).(R/L))⁻ⁿ
k = 338.4 (m³.s)⁻ⁿ and n = 0.84 (4)

Where the correlation coefficient is 0.99 for 17 experiments.

One experiments has been repeated three times under the same conditions to test the reproducibility of the process. The resulting points on the scale-up relationship (**Fig. 8** and **9**) were very close to another.

Three experiments carried out under the optimised conditions give good results in agreement with the dimensionless relationship.

Those equations are applicable for a series of geometrically similar kneader of different sizes. It was possible to check those predictions at a twice scale, with an MX2 kneader. Plot of Np versus the combination of the four remaining dimensionless numbers are presented in **Fig. 9** with those last experiments. The relationship between the power number and the other dimensionless group stay the same as equation 4 where the correlation coefficient is 0.99 for 17 experiments at MX1 scale and 6 experiments at MX2 scale.

The results show that the process is fast, simple and robust. Using dimensionless numbers it can be conducted at the industrial scale with a good economy and appropriately monitored using technologies recommended by FDA's Process Analytical Technology (PAT).

2. The Supercritical Process

SC-CO₂ has recently emerged as a new medium for complexation with CD due to its properties of improved



Fig. 8 Ln (Np) versus Ln (*w*Re.Fr.H/R.R/L) at MX1 scale.



Fig. 9 Ln (Np) versus Ln (ψ Re.Fr.H/R.R/L) experimental results at the MX2 scale.





Fig. 10 Supercritical equipment.

mass transfer and increased solvating power^{9), 10)}. We have implemented a new process by combining a co-crystallisation anti-solvent process SAS¹¹⁾ with a maturing step⁹⁾ and adding finally a stripping step to extract residual solvent.

Experimental set-up and procedures

All experiments were performed in a flexible supercritical machine (Separex, France) shown on **Fig. 10**.

Dimethylsulfoxide (DMSO) as the solvent and SC-CO₂ as the antisolvent were used in the SAS experiments. CD and Eflucimibe were both dissolved in DMSO. This solution was injected into the CO₂ stream in the mixing chamber of a nozzle (Spraying System, France), and sprayed into an expansion vessel. The powder formed was collected in a porous bag placed in the expansion vessel after depressurisation.

For the maturing step, 7 g of Eflucimibe/CD powder (with a molar ratio of 1/2) were wetted by 2.33 g of water (corresponding to 25 mass% of total powder) and placed in a 2 l autoclave. This vessel was filled with SC-CO₂ at the desired pressure and temperature and left for several hours without any agitation. The powder was recovered after gentle depressurisation.

In the final stripping step, the powder was submitted to a continuous flow of SC- CO₂ for two hours in a stainless steel basket.

Powder characterisations

After each step, composition of the powder obtained was determined. Eflucimibe content was measured by HPLC, residual DMSO content by GPC and water content with a Karl Fisher titrator. γ -CD content was then calculated from all these results. Eflucimibe, DMSO and water contents are given in mass percentage of the total powder mixture.

The DSC thermograms were performed on a Perkin-Elmer, DSC-7 calorimeter equipped with a thermal flux cell device. The DSC patterns of the samples (2-3 mg) were obtained between 313 K and 413 K at a heating rate of 5K/min under a N₂ gas stream. They are shown in Fig. 11, for the initial powder mixture (Fig. 11a) and after each processing step (Fig. 11 **b**, **c** and **d**). By integrating the melting peak of drug in DSC thermograms, which is generated by the crystalline form of the powder, and knowing independently the total drug content, it is possible to calculate the amount of non-crystalline Eflucimibe. This last one corresponds to the drug not visible on DSC thermogram, hence drug molecule likely implied in interactions with CD and microcrystalline aggregates dispersed among CD matrix. It acts as an indicator of the level of drug/CD complexation.

To estimate the dissolution rate improvement, *in vitro* dissolution studies were performed at 310 K as described elsewhere¹²⁾. The dissolution rate is defined as the Eflucimibe content dissolved in the medium after a fixed time, expressed in μ g of Eflucimibe per ml of solution. The dissolution curves are





Fig. 11 DSC curve of physical mixture (a); co-crystallised powder (b); powder after co-crystallisation and maturing (c); powder after co-crystallisation, maturing and stripping (d).

presented on **Fig. 12** for the physical mixture (a), and after each processing step (b, c and d).

Co-crystallisation step

This step has been conducted according to previously published procedure by Rodier et al.¹³⁾. On ESEM microphotographs (not shown) an intimate mixture of both components can be seen: large CD particles with drug fibres deposited on them.

The Eflucimibe melting temperature (**Fig. 11a**) of the physical mixture with γ -CD was found to be 402 K. For the co-crystallised powder, we observed a melting temperature of 399.1 ± 0.6 K (mean of 29 experiments). In addition, a part of Eflucimibe contained in the mixture after co-crystallisation is not visible by DSC.

After this step, the dissolution rate was higher than that of the physical mixture with the same profile (**Fig. 12b**). It was no longer correlated to the specific surface of the powder, which can be tuned by the operating conditions with Eflucimibe alone¹⁴) but not in the presence of CD. For instance, the mass ratio CO_2 /DMSO, had no effect on the composition and dissolution rate of the resulting powder. On the contrary, decreasing the mole ratio of Eflucimibe to CD in the initial mixture from 1/1 to 1/3 increased the drug crystallisation yield from 40 % to 70 % (w/w). This yield is defined as the ratio between the mass of powder formed and the mass of powder initially dissolved in DMSO.

Maturing step

This process, first described by Van Hees et al ⁹⁾ is very effective for complexation. Several drugs have been processed successfully with this method^{15, 16)}. After this step, drug fibres are not so clearly distinguishable from CD particles on microphotographs (not shown). Furthermore, only a very small Eflucimibe melting peak can be seen on DSC thermogram (**Fig. 11c**). A strong increase in the drug dissolution profile is noticed with a peak at 500mg/ml



Fig. 12 Dissolution curve of co-crystallised powder (b); powder after cocrystallisation and maturing step (c); powder after co-crystallisation, maturing step and stripping (d); physical mixture (a).



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T, K	P, MPa	$ ho$, kg/m 3	μ, Pa.s	${f S_{Eflucimibe/CO2},}\ imes 10^7$, mole fraction	Non-crystalline Eflucimibe, mass%	Dissolution rate at 2h, µg/ml
373	10	278	2.40 10-5	54	98.8	678.4
313	10	564	$3.78 \ 10^{-5}$	1	88.5	522.9
373	30	644	4.70 10 ⁻⁵	571	88.6	503
353	30	734	5.41 10 ⁻⁵	169	84.1	596.5
313	20	830	6.16 10 ⁻⁵	5	82.3	487.9
333	30	831	$6.26 \ 10^{-5}$	46	83.2	499
212	30	028	7 20 10-5	11	73.8	226.0

Table 2 Effect of the maturing step on Eflucimibe-crystalline content and dissolution rate as a function of CO₂ density and viscosity

Table 3 Maturing step, dissolution rates and specific surface areas as a function of the initial mixture

Eflucimibe	Initial powder	SAS treated	Co-crystallised
Cyclodextrin	Initial Cavamax	SAS treated	Co-crystallised
BET specific surface of the mixture, m ² /g	2.3	17.1	8.6
BET specific surface of the Eflucimibe alone, m^2/g	7.5	54	
Dissolution rate at 2 hours of the mixture, just after mixing the powders, μ g/ml	19	69	100
Dissolution rate at 2 hours of the mixture, after adding maturing water, μ g/ml	33	58	88
Dissolution rate at 2 hours of the mixture, after the maturing step, μ g/ml	141.6	150.3	670

(Fig. 12c).

The influence of CO_2 density and viscosity was evaluated on the dissolution rate. Both the noncrystalline drug content and the dissolution rate increase when CO_2 density and viscosity decrease as shown on **Table 2**. Besides, the non-crystalline drug content is not linked to the solubility of the active substance in CO_2 . This suggests that mass transfer would limit the maturing step and that CO_2 solvent power is not a crucial point.

In addition, the influence of the operating time of this static step has been studied. A classical saturation-shape evolution was noticed: up to 6 hours, the powder composition is modified and dissolution kinetics increases, while both remain constant beyond 6 hours.

We have also studied the effect of the initial mixture composition. Three mixtures having the same mass composition were wetted, placed in the autoclave and submitted to the same conditions (30 MPa, 373 K, 16 hours). The first mixture was composed of the initial drug and CD, the second of drug and CD crystallised separately by SAS process and the third of drug and CD co-crystallised by SAS. **Table 3** shows the dissolution rate after 2 hours for each mixture at different stages: just after mixing, just after adding water and after the static maturing step.

This table provides also the specific surface area of the mixtures. Comparison of the first and the second mixtures before the static step confirms that the amount of dissolved drug increases with the specific surface area. Comparing the second and the third mixtures, it appears that the amount of dissolved drug is no longer correlated to the specific surface area. Therefore, the static step may enhance the dispersion of the drug into the CD matrix and thus it may increase the dissolved drug concentration in all cases. However, the improvement of the compound dissolution is significantly higher for the before hand co-crystallised powder. In conclusion, a strong synergistic effect is obtained by coupling the co-crystallisation and the static steps.

Stripping step

After the stripping step, a homogeneous aspect of the powder was observed (not shown). This can be linked with the complete disappearance of the Eflucimibe melting peak (Fig. 11d) and in a sharper and higher dissolution peak (Fig. 12d). The aim of the stripping step was to decrease the solvent content below 5000 ppm, which is the pharmaceutical standard for a class III solvent. Decreasing the solvent below this threshold is possible, but some drug extraction will be unavoidable, which is the main drawback of this step. In addition, the stripping step has dehydrated the CD: roughly, water content drops from 13%mass to 2-3%mass. Some of the adsorbed water onto CD was dissolved into the SC-CO₂ flowing through the bed of powder, thus dehydrating it. This explains the fast initial dissolution rate due to its enhanced hygroscopicity.

Dissolution kinetics

The dissolution kinetics evolves in the following way. First, the dissolving medium diffuses into the CD matrix containing Eflucimibe. Then, Eflucimibe is dispersed into the dissolving medium and is temporarily stabilized into SDS micelles corresponding to the maximum dissolved drug concentration on Fig. 12. Then follows a recrystallization of Eflucimibe leading back, after a sufficient period of time (at least 20 h), to the solubility of pure Eflucimibe in this dissolving medium, (that is around 100 μ g/ml). According to this scenario, the increase in dissolved drug concentration does not correspond to a true dissolution of the active substance, but to the generation of a metastable colloidal dispersion of SDS micelles including drug. Finally, the acceleration of the dissolution kinetics after the stripping step may be due to the acceleration and amplification of the first dissolution step, which is the diffusion of the aqueous medium through the dehydrated CD matrix

Finally, this new process using supercritical CO₂ and γ -CD leads to a dramatic increase in the drug dissolution rate. This process includes three steps: (1) a semi-continuous co-crystallization by a supercritical anti-solvent process generating a solid dispersion, (2) a batch maturing step during which the powder mixture evolves towards a more intimate mixture, and (3) a final semicontinuous stripping step where residual solvent is extracted with some Eflucimibe and water.

The main novelty of this process lies in the coupling of these three steps, exhibiting a strong synergistic effect in the improvement of the dissolved drug



concentration of the drug.

Comments on both processes

A new innovative and promising supercritical process but not yet fully understood and controlled; a more classical, usual one but better controlled and more advanced in terms of scaling up.

Concerning the supercritical process, the main limiting point is the use of organic solvent in the SAS step. It has to be pointed out that the co-crystallization step leads to an intimate mixing of the API and CD; this can be an advantage when the API is a voluminous molecule that may present difficulties to be efficiently mixed. But this step is not needed in many others cases to improve the efficiency of the maturing step and therefore physical mixtures can be sufficient. This has been confirmed for instance for the binary Ketoprofen- β -CD¹⁰. In addition, the stripping step is needed only when SAS step is performed; it is a typical extraction process where enhanced transfer properties of the supercritical CO₂ are determining parameters. Besides, to be industrially conceivable, SAS and stripping steps imply that supercritical CO₂ is regenerated (a solvent/antisolvent separation is needed) to be recycled. The key-step that is the maturing step is a very simple one, easy to handle, and a "green" one, low energy-consuming (the main energy requirement is when pressurizing the CO₂). In addition, it delivers a ready-to-use product without any further processing: it has been observed with the Ketoprofen- β -CD mixture that no additional water remained in the produced association complex, not needing then a subsequent stripping or drying step ¹⁰. On a scaling-up point of view, in the SAS step, the ratio Solvent/Antisolvent has to be kept constant together with the API concentration in the solvent: these are the predominant invariant parameters and the scaling up could be performed as "scaling out" by setting lab-scale autoclaves with their nozzles in parallel. As for the maturation step, the main invariant parameter that has to be kept constant when changing scale is the mixture (API/CD/Water) composition and duration, with mixing conditions unchanged. Yet, in spite of its already proved efficiency, this step has to be further investigated in order to fully understand the phenomena implied. On a process point of view, the handling of the produced powders could also be improved. The longest step is the maturing one, which is 6 hours. In any case, this newly set-up process has proved to be highly effective concerning the in vivo bioavailability of the Eflucimibe, which was multiplied by 11 (AUC, Area Under the time con-



centration Curve) in dog studies (unpublished data).

As for the kneading process, the device used is more conventional and simple. Scaling-up is relatively easy to perform with the existing commercial devices using traditional approaches of chemical engineering like dimensional analysis and experimental design. This process performed with water avoids the use of organic solvent and works at low temperature level. The produced powder allows a significant enhancement of the API bioavailability. However, it has to be noticed that the operating parameters, in terms of formulation, have to be previously optimized in order to allow the scaling-up based on the capacities of commercial devices: a wrong formulation may induce a very high increase of the required torque, that is not acceptable on the mechanical point of view, by commercial devices.

Conclusion

Both processes resulted in a strong acceleration of the *in vitro* dissolution rate of the drug. Finally, in an *in vivo* test, different Eflucimibe processed formulations have been compared. In comparison with other technologies used (data not published) these two processes appeared to be the most effective, process (a) and (b) giving respectively a 8-fold and 11-fold increase in bioavailability.

Process (a) can be anticipated as a "green process", as it does not use any organic solvent, but only a small amount of water, eliminated by final drying. It is fast, easily scalable and easy to monitor with Process Analytical Technology (PAT) tools; it can be continuously monitored, evaluated and adjusted using validated inprocess measurements, tests, controls, and process end-point. In addition, it needs fewer investments, the material is easy to clean, and it allows the treatment of large quantities.

Process (b) appears to be the most efficient. It uses $SC-CO_2$ as antisolvent that can be recycled in the process and only a small amount of DMSO as solvent eliminated during the final stripping step. A drawback may lie in the fact that it requires high-pressure equipment.

Depending on the physical-chemical properties (solubility...) of the active ingredient and on the context of drug development and production (NDA-New Drug Application, generics) depending on economics, rationality and efficiency, and depending on how easy it is to obtain a good complexation percentage, energy needs, it can be better to use one or the other technique.

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A more detailed description of both processes have been published in two separate articles in the European Journal of Pharmaceutical Sciences.

Abbreviations

ACAT	Acyl-Coenzyme A O-acyltransferase
API	Active Pharmaceutical Ingredient
AUC	Area Under the time concentration Curve
BCS	Biopharmaceutics Classification System
CD	Cyclodextrin
β -CD	Beta-Cyclodextrin
γ-CD	Gamma-Cyclodextrin
CO_2	Carbon dioxyde
DMSO	DiMethylSulfOxide
DSC	Differential Scanning Calorimetry
ESEM	Environmental Scanning Electron Micro-
	scope
FDA	Food and Drug Administration
FTIR	Fourier Transform InfraRed spectroscopy
GPC	Gas Phase Chromatography
HPLC	High Performance Liquid Chromatography
NDA	New Drug Application
PAT	Process Analytical Technology
Ppm	Part per million
SAS	Supercritical AntiSolvent
SDS	Sodium Dodecyl Sulfate
SC-CO ₂	Supercritical Carbon Dioxide
UV	UltraViolet spectroscopy
W/V	Weight/Volume
TT T /	Weight/weight

ΔP	Net blade power consumption	[W]
ρ	Bulk density	[kg.m ⁻³]
Ν	Blade rotational speed	$[rad.s^{-1}]$
R	Blade radius	[m]
D	Blade diameter	[m]
L	Blade length	[m]
Η	Height of powder bed	[m]
g	Gravitational constant	$[m.s^{-2}]$
η	Viscosity	[Pa.s]



Np Power number :
$$Np = \frac{\Delta F}{\rho N^3 R^2}$$

Re Reynolds number : Re = $\frac{\rho . NR^2}{\eta}$

Fr Froude number :
$$Fr = \frac{RN}{g}$$

 I_0/I FTIR absorbance ratio measured respectively at 1572 cm⁻¹ (I₀) and 1537 cm⁻¹ (I)

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Author's short biography



Professor Jacques Fages

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Professor Jacques FAGES graduated from the Institut National des Sciences Appliquées (INSA Toulouse, France) in Biochemical engineering in 1979.

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Professor Jacques FAGES is the author of more than 50 papers in international journals and book chapters and is the inventor of more than 15 international patents. He has given many keynote lectures and has been member of several scientific committees of international conferences. He is member of the high pressure working party of the European Federation of Chemical Engineering. Since June 2007, he is the president of ISASF: International Society for the Advancement of Supercritical Fluids.

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Current Research Interets: Production of divided solids using technologies based on the use of supercritical fluids, Characterisation of particles and porous media (zeta potential, sorption isotherms…).



Alain Chamayou



Born in 1962, Alain Chamayou is a Chemical Engineer from the "Ecole Nationale Supérieure de Génie Chimique" (Toulouse France), received his PhD in Process Engineering at the "Intsitut Nationa Polytechnique" of Toulouse in1993. Actually he is an Assistant Professor in the RAPSODEE research centre of the Ecole des Mines d'Albi where he develops research in the fields of fine grinding, mechanosynthesis and dry-coating.

Historically, he began working on fine grinding with air-jet mills (PhD thesis of L. Godet 2001) with a population balance modelling approach. Then a part of his works were oriented to organic mecanosynthesis (PhD thesis of A. Gil-2002) using this approach in order to improve the bioavailability of drug substances. More generally, mechanical actions are a way to combine (physically and/or chemically) particles in order to obtain new particles with desired user properties. He also extended the basic thematic of grinding (comminution) to co-grinding and then dry-coating (PhD Thesis of A.Vilela 2005) in order to design particles with specific properties. In parallel has developed collaborations with the university of Santiago of Chile to study the influence of ultrasound on grinding and co-grinding, and on products properties.

Michel Baron

Professor Michel Baron is currently Professor and Head of Pharmaceutical Engineering Department at the Ecole des Mines d'Albi, Groupe des Ecoles des Mines, Albi, France.

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He has served for 7 years as assistant professor at the University René Descartes in Paris, France.

He worked in industrial companies in France and Monaco for 7 years, in research and development of pharmaceutical active ingredients.

He then joined the Ecole des Mines d'Albi, France in 1993 where he developped original studies for engineers and pharmacist-engineers double-diploma .

He has served as visiting professor at Tohoku University, Institute for Advanced Materials Processing, Japan, and Keio University, Faculty of Science and Technology, Japan.

His research interest in the Rapsodee Center-CNRS UMR 2392 are directed towards pharmaceutical process engineering and organic mechanochemistry.

He was awarded in 2006 Chevalier de l'Ordre des Palmes Académiques, France.



The Effect of Silanisation on the Catalytic and Sorption Properties of Zeolites[†]

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Abstract

Silanising zeolites can result in significant beneficial changes to their catalytic and sorptive properties. It is, however, necessary to carefully control the reaction conditions when silanising a zeolite. Apart from the different effects of using vapour or liquid deposition procedures and static or flow systems, the deposition temperature and the number of silanisation/calcination cycles are of great importance. By careful control of these conditions, it is possible to systematically modify the diffusional properties of the zeolite while at the same time inertizing the external surface acidity. The diffusional changes are more likely due to a blockage of pore entrances, resulting in a greater diffusion pathway, than to a controlled narrowing of the pore openings. By careful control of the number of silanisation/ calcination cycles, it is possible to systematically change the diffusional properties. The amount of Si deposited/nm² is a good indicator of the process of silanisation. Silanised zeolites are able to significantly increase the yield of particular isomers as a result of the diffusional constraints.

Keywords: Zeolites, Silanization, Catalysis, Sorption

Introduction

The structural characteristic of greatest interest for catalysis by zeolites is the channel system because of the well-known shape-selective properties of zeolites. The size and dimensionality of these channel systems result in molecules being subjected to different diffusional resistances, thus ultimately controlling the selectivity of the reaction. Although the channel system has a large internal surface area, it has been shown that the external surface area of, for example, ZSM-5, is much greater than would be expected if it were assumed to be a perfectly spherical particle¹⁾. Because the external surface is fully accessible to all molecules, it behaves catalytically in a non-shapeselective manner, and it is therefore of great interest to study the effects of passivating or inerting external acid sites in order to promote the shape-selective

reactions. One way to achieve this is to silanise the zeolite. This treatment has the most important secondary effect of narrowing or blocking entrances to pores and thus modifying the diffusional resistances experienced by different molecules, either reducing the pore diameter or increasing the diffusional path length, respectively.

Although a wide range of zeolite structures is known²), for reasons relating to properties such as physical and thermal stability, only relatively few have gained widespread industrial application as catalysts. Examples of these are Zeolite Y, Mordenite, ZSM-5 and Beta. For this reason, it is of great interest to develop methods to modify the channel system of these zeolites so as to produce the same diffusional properties of other more exotic but less stable zeolites.

Inertisation of external surface sites can be achieved by a number of techniques. One method passivates or poisons by sorbing bulky, strong base molecules such as methylquinoline onto the zeolite. The bulkiness ensures that the molecule does not enter into the pores of the zeolite, thus possibly poisoning the internal sites of the crystal. Another method of inerting external acid sites is to remove such sites

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by using chelating agents such as EDTA. It has also been extensively reported that treatment with molecules such as silanes, disilanes, SiCl4 or diborane can result in a modification of the internal surface of a zeolite³⁾. However, passivation of exclusively external surface sites accompanied by modification of the pore opening is generally only achieved using an alkoxysilane complex. This silanisation procedure is generally carried out using chemical vapour deposition (CVD) methods. The silicon source is usually a bulky alkoxy-silane complex such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). With respect to bulkiness, it is important to note that TMOS, for example, has a kinetic molecular diameter of about 0.89nm which must be compared to the pore opening of H-ZSM-5, for example, which is 0.54-0.56nm. TEOS has a kinetic diameter of about 0.96 nm, which makes it even more suitable with regard to minimising the possibility of silanisation of the internal surface.

There are many reports in the literature on the use of such methods and these have been reviewed elsewhere (e.g.³⁻⁶⁾). The zeolites most commonly investigated have been Mordenite and ZSM-5, and the silanising agents generally used have been TMOS and TEOS. In general, there is consensus that the most important effect of silanisation is not so much the inertisation of external surface acid sites, which occurs readily, but rather the changes in the diffusional properties of the zeolite by either narrowing or blocking the pore openings. In the latter case, the resultant greater diffusional path length mimics the effect of using a larger crystal size as far as catalytic shape selectivity of the zeolite is concerned. In this respect, the reactions most widely studied to date have been the disproportionation of alkyl aromatics (e.g.^{6,7,10-12)}) since these reactions lead to the formation, respectively, of a variety of alkyl isomers with different diffusional coefficients and can thus be used to observe the effect of changes in diffusional properties.

To date, few authors have investigated in detail the importance of the careful control of the experimental procedures used in the silanisation process, particularly with respect to temperature and the number of silanisation cycles. Roeger et al.⁷⁾ have shown in a study of silanisation of HZSM-5 using TEOS that the cyclic silanisation/calcination procedure is critical in ensuring a controlled change in diffusional properties. Similarly few if any authors have taken care to measure the internal and external acidity after the silanisation process.

This paper presents results which show that a carefully controlled silanisation procedure using the alkoxy-silane, TEOS, can result in subtle but important changes in the amount of external surface acidity, in the diffusional properties of the zeolite and, consequently, in the catalytic and sorption properties of the treated zeolite.

Experimental Procedures

Modification of the external surface of zeolites was studied using the zeolites ZSM-5, Mordenite and Beta. Specific details on the modification procedures have been described previously⁸⁻¹²⁾. Crystal sizes were approximately log-normally distributed around the mean values indicated in **Tables 1** and **2**. The Si/Al ratios are shown in **Table 1**. Using tetraethoxysilane (TEOS) as the silica source, modification was carried out in three different ways, viz. in a static

procedui						
Deposition Time (h)	Deposition Procedure	Temp. (°C)	Si/Al	% Crystallinity	Pyridine TPD (mmol/g)	MQ TPD (Rel. % MQ)
0 (ZSM-5) ^b			34	100	0.46	100
60	Static Vacuum	100	41	101	0.42	97
60	Static Vacuum	200	37	99	0.41	55
60	Static Vacuum	300	39	102	0.43	40
60	Static Vacuum	400	36	105	0.43	35
8	Vapour Flow	50	43	100	0.39	42
8	Vapour Flow	400	42	94	0.41	20
21	Liquid (water) ^a	25	39	104	0.40	53
21	Liquid (C ₆ H ₁₄) ^a	25	37	96	0.44	29

Table 1 Effect of various silanisation procedures on the Si/Al ratio, relative % crystallinity and acidity of H-ZSM-5 using different deposition procedures

a. Water and hexane, respectively, were diluents; 5 vol% TEOS.

b. Parent material had a crystal size of $1.5 \,\mu\text{m}$ and was used in powdered form.



 Table 2
 Effect of cyclic vs. single silanisation procedure on Si/Al ratio, total acidity (mmol pyridine/g), external surface acidity (relative measure of 4-MQ adsorption), % crystallinity and adsorption of n-hexane and p-xylene of H-ZSM-5, Mordenite and Beta

Zeolite	Si/Al	Total Acidity (mmol/g)	Rel. Ext. acidity	% Cryst.	Adsor Wt. % d	rption change
					n-hexane	p-xylene
ZSM-5 (pure) ^b	34	0.46	100	100	10.3	3
ZSM-5 (400/6×10)	41	0.41	0	98	10.4	2.7
ZSM-5 (400/60)	36	0.43	35	105	10.2	3.0
H-M (pure) ^b H-M(400/6×10) H-M(400/60)	10 11 12	1.03 0.94 1.03	100 0 1	100 95 95	5.7 2.6ª 5.5	$1.7 \\ 1.0^{a} \\ 1.2$
H-Beta (pure) ^b H-Beta (400/6×10) H-Beta (400/60)	18 22 19	0.72 0.67 0.75	100 3 1	100 95 101	11.1 10.0 10.7	3.2 2.5 2.5

a. Adsorption was still far removed from equilibrium after 3 hours

b. Samples were used in powder form. The nominal particle diameter (μ m) was: ZSM-5 = 1.5, H-M = 0.8 (agglomerates of 0.2 μ m), H-Beta =1.7 (agglomerates of 0.2 μ m)

vacuum system, vapour phase flow system and in the liquid phase. After the deposition step, the catalysts were calcined in air. A typical deposition/calcination cycle for a vapour phase flow system is shown in **Fig. 1**. This shows the TEOS breakthrough curve during CVD at 50°C indicating the deposition, flushing and heating/calcination parts of the cycle. The results in **Table 3** were generated using this procedure. The crystal diameter of the H-ZSM-5 was approximately 150 nm. 0.5 g of powder was supported on 4.5 g of inert sand of approx. 200 μ m diameter.

The catalytic activity of the external surface was determined using the cracking of 1,3,5, -triisopropyl benzene (TiPB) as a probe reaction¹¹⁾. TiPB has a kinetic diameter of 0.85 nm and is not expected to enter the channels of the zeolites. Disproportionation^{11, 12)} reactions were used to investigate the influence of silanisation on the shape-selective properties of the modified zeolites. These reactions were carried



Fig. 1 Typical TEOS breakthrough curve during CVD of ZSM-5 at 50°C showing deposition, flushing and heating parts of the cycle.

out in fixed bed reactors and the reaction conditions were chosen variously so as to ensure, as appropriate and desirable, differential operation, constant conversion, or indeed high conversion. TiPB conversions were carried out in the temperature range of 270° C and toluene disproportionation at temperatures in the region of 500° C.

Methods used to characterise the samples with respect to relative % crystallinity, external and total acidity, and sorption capacity have been described elsewhere¹⁰⁾. Pyridine (Py) and 4-methylquinoline (MQ) were used to probe total and external surface acidity, respectively, using temperature-programmed desorption (TPD) techniques. MQ has a kinetic diameter of \pm 0.73 nm which would make it difficult to enter the pores of ZSM-5, but it is possible that it could enter the channels of Mordenite (0.70 × 0.65 nm) and Beta (0.76 × 0.64 nm) after long adsorption times (>24 h). A shorter adsorption time (≈3h), however, combined with the slow diffusion rate of MQ into the channel structure, resulted in MQ adsorption

 Table 3 Number of cycles and number of Si atoms deposited/nm² to obtain approx. 50% xylene selectivity for various deposition temperatures^a

Deposition Temp. (°C)	No. of cycles	Si/nm ² (approx)
50	12	16.1
100	10-11	18.6
200	8-9	18.1
300	3-4	18.8
400	3-4	33.0

Parent catalyst properties: H-ZSM-5; Si/Al=44; crystal diameter=150nm; N₂-BET $[m^2/g]=425$; BJH external surface area $[m^2/g]=128$; NH₃-TPD acidity [mmol/g]=0.74.



occurring mainly on the external surface. Therefore, when relatively shorter adsorption times (\approx 3h) were used, MQ-TPD spectra provided important information on the relative changes in the external surface acidity of Mordenite and Beta after modification.

The capacities of the samples to adsorb n-hexane, p- and o-xylene were used to estimate the extent of pore mouth narrowing and pore blocking. n-Hexane was adsorbed at 80°C and p- and o-xylene were adsorbed at 150°C. At these temperatures, the partial pressures for n-hexane, p- and o-xylene are 60.4, 2.36 and 1.72 mbar, respectively. Sorption and diffusion studies were also carried out using cyclohexane and 1,2,4-trimethylbenzene.

Results and Discussion

Initial studies of silanisation were carried out in a static vacuum system, a vapour phase flow system and in a liquid phase system. Although these different procedures have different mechanisms of silanisation¹⁰ the results are internally consistent and demonstrate clearly, for example, the relative effect of deposition temperature irrespective of the procedure. Table 1 shows these effects on the Si/Al ratio, % crystallinity, total (pyridine TPD) and external (4-methylquinoline TPD) acidity of ZSM-5. However, it is clear from the results in **Table 1** that, irrespective of the silanisation procedure, even though the total acidity has decreased only marginally, the external surface acidity has decreased significantly. The amount of Si deposited was slightly greater when the flow system was used (even after lower deposition times and temperatures) as opposed to the static vacuum system. This has considerable significance for the use of a cyclic procedure. In the flow system, products of the silanisation reaction are constantly removed from the system, and this seems to enhance silanisation, possibly by providing unhindered access to reactive sites for oncoming TEOS molecules. In the cyclic system, this is further enhanced by virtue of the calcination process which results in the formation of new reactive sites as will be discussed later. Liquid phase deposition in a hexane solvent resulted in significant external surface silanisation at ambient conditions, similar to that achieved at 400° in either of the vapour systems. This was an exploratory study and was not investigated further in this work. However, the liquid phase procedure clearly appears to have considerable attraction^{10,12}. With respect to relative % crystallinity, there are indications of significant decreases in the case of the flow system and in the liquid (hexane) system. It is possible that in the case of the static system, a form of epitaxial growth occurs, but that in the flow system amorphous silica layers are preferred as a result of the absence of products of reaction.

As indicated above, there have to date been few reported detailed investigations into the effect of using cyclical methods of silanisation, i.e. cycles of silanisation followed by calcination⁷ Table 2 shows the effect of cyclic silanisation on three different zeolites in a static vacuum system. It compares the properties of the fresh zeolite with those of a sample silanised, firstly, in a single step of 60h, and, secondly, in 6 sequential steps of 10h each. In the case of HZSM-5, the cyclic procedure leads to a greater deposition of silicon and at the same time to a lower total acidity. In the cyclic process, when freshly silanised zeolite is calcined, the reaction products are removed and new sites exposed for further silanisation. This may lead to a more uniform silanisation and explain the greater deposition of silicon. At the same time, there will be a greater possibility of silanisation blocking pores since the reaction will be occurring throughout the external surface and not only on selected high-energy sites. The lower relative % crystallinity in the case of the cyclic process compared to the single-step process is indicative of a tendency to produce an amorphous silica coating in the former case. In the case of the single-step process in which there is no change in adsorption capacity for hexane or p-xylene, and only 65% loss of external acidity, the main silanisation reactions do not seem to be occurring at the pore entrances. On the other hand, the entire loss of external acidity in the case of the cyclic process with no change in hexane adsorption capacity but a decrease in p-xylene adsorption capacity indicates that this method favours the development of a more uniform silica coating, including the narrowing and blockage of some pores, but that the three-dimensional nature of the structure minimises the effect of this on diffusion of molecules. In the case of the 1-dimensional Mordenite, the pore blockage phenomenon associated with cyclic deposition is emphasised by observing that the only major difference between the two procedures is the significant decrease in hexane adsorption capacity. It must, however, be mentioned that in the case of cyclic deposition, the adsorption was so slow that equilibrium was not reached even after 3 hours adsorption time. The 3-dimensional Beta behaved similarly to H-ZSM-5. Interestingly, in each case after the cyclic process, at the stage when there is a total loss of external acidity, the total acidity is



about 90-93% of the initial amount. In the single-step process, the total acidity is very similar to that of the pure sample. This is probably due to the pyridine not being able to access some internal acid sites. This again is consistent with the cyclic process, causing a more significant amount of pore mouth narrowing/ blocking.

As already indicated, a major objective of the silanisation of zeolites is to inert the external surface acidity and to modify the diffusional properties of the zeolite in a controlled manner so as ultimately to modify the resistance to diffusion for the molecules of interest. In this way, the shape-selective properties of the zeolites can be modified. Changes in diffusional resistances can occur either as the result of increased diffusional path lengths resulting from blockage of some pore openings, or of pore narrowing which will inhibit the diffusion of larger molecules through pore mouths. Decoupling these two effects is not simple. It is, for example, well known that the crystal size of a zeolite, and thus the diffusional path length, can significantly influence selectivity in a reaction¹³⁾ **Table** 2 shows that there is little difference between the sorption properties of the various zeolites for the different silanisation methods, although for the 1-dimensional mordenite, there is a significantly lower rate of adsorption of hexane in the case of cyclic deposition. This may be indicative of pore blockage which would have a more significant effect for this dimensionality. Beta also shows a lower hexane adsorption rate for the cyclic deposition sample, whereas there is little difference in the case of H-ZSM-5. In a study of the effect of temperature on silanisation, it was found that the higher the silanisation temperature the higher the initial TEOS conversion, thus resulting in a higher deposition of silica on the surface at each cycle.

The influence of the silanisation of zeolites on their ability to change selectivities in various catalytic reactions has already been alluded to earlier in this paper. Commonly studied reactions have been toluene and ethylbenzene disproportionation. In the present study, the cracking of tri-isopropylbenzene (TiPB) probed the extent of inertisation of external surface acidity, and disproportionation and alkylation of toluene probed changes of diffusivity by monitoring the selectivities to specific product isomers. Fig. 2 shows the cracking activity of 1,3,5 – TiPB as a function of Si deposited/nm². It is clear than once a Si loading of approximately 10 - 15 $atoms/nm^2$ was achieved, the external acidity had essentially been removed. It has been reported that the number of external hydroxyls in H-ZSM-5 is in the range of 1-5.5 OH/nm²¹⁴ and



Fig. 2 Normalised conversion of 1,3,5-triisopropyl benzene over ZSM-5 as a function of Si atoms deposited per nm² of external surface area for different deposition temperatures.



Fig. 3 Si atoms deposited per nm² of external surface area as a function of the CVD cycle number for different deposition temperatures using ZSM-5.

that the number of external cationic sites is about $8.9 \text{ sites/nm}^{2 \text{ 15}}$. These values agree broadly with the number of Si atoms deposited on the external surface which result in the total passivation or inertisation of the external surface catalytic activity. It is of interest to compare these results to those presented in Fig. **3** which shows the number of Si atoms deposited per nm² of external surface area as a function of the CVD cycle number for different deposition temperatures using ZSM-5. Complete inertisation had virtually been reached after about 5 cycles at 50° C and 100° C, after 3 cycles at 200°C and after about 1 cycle at 300°C , all of which equate to $\pm 10-15$ Si/nm². However, at 400° C, as illustrated in Fig. 2, total inertisation of the external surface sites was only achieved at a coverage of ± 40 Si/nm². In every case, the performance of the sample silanised at 400° C showed this sample to behave quite differently. As mentioned earlier, this is most likely due to the fact that at this high temperature, there is a significant degree of homogeneous



Fig. 4 P-xylene selectivity in the disproportionation of toluene over ZSM-5 as a function of Si atoms deposited per nm² of external surface area for different deposition temperatures.



Fig. 5 Xylene selectivities in the disproportionation of toluene over ZSM-5 (Deposition temperature = 200°C) as a function of the number of CVD cycles.

decomposition of the TEOS resulting in a much higher conversion of the TEOS and a much greater but less uniform deposition of Si.

Toluene disproportionation is a useful probe reaction since the selectivity to p-xylene is a good indicator of changes in diffusional properties. Fig. 4 shows the selectivity to p-xylene (given as a fraction of total xylene isomers) as a function of Si deposited/ nm^2 . At the very stage that the 1,3,5-TiPB activity has almost terminated, viz. at a coverage of about 10-15 Si/nm², the p-xylene selectivity increased most rapidly, ultimately reaching a selectivity of > 80% at a Si loading of about 35 Si/nm². Fig. 5 shows the selectivity among the xylenes as a function of the number of CVD cycles using a CVD temperature of 200°C. Even though at this temperature, the TEOS conversion had reached a steady-state value of almost 15% after 3 cycles, it was only after about 7 cycles that the rate of increase of p-xylene relative to the other xylene isomers reached a maximum. Table 3 shows the numKON

ber of cycles and the amount of Si deposited/nm² required to produce approximately 50% p-xylene selectivity for different deposition temperatures. These results show clearly that Si deposited/nm² is the parameter which probably best indicates the effect of silanisation, and is a key indicator of the combined effect of silanisation temperature and number of cycles. It is also significant to observe that the loading of Si occurred in such a continuous manner, as illustrated by the uniformly continuous increase in p-xylene selectivity with the number of CVD cycles.

Conclusions

It has been shown that it is necessary to carefully control the reaction conditions when silanising a zeolite. Apart from considerations such as using vapour or liquid deposition procedures and static or flow systems, on which the authors have previously reported, it is also most important to carefully consider the effect of deposition temperature and the number of deposition/calcination cycles. By careful control of the number of cycles, it is possible to systematically reduce the diffusional properties of the zeolite to whatever extent is desired. It has been shown that the amount of Si deposited/nm² is a good indicator of the process of silanisation. Results shown for a variety of reactions indicate that silanised zeolites are able to significantly increase the yield of particular isomers as a result of the changes in diffusional constraints resulting from the silanisation process and the inertisation of the external surface acid sites. Although not discussed here, the authors have also demonstrated that silanisation is a powerful technique to favourably modify the sieving properties of a number of zeolites.

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Author's short biography



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Technology Innovation in the Nanoparticle Project —Synthesis of Nanoparticles and Nanocomposites—

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Abstract

The five-year METI/NEDO's nanoparticle project started in 2001. In this study, various nanosized particles, e.g. Au, Ag, GaN, ZnO, FePt, CdSe, Y₂O₃:Eu, (Y,Gd)₃Al₅O₁₂:Ce, ZnS:Mn, etc., were prepared by gas-phase methods (thermal and plasma CVD) and by liquid-phase methods (spray pyrolysis, spray drying as well as sol-gel method) using continuous reactors. Nanoparticles and nanoparticle/polymer composite materials were also prepared using polymeric precursor/processing techniques. Using these preparation methods, non-agglomerated and highly-functional nanoparticles were successfully produced in controlled sizes ranging from around 100 nm to a single nanometer with good stoichiometry and high crystallinity.

Keywords: Nanoparticles, Nanocomposites, CVD, Spray Pyrolysis, Sol-gel

1. Introduction

Material synthesis via aerosol and colloidal processing offers a route for production of nanoparticles (with diameters less than about 100nm) of high purity with specifically tailored chemical and physical properties. In particular, single nanometer-sized particles are expected to play an important role in the synthesis of nanostructured materials, as well as in nanotechnology in general, in the 21st century due to unique characteristics such as quantum effects. From this background, the Nanotechnology Particle Project was launched with support provided by the Ministry of Economy, International Trade and Industry (METI) of Japan.

The objective of this project is to establish a platform for developing synthesis and functionalization technologies for nanoparticles, which is important for producing nanostructures and developing nanofunctions. The following research themes have been developed for this project: 1) research and development of high-rate synthesis technology for nanoparticles; 2) research and development of dispersion and surface modification technologies for nanoparticles; and 3) preparation and performance evaluation of nanocomposite materials. In this paper, a brief discussion of the research items in the project and the results of the preparation of nanoparticles using aerosol and colloid methods are reviewed.

2. Nanoparticle Synthesis Technologies

In the synthesis of nanoparticles, both gas-phase synthesis and liquid phase synthesis has been used to elucidate the particular features of each method. This was done by investigating the average particle diameter, particle size distribution, morphology/shape, surface characteristics, compatibility with materials and their link with the surface modification techniques. Novel methods of synthesizing nanoparticles were developed by clarifying field conditions such as pressure and temperature and the composition distribution in the nucleation and growth processes of nanoparticles as shown in **Fig. 1. Fig. 2** shows the TEM pictures of representative nanoparticles prepared with various methods developed in this project.

2.1 Nanoparticle preparation via gas-phase reaction methods

Material synthesis of nanoparticles via high-temperature processing techniques is a promising tool that offers a good route to production of high-purity

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Fig. 1 Various nanoparticle synthesis methods developed in the project.



Fig. 2 TEM pictures of representative nanoparticles prepared using various preparation methods developed in the project.

nanoparticles with specifically tailored chemical and physical properties. However, the transformation of the gaseous precursor to the final particulate is a complex physical process involving nucleation of the particulate phase, condensation of gasses onto particles, and coagulation and coalescence between particles.¹⁾ Nanoparticle synthesis techniques by CVD methods are roughly classified by heat and energy sources, the state of starting materials, and other factors. However, nanoparticles generated by gas-phase processes are usually in the form of aggregates, due to their coagulation at high temperatures. There have been several recent attempts to combine CVD methods with the ionization of gases or the unipolar charging of particles to generate non-agglomerated nanoparticles. The purpose was to suppress collisional growth of agglomerates by mutual electrostatic repulsions of unipolarlycharged particles. Using a newly developed electrospray-assisted chemical vapor deposition (ES-CVD) process, non-agglemerated, spherical nanoparticles of silicon, titanium and zirconium oxides were prepared.²⁾ Non- or only soft-agglomerated nanoparticles are also produced by radio

frequency- and microwave-plasma CVD processes. SiO_2 , GaN^3) and FePt nanoparticles were produced in this project.

2.2 Nanoparticle synthesis via liquid-phase reaction methods

Many techniques for the preparation of nanoparticles have been developed via the liquid phase route. It is important to develop a synthesis method in which particles have controlled characteristics including size, size distribution, morphology, agglomeration and composition. To be industrially relevant, the process needs to be low-cost and involve continuous operation and a high production rate (10 g/h per reactor, in this project).

Nanoparticles prepared via liquid routes and nanoparticle-based nanostructured materials were investigated. Silica (SiO₂) nanoparticles were fabricated using polymer as a model material for the filler in nanocomposites. The other model materials were phosphors (e.g., Y₂O₃:Eu), luminescent semiconductors (e.g., ZnO, CdSe) and metallic materials (e.g., Au, FePt). Some novel techniques for preparing nanoparticles were developed, especially those focusing on controlling the agglomeration.

FePt nanoparticles have been synthesized from a process involving the mixing of two precursor liquids, ferric acetyl ferric acetyl acetonate, Fe(*acac*)₃, and platinum acetyl acetonate, Pt(*acac*)₂, in a polyol solution of sodium hydroxide at high temperatures.⁴⁾ The particle size was monodispersed without agglomeration. An ultrasonic field generator also was applied for preparation of FePt and Au. Our group also successfully prepared Au nanoparticles using dendron-grafted phenyleneethynylenes with alpha, omega-disulfur containing groups, which have an intense blue photoluminescence on the composite film.

A continuous-flow reactor has been designed for producing organically capped CdSe nanocrystals as an isolated CdSe nanocrystal, using trioctylphosphine oxide (TOPO) as the capping organic reagent and the high-temperature reaction solvent.⁵⁾ A relatively high reaction temperature (e.g. 350 degree-C) was necessary for matured crystal growth. The quality of TOPO (i.e. impurity compositions such as phosphonic acids) also influenced the quality of the resulting CdSe nanocrystal. The continuous flow reactor produced highly-luminescent, monodispersed CdSe nanocrystals, which was confirmed by transmission electron microscope observation. The production rate was stable for at least 1 h to allow more than 10 g production. This technique was used for the preparation of ZnO nanoparticles surrounded by shell-



like silicate materials and for the preparation of FePt nanoparticles in the project's largest continuous flow reactor (with the rate of 30 g/h).

Synthesis of europium ion doped yttrium oxide (Y₂O₃:Eu³⁺) phosphor nanoparticles, using a relatively high molecular weight polyethylene glycol, has been previously reported. Y₂O₃: Eu³⁺ materials could be prepared by simply heating in air when a watersoluble polymer was added into a solution containing metal nitrates.⁶⁾ When the polymer was absent, flake particles above 2 micrometers in size were formed. A dramatic reduction in particle size occurred when the polymer was added to the precursor. Particles of about 50 nm in size and nearly spherical in shape were observed when EG/Y=0.0475 and 0.095 mol/ mol. The polymer was expected to form carbonaceous materials around the produced primary particles to reduce agglomeration of those particles. The carbonaceous materials could be removed by heating at higher temperatures, resulting in softly-agglomerated particles in the size range of 20-100 nm.

Cerium-doped yttrium gadolinium aluminum garnet, (Y,Gd)₃Al₅O₁₂:Ce, was systematically prepared by a polymer-complex method using high-molecular weight polyethylene glycol (PEG).⁷⁾ Well-dispersed nano-sized gallium nitride (GaN) and magnesiumdoped GaN (GaN:Mg) particles were successfully prepared from nano-sized gallium oxide (Ga₂O₃) particles in an ammonia gas atmosphere.⁸⁾

In addition to the methods listed above, spray pyrolysis (SP) methods are also promising for nanoparticle preparation, in which the precipitation, thermolysis (i.e. calcination) and sintering stages of powder synthesis can be integrated into a single continuous process. To prepare fine particles by SP, a starting solution is usually prepared by dissolving the metal salts of the product in the solvent. The droplets are atomized from the starting solution with an atomizer, and the droplets are then placed in a furnace. A variety of activities may occur inside the furnace during formation of the final product including evaporation of the solvent, diffusion of solutes, drying, precipitation, reaction between the precursor and surrounding gas, pyrolysis and sintering. Generally, a onedroplet-to-one-product particle (ODOP) conversion is considered the typical particle formation mechanism in conventional spray pyrolysis (CSP). In this project, various modified spray pyrolysis methods were developed and introduced for nanoparticle synthesis, including salt-assisted spray pyrolysis (SASP)⁹⁻¹²⁾ and low pressure spray pyrolysis (LPSP)¹³⁻¹⁸⁾ as well as flame-assisted spray pyrolysis (FASP).¹⁹⁻²⁰⁾

Salt-assisted spray pyrolysis (SASP) is a modified spray pyrolysis method that introduces salts into the precursor solution. It was a versatile method for producing a wide range of nanomaterials, from simple oxide to multicomponent materials. The nanoparticle preparation process by SASP is illustrated in a previous paper by our group.9) The investigation of the mechanism of nanoparticle formation by SASP used NiO as a model material. The addition of inorganic salts leads to substantial changes in product particles, and nanoparticles can be obtained under a variety of conditions. Different types of salts and precursors greatly influence the separation process as well as the characteristics of these products, which, along with synthesis temperature, can be used to control the properties of the final product.¹⁰⁾ The capability of SASP in the preparation of simple oxide nanoparticles was also shown in the production of ZnO¹¹, NiO₂ and CeO₂. Highly crystalline, dense BaTiO₃ nanoparticles in a size range from 30 to 360 nm with a narrow size distribution also were prepared successfully by the SASP method. KNO3 salt was employed in the process synthesis.¹²⁾ This shows the capability of SASP in the production of multi-component oxide materials. The crystal phase was transformed from tetragonal to cubic at a particle size of about 50 nm at room temperature. SASP also can be used to produce a highweight fraction of tetragonal BaTiO₃ nanoparticles down to 64 nm in a single step. The particle size was highly affected by operational conditions. The particle size decreased with decreasing salt concentration, operating temperature and droplet/particle residence time in the hot zones.

Low-pressure spray pyrolysis (LPSP) was applied to the proper nanoparticle synthesis as well.¹³⁻¹⁶⁾ The distinguishing feature of this process is a dramatically different particle formation mechanism. It is expected that a micron-sized droplet will first undergo rapid solvent evaporation upon entering the low-pressure environment. Nucleation and crystallization will be accelerated due to this high evaporation rate. The primary crystals then will undergo Brownian motion inside the droplets. The agglomeration of these primary crystals will be limited due to their very short residence time under the low-pressure conditions. In addition, gas evolution due to thermal reactions and the high drying rate from the furnace will cause some pressure inside droplets/dried particles, which could be the main reason for the dispersion of primary crystals into final nanoparticles. The droplets may break up depending on the properties of the precursor itself. Furthermore, because of the rapid



drying rate at high temperatures, the final particles could be fragmented into multiple nanoparticles, which actually are single primary crystals. Low pressure is considered a driving force for the formation of nanoparticles. Submicron and even micronsized particles may be formed due to the slow drying rate and the physical properties of the precursor. This indicates that the mechanism of particle formation in the LPSP process is obviously complex, including not only process parameters, but also the physicochemical properties of the precursor. Various kinds of materials, from single oxide to multicomponent materials, i.e., nickel,¹³⁾ nickel oxide,¹³⁾ titanium oxide,¹⁴⁾ barium titanate,¹⁵⁻¹⁶⁾ indium tin oxide,¹⁷⁾ and a doped phosphor material (Y₂O₃:Eu³⁺), have been prepared successfully via the LPSP method.¹⁸⁾

Flame-assisted spray pyrolysis (FASP) is another aerosol route for nanoparticle preparation. In this method, a flame aerosol reactor/burner (instead of a traditional electric furnace) allows the input fuel, which provides a high-energy source, to be easily changed and controlled. Aqueous solutions of precursors have been used recently in the flame-spray process for preparation of single and multicomponent nanoparticles by our group.^{19:20)} The use of aqueous precursors is also driven by the low cost of metal salts such as nitrates and acetates and the availability and high solubility of metal salts in water. Submicron and nanosized particles can be produced depending on the operation conditions used and the physicochemical properties of the precursors.

3. Nanoparticle Dispersion & Surface Modification Techniques

For many nanoparticle applications, it is necessary to form a stable colloidal nanoparticle suspension. However, the surface energy of nanoparticles is significantly higher than that of larger particles, so nanoparticles tend to agglomerate in liquid suspensions. Stable nanoparticle suspensions are often formed by adjusting the suspension ionic strength and pH or by surface modification of the nanoparticles themselves. (**Fig. 3**) Mechanical milling processes, such as bead milling, are an alternative to chemical and surface modifications for making stable nanoparticle dispersions.

A new type of bead mill for dispersing nanoparticles into liquids has been developed.²¹⁾ The bead mill utilizes centrifugation to separate beads from nanoparticle suspensions and allows for the use of small-sized beads (i.e. 15–30 μ m in diameter). The



Fig. 3 Dispersion and surface modification techniques in the project.

performance of the bead mill in dispersing a suspension of titanium dioxide nanoparticles with 15 nm primary particles was evaluated through experiments. Dynamic light scattering was used to measure titania particle size distributions over time during the milling process. Bead sizes in the 15–100 μ m range were used. It was found that larger beads (50-100 μ m) were not capable of fully dispersing nanoparticles, and particles reagglomerated after long milling times. Smaller beads (15–30 μ m) were capable of dispersing nanoparticles, and a sharp peak around 15 nm in the titania-size distribution was visible when smaller beads were used. Because nanoparticle collisions with smaller beads have lower impact energy, it was found by X-ray diffraction and transmission electron microscopy that changes in nanoparticle crystallinity and morphology are minimized when smaller beads are used. Furthermore, inductively-coupled plasma spectroscopy was used to determine the level of bead contamination in the nanoparticle suspension during milling It was found that smaller beads are less likely to fragment and contaminate nanoparticle suspensions. The new type of bead mill is capable of effectively dispersing nanoparticle suspensions and will be extremely useful in future nanoparticle research.

4. Preparation of Nanocomposite Materials

Nanoparticles and nanocomposites are expected to be the next generation of materials, because of a variety of characteristics including their mechanical properties and their optical and heat responses. However, nanoparticles are difficult to handle, especially during industrial production. To control this problem, our group investigated building submicron powders from nanoparticles (with sizes from 4 to 100 nm) us-



ing the spray-drying method.²²⁾ The prepared silica powders have a spherical morphology, with the final size (between 0.1 and 2 μ m) controllable by the concentration of the starting colloidal suspension.

Using a similar method, our group successfully prepared microencapsulated powders derived from a precursor of a mixture of two types of sols as well as a mixture of a sol-aqueous solution. Microencapsulated Small-SiO₂/Large-SiO₂, Al₂O₃/SiO₂ as well as ZrO₂/SiO₂ powders were prepared.²³⁾ The light-scattering characteristics of the prepared particles were investigated, and it was found that the refractive index of prepared powders was controllable by their mixture ratio.

Using the spray method, our group investigated the preparation of nanocomposite materials. A mixture of 3 nm of zinc oxide (ZnO) nanoparticles and silica nanoparticle colloid (or TEOS solution) was spray-dried to form a ZnO/SiO₂ powder nanocomposite²⁴⁻²⁵⁾. The green photoluminescence (PL) exhibited by the composite was very stable. Since the excitation and emission luminescence spectral positions of ZnO are dependent on particle size, composites that emit a specific color can be produced. By using ZnO colloids that have been aged for different times, composites containing ZnO particles of different sizes can be produced. Our group has produced composites that emit colors from blue (460 nm) to yellow-green (550 nm).

4.1 Preparation of porous materials

The synthesis of ordered porous materials presents a fascinating and intellectually challenging problem due to its potential for applications in catalysts, chromatography, controlled-release drugs, low dielectric constants, pigments, microelectronics and electro-optics. Our group have developed the methods to produce silica powders as well as silica films that contained ordered pores.²⁶⁻³¹⁾ The spray-drying method was used to prepare ordered porous silica powders. A colloidal suspension of silica nanoparticles and polystyrene latex (PSL) nanoparticles was mixed and sprayed as droplets into a reactor containing two temperature zones, as shown in our group's previous research.²⁶⁻²⁷⁾ The solvent in the droplets was evaporated at the front part of the reactor to produce a powder composite of silica and PSL nanoparticles. The PSL nanoparticles in the powder were evaporated in the downstream portion of the reactor to produce a silica powder of ordered pores. The pores were arranged into hexagonal packing, indicating that a self-organization process occurred spontaneously during solvent evaporation. The entire process was completed in only a few seconds, which is superior to the current methods requiring several hours to several days to achieve.²⁸⁾ Furthermore, our group used a similar method to successfully prepare other materials such as silicon dioxide, titanium dioxide, aluminum dioxide, zirconium dioxide and yttrium dioxide particles containing macropores with ordered, hexagonal closed-packing structures.²⁹⁾

Silica films containing a three-dimensionally (3D) ordered pores, with sizes in the range of 40-1000 nm, were produced using a dip-coating method.³⁰⁻³¹⁾ A silicon wafer or glass substrate was dipped vertically in the precursors containing PSL and silica nanoparticles. The PSL particles were then completely removed at a temperature of approximately 400°C. This method permitted the pore size to be selected through appropriate adjustment of the size of the PSL particles. The presence of an optical band gap is dependent on the dielectric constant periodicity of the material. The film produced using this procedure had a dielectric constant as low as 1.192, confirming that the proposed method also has the potential for producing ultralow dielectric-constant materials. When the films were irradiated with a white light source, the reflective spectrum was changed by varying the incident angle, indicating its possible use as a monochromator. As an advanced result, our group successfully produced an ordered, macroporous, iron-platinum (FePt) film as shown in Fig. 3.³² The prepared film had a magnetic property—a coercivity of up to 10 kOe after annealing at a temperature of 600°C (L1₀ phase).

4.2 Nanoparticle/polymer composite materials

In the past decade, significant progress has been achieved in the synthesis of various types of polymernanocomposites and in the investigation of their optical, electronic and magnetic properties. Our group developed a novel method of preparing a nanoparticle-based nanocomposite polymer in which nanoparticle fillers were grown in a polymer matrix. As an example, zinc oxide (ZnO) nanoparticle-based nanocomposite polymer electrolytes with a very high luminescence intensity were prepared by this method.³³⁾ It was found that non-agglomerated ZnO nanoparticles were widely and evenly dispersed in the polymer. A large number of ZnO nanoparticles served as luminescent centers for inducing high luminescent intensity. Compared to conventional preparation conditions, the luminescent intensity was enhanced about 22 times for the ZnO nanopowder.

In another experiment, nanostructured ZnO/Eu and ZnO/Y2O3:Eu composites were produced by hy-



drolyzing a mixture of zinc acetate, yttrium acetate and europium acetate in an ethanol solution, followed by mixing with lithium hydroxide.³⁴⁾ The powder produced might be used as filler in luminescent polymer electrolyte composites, which can produce two colors: red (Eu emission) when excited using a wavelength of around 254 nm; and, green (emitted by ZnO nanoparticles) when excited using a wavelength of around 365 nm.

Our group also prepared the hybridization of silica nanocomposites in a thermoplastic resin using a melt extrusion method.³⁵⁾ It was found that uniform dispersion of nanoparticles in the resin can be attained by treating nanoparticle surfaces with an organic compound and modifying the resin prior to mixing, as well as the optimization of the screw design of a twinscrew extruder as shown in **Fig. 4**. Since the domain size of silica nanoparticles in the resin is smaller than the wavelength of visible light, the obtained composites are transparent in the visible region, which is important for industrial applications.



Fig. 4 Nanoparticle dispersion and nanocomposites preparation techniques.

5. Summary

The preparation of nanoparticles by aerosol, colloid and polymer processes is becoming more and more important. Through the nanoparticle project, various nanoparticles with high quality have been prepared. The evolution of functional elements of nanoparticles and assembling nanoparticles plays an important role in the synthesis of nanostructured materials. By introducing particle engineering and material science, novel materials and new phenomena can be discovered, and guidelines for scale-up in nanomaterial processing will be readily established.

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Self-assembly Patterning of Nano/Micro-Particles[†]

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Abstract

We developed a self-assembly process of SiO_2 particles to fabricate desired patterns of colloidal crystals having high feature edge acuity and high regularity. A micropattern of colloidal methanol prepared on a self-assembled monolayer in hexane was used as a mold for particle patterning, and slow dissolution of methanol into hexane caused shrinkage of molds to form micropatterns of close-packed SiO_2 particle assemblies.

We further developed spherical particle assemblies and micropatterns of them. Hydrophilic regions of a patterned self-assembled monolayer were covered with methanol solution containing SiO_2 particles and immersed in decalin. Particles were assembled to form spherical shapes and consequently, micropatterns of spherical particle assemblies were successfully fabricated through self-assembly.

This result is a step toward the realization of nano/micro periodic structures for next-generation photonic devices by a self-assembly process.

Keywords: Self-assembly Patterning, Self-assembly, Colloidal Crystal, Photonic Crystal, Self-assembled Monolayer

1. Introduction

"Self-assembly" has been attracting much attention as the next generation nano/micro fabrication process. Modification of solid surface such as particles, substrates and fibers with self-assembled monolayer having desired functional groups has been developed using self-assembly. Colloidal crystals were fabricated by self-assembly of nano/micro particles to form closed pack structure such as fcc(face-centered cubic) or hcp(hexagonal closed packing). Organization proceeds with low energy consumption by the use of various interactions in the self-assembly pro-

 ¹ 2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan TEL: +81-52-736-7237 FAX: +81-52-736-7234 e-mail: masuda-y@aist.go.jp http://staff.aist.go.jp/masuda-y/index.html cesses. For instance, hydrophobic interaction works between OTS (octadecyltrichlorosilane) molecules, and chemical bonds are formed between "molecule and substrate" and "molecule and molecules" in the formation of self-assembled monolayers. Stabilization of energy caused from formation of these bonds (\triangle H<0) is larger than decrease of entropy caused from assembly of molecules which are dispersed. These balance results in \triangle G<0, therefore, molecular layer is formed by the self-assembly mechanism. Formation of molecular layer is seemingly against the second law of thermodynamics, however, it proceeds spontaneously due to the stabilization of the system caused from chemical bonds formation.

Additionally, formation of close packed colloidal crystal by the precipitation of particles in the solution proceeds by the effect in which particles precipitate to minimize total potential energy of every particle.

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Moreover, there are a great deal of self-assembly phenomena in nature, for instance, crystallization of solids in supersaturated solution, crystals of snow having various morphologies, patterns of butterflies, zebra, giraffe, and beat of the heart.

In the particle science, novel nano/micro fabrication has been developed by the use of "self-assembly". Opal is constructed of close packed particle assembly to form fcc (hcp). Periodic architecture is formed by the combination of particles and air to be photonic crystal. Photonic crystal has photonic band gap and diffracts visible light to show structural color. There are many photonic crystals in nature, for instance, opal, morpho butterfly, blue damselfish, chrysochroa fulgidissima (schonherr), peacock etc. In order to apply photonic crystal for next generation device, patterning process of photonic crystal is required to fabricate photonic devices. In this study, we developed patterning process of colloidal crystals by the use of self-assembly. Two-dimensional patterns of colloidal crystals, spherical particle assemblies and their micropatterns were fabricated from the colloidal solution.

2. Particle Assembly for Photonic Crystal

Nano/micro periodic structures have attracted much attention as next-generation devices^{1, 2)} such as photonic crystals³⁻⁵⁾ in which the refractive index changes periodically to show a photonic band gap. Various scientific and engineering applications, such as control of spontaneous emission, zero-threshold lasing, sharp bending of light, and so on, are expected to become possible by using the photonic band gap and the artificially introduced defect states and/or light-emitters. The structures were prepared by semiconductor nanofabrication techniques such as lithography and etching $processes^{6,7}$, advanced wafer-fusion technique⁸, lithographic layer-by-layer approach⁹⁾, holographic lithography¹⁰⁾, advanced silicon microelectromechanical systems¹¹⁾, glancing angle deposition¹²⁾ or auto cloning technique¹³⁾, and theoretical studies were performed to estimate the properties of the structures. These studies confirmed the high potential of nano/micro periodic structures as future devices.

However, a simple process which requires a short time for fabrication, low energy and less amount of material needs to be developed to enable mass production. Additionally, the processes of patterning the structures need to integrate various elements for application to commercial devices. The regularity and feature edge acuity of periodic structures should also be improved in order to enhance the performance.

Nano/micro periodic structures can be prepared with short fabrication time and low energy by selfassembly of mono-dispersed particles in which particles and air (wall and air for inverse opal) are arranged periodically^{14, 15)}. Self-assembly and patterning of nano/micro particles have attracted much attention recently^{1, 2, 16, 17)}. Micropatterns of close-packed particle assemblies with high arrangement accuracy have been realized by using templates such as micromolds¹⁸⁾, grooves¹⁹⁾, cylindrical holes²⁰⁾ or trenches²⁰⁾. However, substrates having micromolds or grooves are necessary in these processes, and feature edge acuity and regularity need to be improved further in order to fabricate various complicated structures for photonic devices.

We have developed several patterning methods, without the use of a template, having microstructures such as molds or grooves in static solution systems²¹⁻²³⁾ or in drying processes^{24, 25)} to apply them for photonic crystals. Microstructures constructed from particles such as micropatterns of particle layers, narrow particle wires, array of particle wires and so on were prepared under moderate conditions using self-assembled monolayers (SAMs). Chemical reactions and/or electrostatic interactions between particles, substrates and solutions can be easily utilized and experiments can be conducted under wellcontrolled conditions in the static solution system because of its static reactions. On the other hand, meniscus force and capillary force can be easily utilized for assembling particles into a close-packed structure in the drying process. However, interactions between particles, substrate and solution are difficult to use effectively and the patterning conditions are hard to control precisely because of its dynamic system so that exact nano/micro patterns are difficult to fabricate. Each patterning system has its own advantages and disadvantages. These self-assembly solution processes do not need preprocessing of micromolds or grooves. However, further progress based on novel concepts is strongly required.

Here, we developed a novel process to realize micropatterning of particle assemblies using droplets of colloidal solution and a patterned SAM. This two-solution process was developed to have the advantages of both the static solution process and the drying process. Interfacing between two solutions and shrinkage of droplets were utilized to obtain meniscus force to form densely packed particle assemblies, and ad-

ditionally, the static solution system allowed precise control of the conditions. Furthermore, we proposed a novel concept for future photonic crystals. Photonic crystals in which the refractive index changes periodically have been usually prepared by the assembling of primary particles. However, spherical particle assemblies were prepared from primary particles, and periodically structure was fabricated by the orderly array of the spherical particle assemblies with our method. Spherical particle assemblies have photonic band gap derived from size, periodicity, refractive index, etc. of primary particles, and the large periodical structure fabricated from spherical particle assemblies have photonic band gap derived from size, periodicity, refractive index, etc. of spherical particle assemblies. Our newly developed method will be an initial shot for multi band gap photonic crystals.

3. SAM Preparation

An Si wafer (p-type Si [100], NK Platz Co., Ltd.) was sonicated in water, ethanol or acetone for 10 min, respectively, and exposed for 2 h to UV light (184.9 nm) (low-pressure mercury lamp, NL-UV253, Nippon Laser & Electronics Lab.) to clean the surface. The OTS-SAM²¹⁻²⁵⁾ or HFDTS-SAM²⁶⁾ were prepared by immersing the Si substrate in an anhydrous toluene (Aldrich Chemical Co., Inc.) solution containing 1 vol% OTS(Acros Organics) or HFDTS(Lancaster synthesis Ltd.) for 5 min under an N₂ atmosphere (**Fig. 1**). The substrate with the SAM was baked at 120°C for 5 min to remove residual sol-



Fig. 1 Conceptual process for two-solution self-assembly method to fabricate patterned colloidal photonic crystals.



vent and promote chemisorption of the SAM.

SAMs on the silicon substrate were exposed for 2 h to UV light through a photomask to be used as a template for micropatterning of spherical particle assemblies. UV-irradiated regions became hydrophilic due to silanol group formation, while the non-irradiated part remained unchanged. Formation of the SAMs and the modification to silanol groups by UV irradiation were verified using the water drop contact angle (θ w). The initially deposited OTS-SAM or HFDTS-SAM showed a water contact angle of 105° or 112°, but the UV-irradiated surface of SAM was wetted completely (contact angle (5°)).

4. 2D Patterning of colloidal photonic crystals

4.1 Preparation of 2D pattern of colloidal photonic crystals

SiO₂ particles $(1 \ \mu \text{ m} \text{ in diameter}) (0.002 - 0.2 \text{ mg})$ were thoroughly dispersed in methanol $(20 \ \mu \text{l})$ and dropped on a patterned OTS-SAM (**Fig. 1**). The solution was lightly repelled by hydrophobic regions and mainly exists on hydrophilic silanol regions. The substrate was then immersed into hexane and carefully swung to remove the residual solution. The solution was repelled well by octadecyl regions in hexane. The contact angle of the methanol solution on OTS-SAM was confirmed to increase from 51.6° in air to 129.5° in hexane (**Fig. 1**), indicating that the methanol solution tends to exist on silanol regions selectively.

Methanol was then gradually dissolved into hexane to shrink the colloidal solution mold containing particles. The shrinkage of the mold increased the concentration of particles in the solution. The particles then attracted each other by meniscus force to form a close-packed fcc (face-centered cubic) or hcp (hexagonal closest packing) structure during the drying process of methanol. Close-packed structures were thus formed on hydrophilic silanol regions selectively (**Fig. 2, A to H**).

4.2 Structure evaluation

2D micropatterns of multi particle-layers (Fig. 2, A and B), partially double particle-layers (Fig. 2, C and D), or single particle-layers (Fig. 2, E to H) were successfully fabricated by changing the particle concentration in the solution and solution volume per unit of hydrophilic area (SiO₂/methanol 0.2 mg/ 20μ 1 for Fig. 2, A and B, 0.02 mg/ 20μ 1 for Fig. 2, E to H). 2D patterns of colloidal crystals with high regularity





Fig. 2 SEM micrographs of patterned colloidal photonic crystals constructed from (A-B) multi particle-layers, (C-D) partially double particlelayers or (E-H) single particle-layers. Image (B) is a magnified area of (A).

in particle assembly have not been prepared by our processes previously reported²¹⁻²⁵⁾. The feature edge acuity of patterns and regularity in particle assembly21-25 presented here are clearly higher than those previously reported²¹⁻²⁵⁾. Fig. 2B shows a magnified area of the patterns constructed from thick particle-layers (Fig. 2A). The edge of patterns (Fig. 2, A to H) shows high feature edge acuity due to close-packing induced by meniscus force in the drying process. The core area of the particle circle (Fig. 2D, Fig. 3) was a double particle-layer of close-packed hexagonal lattice, i.e., the arrangement of fcc{111}, and the outer shell of the circle was a single particle-layer of hexagonal lattice (fcc{111}). The boundary area of these two flat terraces, i.e., inner shell, was

constructed from a nested structure of square lattice, i.e., the arrangement of fcc{100}, to form a gentle slope between the core double-layer and outer shell single-layer. The lattice constant of the square lattice at the inner shell increased gradually with distance from the core of the circle to form a gentle slope. The difference in height was caused by the assembling process and the shape of the liquid mold in which the center is higher than the outside. The particle arrangement in the patterns constructed from a single particle-layer (**Fig. 2, E to H**) were assigned to the arrangement in fcc{111} which is a close-packed structure. The border line of particle layer in **Fig. 2E** showed different shape with that in **Fig. 2F, G** because the border line of particle layer in **Fig. 2F,**



G was fcc <1, 1, 0> and that in **Fig. 2E** was fcc <1/2, 1/2, 1> which is orthogonal to fcc <1, 1, 0>. There were far fewer defects in the particle patterns than in our former processes²¹⁻²⁵⁾ because of the effective meniscus force. The standard deviation for the edge of the pattern constructed from a single particle-layer (**Fig. 2F**) was calculated in the same manner as we reported previously²⁴⁾. The center position ((*x*_i, *y*_i) μ m) of each particle at the edge was plotted to estimate the standard deviation. The particle at the far left in the edge line of **Fig. 2F** was set to be the origin of the x-y coordinate.

The approximated straight line (f(x)) and its slope (θ) are represented as follows.

$$f(x) = 0.0273x - 0.09 , \qquad (1)$$

$$\cos\theta = 0.996 , \qquad (2)$$

The standard deviation from the approximated straight line is given by the expression,

S (standard deviation) =

$$\sqrt{U} = \left[\frac{\sum_{i=1}^{n} \{\cos \left(f(x_i) - y_i \right) \}^2}{n-1} \right]^{\frac{1}{2}}, \quad (3)$$

where *n* is the number of particles (*n* = 35). Unbiased variance (U) was used because the number of particles (*n*) is smaller than universe. The accuracy of the particle arrangement in **Fig. 2F** was estimated to be S = 8.75 × 10³. This is lower than that of the pattern constructed from a single particle-layer prepared in the solution using chemical reactions (S = 3.89×10^{-2} , **Fig. 7** (a) in ref. 5(Masuda, Y.; Itoh, M.; Yonezawa, T.; Koumoto, K. Langmuir 2002, 18, 4155-4159.)). The standard deviation for the edge of the pattern constructed from a single particle-layer (**Fig. 2H**) was calculated in the same manner. Distance (*r*_i) from center of a circle ((*x*_o, *y*_o) μ m) to each particle ((*x*_i, *y*_i) μ m) at the edge and its average (\vec{r}) are presented as follows.

$$\mathbf{r}_{i} = \left((\mathbf{x}_{i} - \mathbf{x}_{o})^{2} + (\mathbf{y}_{i} - \mathbf{y}_{o})^{2} \right)^{1/2}, \qquad (4)$$

$$\overline{r} = \frac{i}{(x_{\rm i} - x_{\rm o})^2 + (y_{\rm i} - y_{\rm o})^2)^{1/2}}{n},$$

$$\overline{r} = \frac{i}{n},$$

$$x_o = 21.9 \,\mu\,{\rm m}, \, y_o = 17.7 \,\mu\,{\rm m}, \, \overline{r} = 16.53 \,\mu\,{\rm m}$$
(5)

The standard deviation from the approximated circle is given by the expression,

S (standard deviation) =

$$\sqrt{V} = \left[\frac{\sum_{i=1}^{n} \left\{ \left((x_{i} - x_{o})^{2} + (y_{i} - y_{o})^{2} \right)^{1/2} - r \right\}^{2}}{n} \right]^{1/2},$$
(6)

where *n* is the number of particles (n = 112). Variance (V) was used instead of unbiased variance because the number of particles (*n*) is the same as universe, i.e., all particles at the edge. The accuracy of the particle arrangement in **Fig. 2H** was estimated to be S = 3.89×10^{-1} . This is higher than that in **Fig. 2F** because a perfect circle can't be constructed from a small number of particles which were packed in hexagonal arrangement.



Fig. 3 Particle arrangement view (top) prepared from SEM micrograph (bottom) of patterned colloidal photonic crystals constructed from partially double particle-layers. Center positions of particles in an upper layer show hexagonal or square lattice arrangement regions. The cross-sectional view shows the difference in height caused from the difference in particle arrangement modes. The three colored areas show regions of (A) double layers of hexagonal lattice, (B) nested structure of square lattice and (C) single layer of hexagonal lattice.
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Assembly process

The assembly process can be assumed from the details of structures and defects. Particle circles (**Fig. 2**, **D** and **H**) showed no defects at their core, implying that particles were probably assembled from the core of the particle circle and not from the outer shell. The particle circle (**Fig. 2D**, **Fig. 3**) would be formed not layer-by-layer, and the upper layer at the core was also formed before the outer shell was assembled, since the first layer at the boundary area was not a close-packed assembly. A close-packed hexagonal lattice would be formed in the lower layer as shown in the single particle circle (**Fig. 2H**) in the case particles were assembled layer-by-layer. Other particle patterns (**Fig. 2**, **A to C**) would be assembled from the core area in the same manner.

5. Self-Assembly Into Spherical Particle Assembly and Their Micropatterning

5.1 Self-assembly into spherical particle assembly

SiO₂ particles $(1.13 \,\mu \,\mathrm{m}\,\varphi)$, Hipresica UF N3N, CV: 3.57%, specific gravity: $1.8 \pm 0.1 \mathrm{g/cm^3}$, Ube-Nitto Kasei Co., Ltd.) (0.2mg, 1.5×1010 particles) were thoroughly dispersed in water (20 μ 1) and dropped on a hydrophobic OTS(octadecyltrichlorosilane)-SAM

(Fig. 4). The OTS-SAM with droplets was then immersed in hexane (20 ml, solubility of hexane in water at 20° C: 0.0013g/100ml, specific gravity: 0.7) and ultrasonicated for 1 min. Large water droplets containing SiO₂ particles were separated into many small emulsions that kept them spherical on hydrophobic OTS-SAM. Water in the emulsions was gradually extracted to hexane to reduce the size of emulsions forming spherical particle assemblies²⁷⁾. After having been immersed for 12 h, spherical particle assemblies with different diameters were observed on OTS-SAM; it was also observed that the assemblies were constructed from various numbers of particles such as 3, 5, 6, 8 or many particles (Fig. 4). Quantities of 3, 5, 6 or 8 particles were assembled into triangular, pyramidal, octahedral or decahedral particle clusters, respectively. The number of particles in spheres can be controlled by the change of emulsion size or particle concentration in water²⁷⁾. The spherical shape of particle assemblies was caused by the high contact angle of water emulsion on hydrophobic OTS-SAM in hexane. Consequently, various sizes of spherical particle assemblies can be prepared using this emulsion process.



Fig. 4 Conceptual process for fabrication of spherical particle assemblies (first step). SEM micrographs of spherical particle assemblies with different diameters. Second left: Particle assemblies constructed from a small number of particles such as 3, 5, 6, 8 and so on. Third left: Spherical particle assembly and tilted images. Right: A large spherical particle assembly.





Fig. 5 Linear disclinations on a large spherical particle assembly.

5.2 Formation process of small clusters of particles

The particles would be strongly bound to the droplet interfaces by surface tension in emulsions²⁸⁾. In the formation process of small clusters of particles (**Fig. 4**), the water in emulsions dissolved into hexane to reduce droplet size and this restricted the area in which particles could exist²⁷⁾. Particles touched together by the reduction of emulsion size and formed a spherically packed assembly. Deformation of the interface then led to the rearrangement that formed close-packed particle assemblies. The clusters were formed using emulsions not dispersed in the solution but adsorbed on the flat substrate, and thus some of the clusters showed imperfect symmetry such as pyramidal, octahedral or decahedral, which have a large flat face touching the substrate.

5.3 Linear disclinations on spherical particle assemblies

Additionally, large spherical particle assemblies (for instance $\sim 57 \mu m \varphi$ in **Fig. 4 (Right), Fig. 5**) were prepared from large methanol emulsions (\sim $100 - 300 \mu m \varphi$) in decalin (decahydronaphthalene) without the use of ultrasonication, which makes emulsions smaller. Many linear disclinations, i.e., grain boundaries, were formed on the surface to reduce elastic strain energy because a close-packed triangular particle lattice composed of a particle surrounded by 6 particles in plane cannot cover a spherical surface²⁹⁾. Linear disclinations were composed of an alternative arrangement of the particle surrounded by 5 particles in plane (red, this particle can be assumed to have a charge of +1) and the particle surrounded by 7 particles in plane (yellow, charge -1). Both ends of a linear disclination were particles surrounded by 5 particles in plane to make the total charge of each linear disclination +1 as observed in²⁹⁾. The minimum number of linear disclinations can be calculated for the large sphere ($\sim 57 \,\mu m \varphi$) (Fig. 5) to be 22 (N: minimum number of linear disclinations N=12+0.41r/d=22, r: radius of sphere $\sim 28.5 \,\mu$ m, d: mean particle spacing 1.13 μ m) from geometric calculations^{29, 30)}. The surface area in a purple circle can be also calculated to be about 10.5 % of the total surface area of the sphere from the formula (chapter 5-5) (surface area ratio: S_2/S_1 , surface area of the sphere: $S_1=4\pi r^2$, surface area in a purple circle: $S_2=2\pi r(r-r_1)$, radius of the purple circle shown in Fig. 5 $\sqrt{r^2 - r_1^2} = 17.5 \,\mu$ m). The minimum number of linear disclinations on the surface area in a circle can therefore be estimated to about 2.3(n : minimum)number of linear disclinations in a purple circle $n=N \cdot S_2/S_1$). However, many linear disclinations were observed in an SEM micrograph (Fig. 5). It is suggested that our assembly method can be further





Fig. 6 SEM micrographs showing the inside of spherical particle assemblies formed from methanol emulsions in decalin.

optimized to reduce linear disclinations.

Furthermore, the upper sides of spherical particle assemblies were removed using a manipulator installed in an optical microscope (BX51WI Microscope, Olympus Optical Co., Ltd.) to evaluate the packing structure. Particle assemblies have a densely packed structure (**Fig. 6**). Particles would be completely rearranged to form a densely packed structure during the reduction of emulsion size due to the high dispersibility of particles in emulsions.

5.4 Micropatterning of spherical particle assemblies

SiO₂ particles $(1.13 \mu m \varphi, 1 \text{ g/l})$ were thoroughly dispersed in methanol solution $(10 \mu 1)$ and dropped onto a patterned HFDTS(heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane)-SAM²⁶⁾ having hydrophobic HFDTS-SAM regions and hydrophilic silanol

regions, photopatterned using a mesh for transmission electron microscopy as a photomask (Fig. 7). The patterned SAM covered with the solution was then carefully immersed in decalin so as not to remove the solution because the density of methanol (0.79) is lower than that of decalin (0.88) causing methanol to float on decalin. The patterned SAM was then gently vibrated to remove additional methanol solution and assist the movement of droplets to silanol regions. The methanol solution was selectively contacted on hydrophilic regions to form a micropattern of the solution, which became clearer after immersion for a few hours. The methanol solution containing particles formed a spherical shape because of the surface interaction between methanol, decalin and surface of a SAM and the buoyant force of methanol in decalin. Methanol in emulsions was gradually dissolved into exterior decalin phase to form



Fig. 7 Conceptual process and SEM micrographs of micropattern of spherical particle assemblies. Top left: Micropattern of spherical particle assemblies. Bottom left: Magnified area of top left. Top right: Tilted micropattern of spherical particle assemblies. Bottom right: Magnified area of top right.

particle assemblies. After having been immersed for 12 h, particle assemblies having a dome shape were formed at the center of each silanol region (Fig. 7). The distance between the centers of each spherical particle assembly was same to the distance between holes of a mesh. The diameter of spherical particle assemblies was about $18 \,\mu m \varphi$. It was smaller than that of hydrophilic regions (about $100 \,\mu\text{m}$) due to low particle concentration in methanol and the shape of methanol droplets on a substrate. This indicates the arrangement regularity of spherical particle assemblies can be improved more by the use of the photomask having small holes to decide positions of each droplet precisely. Some extra particles, i.e., noise particles, were also deposited on hydrophobic regions.



(Fig. 8b)

The process should be further optimized to control many factors such as volume of methanol solution on a substrate, quality of a SAM or aggregation of particles in the solution to avoid noise particles. Particle assemblies were shown to have a densely packed structure by destructive inspection using a manipulator. Consequently, the dot array of spherical particle assemblies was successfully fabricated by this selfassembly process.

5.5 Calculation of partial surface area of a sphere for the estimation of linear disclinations (Fig. 8)

$$\begin{aligned} y &= f(x) = \sqrt{r^2 - x^2} & \text{(Fig. 8a-1, 2)} & f(x) = \sqrt{r^2 - x^2} & \text{(Fig. 6a-1, 2)} \\ a & x & b & \\ a &= r_i & \\ b &= r & \\ r &= 28.5 \mu\text{m} & \\ f(r_i) &= \sqrt{r^2 - r_i^2} = 17.5 \mu\text{m} & \\ r_i &= \sqrt{r^2 - r_i^2} = 10.105 & \\ \frac{1100}{100} & \frac{1100}{100} & \frac{1100}{100} & \\ \frac{1100}{100} & \frac{1100$$





Fig. 8 Calculation of partial surface area of a sphere.

6. Conclusion

We proposed a novel self-assembly process to fabricate micropatterns of particle assemblies, without the use of a template, having microstructures such as molds or grooves. 2D micropattern of colloidal crystal and a two-dimensional array of spherical particle assemblies were fabricated by self-assembly with this method. Interfacing between two solutions and shrinkage of droplets were utilized to obtain meniscus force to form particle assemblies, and additionally, its static solution system allowed precise control of the conditions. These showed the high ability of self-assembly processes to prepare microstructures constructed from colloidal crystals. Further investigations of the solution-solution, solution-SAMs and solution-particles interfaces and the behavior of particles and solutions would allow us to develop this two-solution system to prepare desirable particle assembly structures.

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Organic – Inorganic Nano-Hybrid Materials[†]

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Abstract

Nano-ordered composite materials consisting of organic polymers and inorganic materials have been attracting attention for the purpose of the creation of high-performance or high-functional polymeric materials. Especially, the word of "polymer hybrid" claims the blends of organic and inorganic components at nano-level dispersion. By using this idea, an enhancement of mechanical strength of organic polymers with silica particles is possible. High transparency of this material is another important property and indispensable for development of optical waveguides, optical biosensors, non-linear optical materials, and contact lenses. Hybrid materials are also potential candidates for catalysts and gas separation membranes.

The sol-gel reaction makes possible to incorporate the organic polymer segments in the network matrix of inorganic materials. The high homogeneity of the hybrid strongly suggests that the organic polymer segments and inorganic one are blended at the nano-meter level. The organic polymer nano-hybrids can be considered not only as the combination of organic polymer and inorganic materials, but as quite new materials.

Keywords: Hybrids, Composites, Sol-Gel Reaction, Nano-Materials, Silica Gel, Hydrogen Bonding, π - π Interaction, Ionic Interaction, IPN Structure

1. Introduction

Recently, the word "hybrid" is seen very often. Some examples are the hybrid car, or hybrid version of a computer software, etc. There are also hybrid type ball-point pen, hybrid type mobile phone, hybrid type investment trust fund, etc. The dictionary meaning of the word "hybrid" is "a mongrel" or "a thing made by combining two different elements" . If so, what is the meaning of "hybrid" in materials science? It is literally "something that is obtained by mixing different types of materials", and becomes a new material that can be called a "mongrel" . Therefore, a hybrid of organic and inorganic is a combination of organic materials and inorganic mate-

rials. In particular, they may also be called polymer hybrids to emphasize that polymer constituents are involved. However, in order to distinguish them from the conventionally known composites that are mere mixtures, it is necessary to call the materials "hybrid materials" when the level of mixing of the different types of materials is at the nanometer level, or sometimes at the molecular level. A scale of the domain size is shown in Fig. 1, where the continuous line part in the figure is particularly called hybrid materials region. In such hybrid materials, it is possible to expect very interesting characteristics that are not found in the organic polymer or the inorganic material independently. For example, they can have features such as being flexible like a plastic but have excellent mechanical strength and thermal stability.



Fig. 1. Domain size in hybrid materials.

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The following are the background points about why such hybrid materials have attracted attention.

- (1) It has become possible to carry out high precision molecular design (structural control) even at the nanometer levels.
- (2) Instruments have been developed that are capable of characterization of nanometer or even lower sizes.
- (3) Interesting and unique phenomena have been found one after another in the nanometer region, such as energy movement, opto-chemistry, etc.
- (4) Instead of developing a totally new material, by controlling the conventional composite materials at the molecular level in finer detail, the possibility has now become strong, as a consequence, of obtaining extraordinary improvement in the material characteristics.

In this paper, we consider the organic-inorganic polymer hybrid materials which are attracting much attention recently, and describe the principles of their preparation, new methods of synthesis, and the possibilities that can be expected as materials¹⁾.

2. Organic-Inorganic Polymer Hybrids Using Hydrogen Bonding

Although various types of materials such as silica, alumina, titania, zirconia, etc. can be used as the inorganic component of an organic-inorganic polymer hybrid, the case of silica which is a typical one among these is described here. Although much silica is powdered fine, it is impossible to powder it to the molecular level. However, it is possible to disperse it at the molecular level using a method called the sol-gel. The sol-gel method, as is shown in Eqn. (1), is made of the elemental reactions of hydrolysis of silicate followed by condensation reaction of silanol group, and as a result, is a reaction of forming a three-dimensionally cross-linked silica gel matrix with silicon-oxygen bonds as the unit of repetition. By making an organic polymer present simultaneously in this sol-gel reaction, it is possible to synthesize an organic-inorganic polymer hybrid in which there is a molecular dispersion of organic polymer and silica gel^{2), 3)}. This reaction is schematically expressed in Eqn. (2).





However, using this method it is not necessarily possible to obtain a uniform polymer hybrid from all organic polymers. When poly(2-methyl-2-oxazoline) [1], poly(N-vinylpyrrolidone) [2], poly(N, N-dimethyl acrylamide) [3], etc. were used, a colorless transparent uniform glass shaped material was obtained with a wide range of composition of 0 to 100% of these organic constituents. That is to say that a colorless transparent uniform material is obtained with any composition from glass to plastic. In the case of organic polymers other than [1] to [3], although it is possible to mix uniformly with silica gel by about a few %, the material becomes non-uniform after a certain constituent level, and generally becomes turbid white in appearance. The superior uniformity of the polymer hybrid using [1] to [3], is considered to be because the interaction is strong due to hydrogen bonding between the amidocarbonyl group of the organic polymer and the residual silanol group in the silica gel matrix, as is shown schematically in Fig. 2 for the case of [1], and as a result, the organic polymer is uniformly dispersed at molecular levels in the silica gel. This interaction due to hydrogen bonding can be confirmed by the fact that, in FT-IR measurement, compared to the case of only organic polymer, the stretching vibrations of the amidocarbonyl group



Fig. 2. Hydrogen bonding in hybrid materials.



shifts to the low wavenumber side due to hybridization^{4), 5)}. Further, the fact that the organic polymer is uniformly dispersed in the hybrid can also be confirmed by the fact that by sintering the polymer hybrid it is possible to obtain porous silica having very small holes of molecular order⁶⁾.

Apart from the amide group which is the repeting unit in the organic polymer in [1] to [3], it is possible to consider various types as the functional group that acts as the acceptor group of hydrogen bonding. For example, it is known that even with polyurea, polyurethane, polyamide⁷⁷, polyimide⁸⁹, polycarbonate, etc., it is possible to obtain uniform polymer hybrids with silica gel. However, these functional groups have weak hydrogen bonding accepting ability compared to amide groups, and uniform mixing with silica gel over a wide range from 0% to 100% is not possible as [1] to [3].

3. In-Situ Prepanation Method of Polymer Hybrids

3.1 Synthesis of polymer hybrids by the in-situ polymerization method

It is possible to synthesize a uniform polymer hybrid even using the so called "in-situ polymerization method" of polymerizing organic monomers as well as forming an inorganic matrix by a sol-gel reaction. For example, if radical polymerization of organic monomer is made simultaneously with the sol-gel reaction (considered to be polycondensation), it is possible to obtain a hybrid material in which the organic polymer and the inorganic material are dispersed uniformly. The merit of this method is that, compared to the organic polymer, the monomer has superior solubility and dispersibility, and hence it is easy to obtain a more uniform hybrid. Using this "insitu polymerization method" it is possible to synthesize a polymer hybrid of polydimethylacrylamide⁹, or polystyrene¹⁰ with silica gel. Particularly in the case of polystyrene, it is difficult of obtain a uniform polymer hybrid in the method that uses organic polymer as the starting material.

In addition, as the organic monomer, by combining things having dual functionality for example dimethylacrylamide and methylenebisacrylamide, it is also possible to make the organic matrix have a crosslinked structure. Although the gel of the organic material and the inorganic silica gel are not bonded together covalently, they are interpenetvated with each other. This becomes the so called IPN (interpenetrating polymer network) type of hybrid. If we consider that the material becomes non-uniform if an attempt is made to synthesize the hybrid using a nonsoluble organic gel as the starting material, it can be said that the IPN hybrid can be obtained only using the "in-situ polymerization method".

Such IPN hybrid has the merit that it is extremely good in resistance to solvents as compared to the hybrid material of the usual linear chain organic polymer^{11, 12}.

3.2 Synthesis of poly (vinyl alcohol) hybrid using an in-situ hydrolysis method

If an attempt is made to synthesize a polymer hybrid using poly (vinyl alcohol) as the organic polymer, usually, phase separation occurs because of the gathering due to hydrogen bonding among themselves of the hydroxyl groups of poly (vinyl alcohol), and only a non-uniform material can be obtained. However, by taking poly (vinyl acetate) as the starting material and using an acidic catalyst in the sol-gel reaction, and carrying out the hydrolysis of the ester functional group of the organic polymer simultaneously with the formation of the inorganic matrix, it becomes possible, as a result, to obtain a uniform and transparent polymer hybrid of poly (vinyl alcohol) and silica gel¹³⁾. It goes without saying that this thinking of protection group in organic chemistry can also be applied to organic polymers other than poly (vinyl alcohol).

4. Interaction for Synthesis of Polymer Hybrids

4.1 Synthesis of polymer hybrid using π - π interaction

Although thus far we described mainly the examples of using hydrogen bonding as the interaction between the organic polymer and the inorganic matrix in a polymer hybrid, it is of course possible to consider interactions other than this. That is, it is considered easy to obtain a uniform hybrid material if a structural design is made such that interaction occurs between the organic polymer and the inorganic material. One such example is described here of synthesizing a hybrid using stacking between phenyl groups, that is, using π - π interaction. For example, when polystyrene is used as the organic polymer, if a substance having phenyl group is used such as phenyltrimethoxysilane as the starting material of the sol-gel reaction, as is shown in Fig. 3, π - π interaction occurs between polystyrene and the inorganic matrix, and as a result, a uniform and transparent polymer hybrid is obtained¹⁴⁾. In general, very often





Fig. 3. π - π interaction in hybrid materials.

a hydrophilic organic polymer is used in the case of a polymer hybrid using hydrogen bonding, and if we consider that there are problems in resistance to water, hydrophobic polymer hybrids such as polystyrene are very interesting. If this π - π interaction is used, it is possible to obtain easily hybrid materials of polymers containing benzene rings such as poly(diallyl phthalate) or polycarbonate, etc., other than polystyrene.

4.2 Synthesis of polymer hybrids using ionic interaction

It is also possible to consider ionic interaction, that is, interaction between anions and cations, as the interaction between organic polymer and inorganic material. For example, as is shown in **Fig. 4**, when polystyrene sulfonate is used as the organic polymer, if amino group is introduced in the inorganic matrix, in the hybrid material, the sulfonate group and the amino group respectively carry out anion-cation interaction, and as a result, it is possible to obtain a uniform and transparent material¹⁵.

As the interaction in a polymer hybrid, apart from the above, it is also possible to consider hydrophobic interactions, coordinate bonding between metal and ligand, electron transfer between donor and acceptor, etc., and it is expected that the combinations of organic polymer and inorganic material that become



Fig. 4. Ionic interaction in hybrid materials.

a hybrid material will expand more and more.

5. Characteristics Expected of Hybrid Materials

5.1 Surface coating

Various interesting characteristics can be expected from a material in which an organic polymer and an inorganic matrix are dispersed in the molecular level. For example, if surface hard coating of plastics is considered, compared to the usual silica coating, a hybrid material exhibits a higher affinity to plastic which is the base material. The surface becomes dense because of hybridizing, there are even examples of improvement in the surface hardness and abrasion resistance, and in particular, this is a technology which becomes very important when carrying out surface coating having functionality.

5.2 Hybrid filler

Very often trials are made to improve the mechanical strength and thermal stability of plastics by adding an inorganic filler material. Instead of this inorganic filler material, if an organic-inorganic polymer hybrid is used, it is of course possible to expect the affinity to increase with the plastic which is the organic material, and consequently, it is possible to use it as a filler material with a high dispersibility. The manifestation of large effects with small quantities can of course be expected as high performance fillers, and is likely to be a method that will attract more attention from now on.

5.3 Gas barrier characteristics

When an organic polymer and an inorganic matrix get dispersed in each other at the molecular level, a high density material is obtained as a result. Such materials can be expected to be superior as barriers against gas permeation. It is very interesting if the barrier characteristics to air, particularly to oxygen, is improved, because it is possible to expect fire vetardancy at the same time.

5.4 Resistance to solvents

By hybridization, it is said that the resistance to solvents increases compared to the organic polymer itself. This is considered to be the effect of the inorganic constituent having a higher density, in addition to the effect of the inorganic constituent being dispersed in the organic polymer matrix. In addition, as was described above, it goes without saying that a hybrid material with the IPN structure in which the organic gel and the inorganic gel are interpenetrated,



exhibits extremely superior resistance to solvents.

5.5 Adhesion of different types of materials

Because an organic-inorganic polymer hybrid is a combination of an organic polymer and an inorganic material, it goes without saying that it has affinity with both organic polymer and inorganic material. In other words, this indicates that there is the possibility of using a hybrid material as an adhesive between different types of materials.

5.6 Gradient material

If the extent of mixing of the organic polymer and the inorganic component is controlled in a hybrid material, it is possible to obtain a so-called gradient material. In other words, it is possible to design a material in which the "front" is the organic polymer itself and the "back" is the inorganic material, and the part in between them is hybridized in a gradient manner. Such gradient hybrid materials will become a very important technology when its surface functions and adhesive functions are viewed with emphasis.

6. Conclusions

An outline of the new material called organicinorganic polymer hybrid was given in the above. Its basic principle of operation is hydrogen bonding or π - π interaction, etc., and this indicates that, in general, this can be applied to many varieties of organic polymers. In addition, by applying the principle of interaction in a hybrid material in the molecular level to the boundary surface between different types of materials, it is considered possible to obtain very interesting knowledge in terms of materials science as, for example, increasing the adhesion characteristics, formation of functional interfaces, application to gradient materials, etc.

The method of preparing a hybrid material is extremely simple and is that of mixing the starting materials in air and leaving them aside for several days, and this has big advantages in terms of its industrial utilization. In addition, even flexible polymer hybrids have been obtained that have superior film formation and spinnabilities, and it is also considered important in terms of material science that they can be formed easily by spin coating or dipping. Molecular level organic-inorganic polymer hybrids can be used as alternate materials in almost all areas in which the conventional organic polymers are used as the materials or in the fields in which inorganic materials are being used as the materials, and it can be expected that its characteristics are completely different from the characteristics of the organic polymer itself or of the inorganic material itself, and the possibilities of such hybrids are infinite.

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Author's short biography

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Yoshiki Chujo completed his PhD at Kyoto University in 1980 and then joined Nagoya University as an assistant professor in 1981. In 1983, he joined the group of Prof. J. E. McGrath at Virginia Tech in the U.S.A. as a postdoctoral research fellow. He returned to Kyoto University as a lecturer in 1986 and has been Professor of Polymer Chemistry there since 1994. His research interests focus on polymer synthesis, inorganic polymers, and polymeric hybrid materials.



Characteristics and hydrogen desorption property of nanostructured graphite produced by grinding in vacuum atmospheres[†]

Minoru Shirahige^{1, 2}, Junichi Iida¹, Toshiyuki Fujimoto², Yoshikazu Kuga^{*,2}, Mikio Kawai³ and Junji Katamura³

Abstract

The natural graphite ground in vacuum atmosphere by a vibration ball mill is found to have the porous nanostructure consisting of the agglomeration of primary particles of approximately 20nm in size. Such nanostructured graphite particles were used as a raw material to experientially investigate the hydrogen desorption characteristics of the products ground in high pressure hydrogen atmospheres by 3 types of milling machines including a ball mill, a vibration ball mill and planetary ball mill. We experimentally investigated the relationship between the nanostructured graphite in hydrogen atmosphere. The micropores and mesopores in the nanostructured graphite prepared by a vibration ball milling in vacuum atmosphere. The starting temperature of hydrogen desorption of the ground products of the nanostructured graphite, which was prepared by a vibration ball mill in vacuum atmosphere, decreased to 470K from 600K, which had been previously reported.

Keywords: Natural graphite, Grinding, Nanostrucuture, Hydrogen desorption

1. Introduction

Many development works are in progress for fuel cell vehicles and research efforts for hydrogen storage materials are also actively underway, given the increasing need for lighter and less expensive hydrogen storage materials. With this in mind, carbonbased hydrogen storage materials have aroused growing anticipation. Since Dillon et al.¹⁾ reported the

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potential for the ordinary temperature storage of hydrogen within single-walled carbon nanotubes, many pieces of research have been studying the potential hydrogen storage performance of carbon-based materials²⁻⁴⁾, and in the earlier days, these carbon-based materials seemed to have a higher hydrogen storage capacity. Regrettably, however, recent research, including that by Tibbetts et al.³⁾, cites a hydrogen storage capacity with certain carbon-based hydrogen storage materials at ordinary temperature and pressure of 11 MPa as 1wt% or lower; even worse, according to the report by Kajiura et al.⁴⁾, the hydrogen storage capacity levels of similar materials are even lower, reaching only 0.43wt% at best. In response to these reports, Orimo, Fujii et al.⁵⁻⁸⁾ reported that a hydrogen storage capacity as high as 7.4wt% can be attained by subjecting graphite to a mechano-milling process with a planetary ball mill in a hydrogen atmosphere; while the investigation of the mechanism of this process is in progress⁹. However, in this research, it has been verified that the stored hydrogen is desorbed at temperatures of approx. 600K and 950K, meaning there is a particular engineering chal-

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lenge for hydrogen storage materials, namely, the capability for the storage/desorption of hydrogen at lower temperatures.

The realization of a lower hydrogen desorption temperature appears to raise the need for control of nanostructured graphite that stores hydrogen. Many researchers have attempted to clarify the behaviors of graphite during the grinding processes¹⁰⁻¹⁹⁾. As a result of grinding in a vacuum atmosphere, the moisture and/or oxygen are stripped off the surface of the graphite due to the operation in vacuum, meaning the friction coefficient of graphite tends to be greater¹⁹⁾. There have also been reports that this effect leads to a greater grinding rate, and the shape of the resultant individual particles tends to be more solid^{10, 13)}.

Thus, the authors initially attempted to obtain a nanostructured graphite material featuring a greater pore volume by grinding natural graphite with a ball mill in a vacuum atmosphere, where a greater grinding rate is achieved. Subsequently, they further ground the powder product thus-obtained as a starting material in a hydrogen atmosphere with dissimilar milling machines in a hydrogen atmosphere to prepare nanostructured graphite specimens, whose individual particles contain hydrogen. Subsequently, they experimentally investigated the relation between the nanostructure and the hydrogen desorption property using these specimens.

2. Specimens and Test Methods

2.1 Preparation of vacuum-ground graphite products

Using a vibration ball mill (VM) (capacity; 450 cm³, steel ball size; 4.8 mm, vibration amplitude; 5 mm, vibration frequency; 1200 Hz), loads of 10 g and 33 g of feed graphite were ground in a vacuum throughout a duration lasting from 1 to 120 hours. The starting material was natural graphite material from Brazil, consisting of flake-shaped particles (mean grain size; 16 μ m, purity; 99.5%). The material was dried for 1 hour at 300° C, the required amount of the material was loaded in a pot, and heated to 150°C, meaning this lot was vacuum-dried for 1 hour with a turbomolecular pump, and then subjected to grinding.

2.2 Grinding of vacuum-ground product in hydrogen atmosphere

Using a vibration ball mill, a feed of 33 g was ground in a vacuum for 96 hours to obtain a powder product (VM-33-96). This product was used as the starting material, and three grinding mills — a planetary ball mill (PBM), vibration ball mill (VM) and ball mill (BM) were employed. 1 MPa of hydrogen was introduced into a pot according to the procedure described below, whereupon the material was ground. Firstly, as a raw feed, VM-33-96 was dried for 1 hour at 300°C, and then 5 g of the material was loaded into the ball mill (BM) (capacity; 440 cm³, steel ball size; 4.8 mm), 3 g into the planetary ball mill (PBM) (capacity; 220 cm³, steel ball size; 11.1 mm), and 10 g into the vibration ball mill (VM) (capacity; 450 cm³, steel ball size; 4.8 mm) respectively. After each mill was closed, the pot was heated to 150°C, and then, by using a vacuum line, the pot was heated for 1 hour under a vacuum with a turbo molecular pump. After the pot was allowed to cool off, 1 MPa of hydrogen was introduced into the pot, whereupon the powder material was subjected to grinding for 24 hours. The grinding conditions were: a running speed of 120 rpm for the ball mill; rotation speed of 200 rpm and revolution speed of 400 rpm for the planetary ball mill; vibration amplitude of 5 mm and vibration frequency of 1200 Hz for the vibration ball mill. After the grinding operation, each specimen was unloaded from each mill in a glove box filled with argon atmosphere to avoid oxidation or absorption of moisture in the air.

2.3 Analysis for specific surface area and crystalline structure of specimens

The specific surface area of each specimen, having undergone N₂ adsorption, was measured through the BET method by using the model ASAP2010 from Micromeritics. Also, the pore distribution for each specimen was analyzed with the BJH technique²⁰, assuming the shape of all the pores to be cylindrical. For analysis of the crystalline structure of the particles of the specimens using the X-ray powder diffraction method, an X-ray diffraction device (XRD), model MXP18VAHF from McScience, was used, which employed a Cuk α X-ray, thereby the mean interlayer distance d(002) and the thickness of crystallite in the c-axis L_c(002) were determined. In addition, to facilitate analysis of the surface structure of the ground product, the area of ground product in the D band (1360 cm^{-1}) and that in the G band (1580 cm^{-1}) were determined using Raman spectroscopy, thereby the R value, which is the ratio of the former area to the latter (I_{1360}/I_{1580}) , was determined for the intended analysis. The R value is widely known as a means of measuring the degree of graphiteness on the surface of a carbon material²¹⁻²²). The analyzer used was the Raman Spectroscope NRS-2100 from Renishow, wherein a 514 nm Ar ion laser beam was used.



2.4 Evaluation method for hydrogen desorption property

The hydrogen desorption property of the specimens was analyzed by using a TG-mass analyzer from McScience, and Ar was used as the carrier gas, wherein the carrier gas was heated to 1000° C with a heat increase rate of 10° C/min, whereupon the amount of desorbed hydrogen was determined by a mass-analysis technique (mass = 2).

3. Experimental Results and Discussion

3.1 Preparation of nanostructured graphite by grinding in a vacuum, and property of resultant product

In an attempt to obtain more porous nanostructured graphite, 10 g and 33 g raw feeds were each ground with a vibration ball mill in a vacuum. **Fig. 1(a)** illustrates the relation between the specific surface areas of ground products and grinding times. With a grinding operation for 10 g raw feed, the specific surface area peaks at a grinding time of 8 h, and eventually decreases. With a grinding operation for 33 g raw feed, the specific surface area almost peaks at the grinding time of 96 h. In other words, the smaller the amount of raw feed for the grinding

operation (10 g), the shorter the time featured for the specific surface area to maximize and the greater the grinding rate. With both amounts of raw feed, the maximum value of the specific surface area was as great as approximately 700 m^2/g , that is, a level significantly high compared with a specific surface area of approximately $4 \text{ m}^2/\text{g}$ with the material before undergoing grinding. Fig. 1(b) illustrates the variation in pore volume with ground products that is governed by the grinding time. It should be understood that like the tendency of specific area that is dependent on the grinding time, the pore volume with 10 g feed maximizes at the grinding time of 8 h, and that with 33 g feed maximizes at the grinding time of 96 h, and then pore volumes with both 10 g and 33 g raw feeds eventually decrease.

To be able to obtain more detailed knowledge about maximization of the pore volume, the authors determined pore radius distributions, taking the grinding time as a parameter. The resultant pore radius distributions are graphically plotted in **Fig. 2**. With the plotting for 10 g raw feed (**Fig. 2(a)**), a significant amount of metho- and macro-pores are present at an earlier stage of grinding operation (O), namely, 8 hours after the start of grinding. At more advanced stages of grinding operation, namely, grind-



Fig. 1 Changes of (a) the specific surface area and (b) the pore volume of the ground products during grinding.



Fig. 2 Pore radius distributions of products ground for 0-120h in vacuum using a vibration ball mill.(a) feed graphite: 10g(b) feed graphite: 33g

ing times of 72 h (∇) and 120 h (\Box), the numbers of metho- and macro-pores of sizes typically 3 nm or greater tend to decrease. As shown in Fig. 2(b), in grinding operations with a 33 g feed, an increased number of pores occur as the grinding time is longer, wherein the pore volume with metho- and macropores is maximized at the grinding time of 96 h, and diminishes at the grinding time of 120 h (\Box). These results mean that grinding rate can vary depending on the amount of raw feed. Nevertheless, it should be understood that as a grinding operation with a vibration ball mill in a vacuum advances, the specific surface area and pore volume of a ground product increase, maximize and eventually decrease. This learning, namely, as the grinding operation advances, the specific surface area of a ground product will increase, maximize, and then level off or decrease, does not conflict with commonly known results^{23, 24}.

3.2 Observation of shapes of nanostructured graphite

Next, the authors evaluated the nanostructures of ground products, based on the results of observation with products obtained from grinding in a vacuum through SEM and TEM techniques, as well as on information concerning crystallite sizes calculated from the XRD pattern. **Fig. 3** illustrates one example of such evaluation effort: the photos in this figure show the thicknesses L_c of crystallites in the c-axis direction that have been determined based on the SEM images and the XRD of ground products obtained from raw feeds, each weighing 33 g. **Fig. 3**(a) shows



Fig. 3 Typical SEM images and crystallite size of the samples ground in a vacuum using a vibration ball mill.
(a) raw graphite (L_c>100nm)
(b) product ground for 4 h (L_c=35nm)
(c) product ground for 8 h (L_c=20nm)
(d) product ground for 96h (L_c=4nm)



a picture of flake-shaped graphite (raw feed), whose median diameter D_{50} measures 16 μ m; it is apparent that as a result of an advanced grinding operation, the diameters of the 4 h and 8 h grinding operations in (b) and (c), respectively, are much smaller. Incidentally, for the 96 h ground product (d), the thickness L_c of the crystallites was as small as 4 nm, as learned from the XRD result; however, the particles in this ground product were granules strongly agglomerated as compared with ground products obtained from grinding times of 4 h and 8 h. In terms of the particle shapes, the shape of the raw feed (a) is flake-type; the ground graphite product (b) after 4 h of grinding contains a large portion of lump-shaped grains; the 8 h ground product (c) consists of solider fine particles; and the 96 h ground product (d) comprises lumpshaped granules derived from fine particles.

The primary objective of the authors' experiments was to prepare more porous nanostructured graphite. To this end, the authors selected a specimen (VM-33-96) which was obtained by grinding 33 g raw feed for 96 h, wherein the specimen was a ground product featuring a greater specific surface area, increased numbers of metho- and macro-pores as well as a greater pore volume, meaning the authors evaluated this specimen in detail. SEM images of the VM-33-96 are given in **Fig. 4**, and TEM images are shown in **Fig. 5**. Based on the SEM images in **Fig.**



Fig. 4 Typical SEM images of the products ground in a vacuum using a vibration ball mill (feed graphite :33g, grinding time : 96h).



Fig. 5 Typical TEM images of the products ground in a vacuum using a vibration ball mill (feed graphite :33g, grinding time : 96h).



	VM-33-96	Raw graphite	
FWHM of the G band [cm ⁻¹]	50	25	
R value (I ₁₃₆₀ / I ₁₅₈₀) [–]	1.19	0.23	
d(002) [nm]	0.339	0.335	
L _c [nm]	4	>100	
Specific surface area [m ² /g]	777	3.9	
Total pore volume [cm³/g]	0.9233	0.00228	
Average pore radius [nm]	3.53	11.13	

Table 1	Summary of physical	properties of nanostructured	graphite (VM-33-96)
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4, it should be understood that the ground products consist of granules whose sizes are in a range of 10 to $20 \,\mu$ m deriving from agglomeration of primary particles of size approximately 20 nm.

In addition, the TEM image in **Fig. 5(a)** shows an agglomeration structure consisting of primary particles whose sizes are approximately 20 nm. Based on **Fig. 5(b)**, which is an enlargement of **Fig. 5(a)**, the primary particles occurring from grinding comprise not only a crystalline graphite portion but also a more amorphous structure, where the interlayer regularity has been lost.

Table 1 summarizes the physical properties of the authors' specimen (VM-33-96). Compared with raw graphite, the nanostructured graphite generated by grinding in a vacuum has a greater specific surface area and pore volume, thereby it can be concluded that the VM-33-96 is a more amorphous graphite material whose crystallite thickness L_c measures 4 nm. Since featuring a greater half band width and R value with the G-band in the Raman spectrum, the VM-33-96 appears to have a unique structure; characterized by a lower graphiteness and an increased number of graphite edge faces. These findings coincide with the information in the SEM and TEM images.

3.3 Grinding of nanostructured graphite in a hydrogen atmosphere, and the hydrogen desorption properties of this substance

With several grinding mill types, the authors ground their nanostructured graphite (VM-33-96) in a hydrogen atmosphere at 1 MPa, and then evaluated the hydrogen desorption temperatures of the so-obtained ground products. **Fig. 6** shows the results following TG-Mass analysis with the so-obtained ground products.

With a product ground in hydrogen with a planetary ball mill (\triangle), hydrogen desorption started at approximately 600K, and peaks for the hydrogen mass desorbed emerge at 700K and 1050K. This data coin-

cides well with the experimental results⁵⁻⁷⁾ obtained by Orimo et al. Also, Fukunaga et al. insist, based on the results of their neutron scattering experiments, that the hydrogen atoms whose desorption peak occurs at approximately 700K exist between the graphite layers, in a weak chemically bonded mode (adsorption), around the edge dislocations⁹. Incidentally, the authors have learned that with the product (\bullet) ground in hydrogen by a ball mill featuring a lower grinding energy, the hydrogen desorption temperature is at around 470K and its hydrogen desorption peaks at 500 K (which is 200K lower compared with the achievements by Orimo, Fukunaga et al.), though the amount of hydrogen desorption with this product is low. This learning suggests that there can be a position whose chemical bond (adsorption) is weaker compared with the hydrogen position proposed by Fukunaga et al. The hydrogen peak with a ground product (\Box) from the vibration ball mill of a stronger grinding power was as high as 1180K. Based on these findings, it is apparent that the hydrogen desorption temperature can vary significantly depending on the grinding conditions, including the type of grinding mill used, when the nanostructured graphite is further ground in a hydrogen atmosphere. Thus, the authors attempted observation through SEM and TEM into variations in the shape and structure of graphite,



Fig. 6 Hydrogen desorption properties of the products ground in hydrogen atmosphere using the nanostructured graphite as a feed material.





Fig. 7 (a) SEM images and (b) TEM images of the products ground in hydrogen atmosphere using the nanostructured graphite as a feed material.

- (1) product groundin a hydrogen(1MPa) using a ball mill
- (2) product ground in a hydrogen(1MPa) using a planetary ball mill
- (3) product ground in a hydrogen(1MPa) using a vibration ball mill

depending on the grinding mill used. The results are summarized below. An SEM image of a product ground by a ball mill in a hydrogen atmosphere is shown in Fig. 7(a)-1, while a TEM image of the same product is given in Fig. 7(b)-1. Compared with the images of raw feeds before undergoing grinding, as shown in Figs. 4 and 5, the SEM image in Fig. 7(a)-1 appears to exhibit somewhat advanced agglomeration; however, the TEM image in Fig. 7(b)-1 still shows parallel graphite crystal structures running in parallel with each other. In contrast, the product ground by a planetary ball mill (Figs. 7(a)-2 and (b)-2) and the product ground by a vibration ball mill (Figs. 7(a)-3 and (b)-3) show advanced agglomeration of particles, and the TEM images (Figs. 7(b)-2 and (b)-3) appear to have virtually no graphite crystals (parallel graphite structures) and suggest that the structures in these TEM images exhibit advanced amorphous structures. This trend is most significant with the product ground by the vibration ball mill.

The pore radius distributions of these ground products are graphically plotted in **Fig. 8**. As already mentioned, the raw feed, namely, nanostructured graphite (VM-33-96), has many metho- and macropores. The pore radius distribution with the product (BM-H₂) ground by a ball mill in hydrogen atmosphere and using the VM-33-96 as a starting material remains virtually unchanged, while the mean pore diameter constantly measures 3.50 nm. Considering the results in **Figs. 7 and 8**, it seems that no



Fig. 8 Pore radius distributions of the products ground in hydrogen atmosphere (1MPa) using the nanostructured graphite as a feed material.

severe collapse of crystal structure occurs, leading to any amorphousness of particles or agglomeration of particles and causing the pores to be collapsed. In contrast, the numbers of pores measuring 2 nm or greater are smaller with the product (PBM-H₂) ground by the planetary ball mill and the product (VM-H₂) ground by the vibration ball mill respectively. To sum up, based on these results, it appears that as a result of a grinding operation with a planetary ball mill, which features a greater load energy, pores of 2 nm or greater on nanostructured graphite decrease, due to the agglomeration of particles and/or pulverization and the fusion of graphite crystallites. The nanostructured graphite stores hydrogen during the grinding process and starts desorbing the stored hydrogen at approximately 600K, while the hydrogen desorption peaks at 700K and 1050K; which fairly matches the experimental result by Orimo et al. Thus, the modes of existence of the hydrogen in specimens obtained by grinding nanostructured graphite as a starting material by a planetary ball mill in a hydrogen atmosphere seem to be weak bonds between graphite layers around edge dislocations and bonds to carbon atoms at the terminations of the hexagonal graphite layer^{5,9}. In contrast, the grinding parameters in a grinding operation with a ball mill include a relatively low grinding energy that results in the rare occurrence of the agglomeration of nanostructured graphite particles or collapse of crystals: therefore, it appears that hydrogen atoms stored in the nanostructured graphite are present as adsorbed by a weak force in nanostructures, which are activated by grinding and have pores measuring approximately 2 nm and/or spaces having relatively greater clearances between layers. Moreover, it seems that hydrogen desorption temperatures are consequently lower with the products obtained from grinding with



Table 2	Summary of characteristics	of the products groun	d in hydrogen atmos	sphere using the nand	structuredgraphite as a feed material
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	feed,VM- 33-96	BM-H ₂	PBM-H ₂	VM-H ₂
Specific surface area $[m^2/g]$	777	738	406	498
Total pore volume $[cm^3/g]$	0.9233	0.8225	0.2850	0.1624
Average pore radius [nm]	3.53	3.50	3.64	2.10
Median particle diameter D_{50} [μ m]	6.18	6.57	5.23	8.63
Starting temperature of hydrogen desorption [K]	_	470	600	730

a ball mill.

Table 2 summarizes the information concerning the specific surface area, total pore volume, average pore radius, median particle diameter and hydrogen desorption starting temperature for these ground products. The authors have learned that a lower hydrogen desorption temperature is achieved from a grinding operation with a ball mill using nanostructured graphite in a hydrogen atmosphere, wherein the grinding operation features the limited agglomeration of particles, and smaller losses in specific surface area and pore volume respectively. The authors have further learned that the hydrogen desorption start temperature with a specimen obtained from nanostructured graphite ground by a ball mill in a hydrogen atmosphere is 470K, significantly lower than 600K, which is obtained with grinding by a planetary ball mill and 730K, which is attained with a vibration mill.

4. Conclusion

- By grinding in a vacuum, we prepared a nanostructured graphite specimen that featured a greater specific surface area and pore volume.
- (2) The nanostructured graphite specimen thusobtained featured crystallites whose thickness L_c measured approximately 4 nm, and that was a porous material, consisting of agglomerated primary particles of size about 20 nm.
- (3) We learned that the hydrogen desorption start temperature of nanostructured graphite can vary within the range 470K to 730K, depending on the type of grinding mill used.
- (4) The hydrogen desorption start temperature of a ground product from a ball mill is as low as 470K. We learned that to lower a hydrogen desorption start temperature, unique grinding parameters that inhibit the agglomeration of particles are needed.

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Numerical Simulation of Constitution Relationship between Stress and Strain of Particulate Matters[†]

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Abstract

The relations between normal stress and normal strain and that between shear stress and shear strain, which are the constitution relationships, have been obtained in a simple and general particulate field by the numerical simulation using Distinct Element Method. One would be able to calculate the hehamors of particulate matters using the continuum model based on these relations. Furthermore, the numerically calculated constitutive relations are formulated in order to use them for the continuum model simulation. The constitution relationships presented in this work confirm the following.

- (1) Stresses are functions of strains and packing ratios.
- (2) The constitution relationship of particulate matters has a hysteresis because of the change in the internal state of the particulate matters.
- (3) Particulate matters are deformed more easily by the shear stress than the nomal stress.
- Keywords: Constitution Relationship, Stress Strain Relation, Numerical Simulation, Distinct Element Method, Particulate Matter

1. Introduction

Particulate matters are used in various ways in manufacturing industries, etc., and they appear in their processes. Therefore, if their mechanisms are made clear both quantitatively and accurately, it might contribute largely to advances in manufacturing technology, etc. Based on a continuum approximation of particulate matter, the behavior of particulate matter was obtained¹⁾ by assuming a plastic equilibrium state in statics. However, since there is no constitution relationship in the proper sense in this model, it is not possible to close the system and

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calculations could not be done unless a big assumption is made, for example, an assumption related to the direction of the principal stress. Further, this model can only be applied to the plastic equilibrium state just before starting to flow. For dynamic behavior, there are calculation methods using an analogy to kinetic theory²⁻⁴⁾. Since such methods are based on the kinetic theory of molecules which collide like rigid body ions, we can only apply to the dilute condition. Therefore, there are difficulties in applying to the clarification of the most important phenomena such as pile of particulate matter or dense partirulate flow.

On the other hand, we know the Distinct Element Method⁵⁾ (abbreviated as DEM) for the calculation of each single particle in the Lagrangian way. Since this method can calculate motion of individual particles considering directly, although approximately, the mutual interaction among particles using the Soft Sphere model, it is possible to express appropriately the dynamic behavior of particulate matter. However, as all the particles have to be computed individually, there is a limit on the number of particles for which the calculations can be made. In an actual system of

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particulate matter, the number of particles is nearly innumerable. Therefore it is difficult to apply DEM to an actual system.

The authors considered obtaining the constitution relationship of particulate matter using DEM, that is, the relationship between stress and strain for a continuum approach. The constitution relationship needs to be obtained in a general field in which the boundary conditions do not have any effect. Although generality of field and accuracy of calculations are required, a large number of particles is not necessary in this calculation. This is considered to be suitable for using DEM. When the constitution relationship is obtained, it is possible to calculate the behavior based on a continuum approximation for particulate matter.

We set up a simple and general field and used DEM to obtain the relationship between the normal stress and normal strain layer, and the relationship between the shear stress and the shear strain. From the result we present some knowledge about particulate matters.

2. Computational Domain

2.1 Normal stress

The computational domain used for the calculation of normal stress and strain is shown in **Fig. 1**. It is a cube with each side being equal to 4.8mm $(=3\Delta x=3\Delta y=3\Delta z)$ and spherical particles with a diameter of 0.2mm are placed in it. The following four types were used as the initial particle configuration. The result of 1) is omitted in this report.

- 1) Case where 8000 particles are placed at random.
- 2) Case where 9548 particles are placed at random.
- 3) Case where 10% of the particles are removed randomly from a body centered cubic structure.
- 4) Case where 10% of the particles are removed randomly from a hexagonal close packed structure.

In each of the above cases 1) to 4), the calculations were made with the condition that gravity does not act.

The walls of three axis were compressed with a force of *F* as shown in **Fig. 1**. The weight of the wall (=8000mwg) as the weight of 8000 particles was taken as the reference for *F*. 10 times this value (= 8.2×10^{-3} N), 20 times (= 16.4×10^{-3} N), and 30 times (= 24.6×10^{-3} N) were loaded. The stress, strain and the packing ratio were computed for their relationship when these loads are applied. The unloaded process was obtained by calculating in a similar manner as the case of removing *F*. The control volume at the



Fig. 2. Stress computational domain

 Δx

center of **Fig. 1** in which the relationship between stress and strain are cacaulated is shown in **Fig. 2**. This is a cube with each sides of 1.6mm. The sizes of the computational domain and the control volume were varied, and the above size was determined as the values at which the sizes do no affect the results.

2.2 Shear stress

The computational domain is shown in **Fig. 3**. The control volume for the relationship between stress and strain is the same as the case of the normal stress shown in **Fig. 2**. In this case, the initial configuration of particles in the control volume is obtained by making 13824 particles randomly settle down due to gravity from above using random numbers and after that by making the gravity acting on the particles 0 gradually over a time of $2.0 \times 10^5 \Delta t$ (=0.4s). As the shear test, the normal stress is changed to the three values of $\sigma_{zz} = 990$ Pa, 1650Pa, and 2180Pa. Similar to a shear test using a conventional shear tester, the computational domain is divided into a top part and





a bottom part, and the shearing was done by moving the top cell horizontally at a constant speed Vs (Vs=0.5mm/s in this research). When the deforma-

tion of the particulate matter was highly plastic, a speed is applied in the opposite direction. Similar calculations were made, and these were repeated. The relationship between the stress, strain, and packing ratio was obtained. The computation conditions in both the normal stress and the shear stress are shown in Table 1.

3. Method of Computation

The deformation and the interaction of forces of each individual particle were computed by DEM. The method of DEM computation will not be described here as it has been described in detail in, for example, a paper⁶⁾ by the authors. A side of the partition in DEM computation is taken to be equal to the particle diameter to make the number of judgments a minimum. The conditions of DEM computation are also shown in Table 1.

Table 1. Computational conditions				
		$\Delta x (mm)$	1.6	
Width of stress	computational cell	$\Delta y (mm)$	1.6	
		$\Delta z (\mathrm{mm})$	1.6	
		i	3	
Number of stress	s computational cell	j	3	
		k	3	
Particle diameter		$D_{ m p}$ (μ m)	200	
Particle density		$ ho_{\rm p}({ m kg}/{ m m}^3)$	2.5×10^3	
Elastic constant		$E_{\rm p}$ (Particle) (Pa)	1.0×10^{6}	
		$E_{\rm w}$ (Wall) (Pa)	1.0×10^{6}	
Poisson's ratio		ν	0.25	
Friction coefficient		$\mu_{\rm p}$ (Particle)	0.25	
		$\mu_{\rm w}$ (Wall)	0.30	
Fo	r calculation of relation between n	ormal stress and str	rain	
	at random (case 1)		8000	
Particle number	at random (case 2)	N	9548	
	simple cubic latice		12441	
	hexagonal closed-packed latice		16271	
Time step		Δt (s)	$1.0 \sim 2.0 \times 10^{-6}$	
For calculation of relation between shear stress and strain				
Particle number		Ν	13824	
Time step		Δt (s)	1.0×10^{-6}	
Normal stress		σ_{zz} (Pa)	990, 1650, 2180	
Shear velocity		$V_{\rm s}({\rm mm}/{\rm s})$	0.5	



3.1 Computation of stress

In the kinetic theory of molecules, the stress in a continuum approximation is computed from the force of each individual molecule and its position⁷). It is also possible to calculate the stress in the case of particulate matter using a similar method. The following equation⁷ give the atress.

$$\sigma_{ij} = \frac{1}{2\Delta x \Delta y \Delta z} \sum_{m} \sum_{n} (x_i^m - x_i^n) F_j^{mn} \qquad (1)$$

, where *x* and *F* are the distance between centers of two particles that are contacting each other and the force acting between them, and the respective particle numbers are indicated by the subscripts m, n and *i*, *j*, and the direction by (*x*, *y*, *z*). σ_{ij} represents the normal stress σ_{xx} , σ_{yy} , and σ_{zz} when i = j, and the shear stress τ_{xy} , τ_{yz} , and τ_{zx} when $i \neq j$.

3.2 Computation of strain and packing ratio

The increase in the normal strain between its opposing faces, for example, between (1) and (2) shown in **Fig. 4**, during Δt is computed using Eqn. (2).

$$\Delta \varepsilon_{xx} = \frac{u_{xx1} - u_{xx2}}{\Delta x} \Delta t \tag{2}$$

The normal strain during $n \Delta t$ can be obtained using Eqn. (3).

$$\varepsilon_{xx} = \sum_{n} \frac{u_{xx1} - u_{xx2}}{\Delta x} \Delta t \tag{3}$$

Similarly the increase in the shear strain between the faces (1) and (2) shown in **Fig. 5** during Δt is computed using Eqn. (4).

$$\Delta \gamma_{zx} = \frac{u_{zx1} - u_{zx2}}{\Delta z} \Delta t \tag{4}$$

The shear strain over a time of $n \Delta t$ can be obtained



Fig. 4. Stress computational domain

using Eqn. (5).

$$\gamma_{zx} = \sum_{n} \frac{u_{zx1} - u_{zx2}}{\Delta z} \Delta t \tag{5}$$

The velocities of the two opposing surfaces of the control volume were expressed by the average velocity of all the particles included in the two areas shown by dotted lines in **Figs. 4** and **5**.

The packing ratio in the controlvolume was obtained by the ratio of the particle volume to the control volume.

4. Results of Constitution Equations and Discussion

4.1 Normal stress

The calculated results are shown in **Fig. 6** to **Fig. 8**. The numbers attached to the curves indicate the packing ratios at the respective states. Although the relationship between the normal stress and strain is a nonlinear relationship, it is not largely deviated from a linear relationship. The region in which a linear approximation can be made is wide. The relationship between stress and strain during the compression process is different from that during the expansion process. The hysterisis is exhibited because the internal state of the particulate layer is different during compression and expansion. If the packing ratio becomes higher, the large difference in the deformation process disappears. The hysterisis becomes almost nonexistent as is shown in **Fig. 8**. If compression



Fig. 5. Stress computational domain



Fig. 6. Relation between normal stress and strain (random packed, *F*=30*m*_wg)



Fig. 7. Relation between normal stress and strain (simple cubic lattice, *F*=30*m*_wg)



Fig. 8. Relation between normal stress and strain (hexagonal closed-packed lattice, $F=30m_wg$)

and expansion are repeated, the inclination of the stress-strain curve becomes higher and the width of hysterisis becomes small because the internal state of the particulate layer becomes a highly packed state. When the highly packed state is reached, it becomes difficult for the particulate layer to get deformed. From these results, it is possible to express KONA S

the normal stress approximately using the strain and the packing ratio.

We tried to express the calculated results by a simple equation. That includes also the data that have been omitted from this paper. The packing ratio of particulate layer in the initial state ranged from 0.49 to 0.70. The packing ratio is 0.524 when the layer is formed by particles in a simple cubic lattice. It can be understood that a packing ratio of 0.49 corresponds to the case where the particles initially form lagers by contacting irregularly and unevenly. The packing ratio of 0.70 can be considered to be roughly the maximum value. Based on the above facts, we expressed the computed value of the normal stress as a function of strain at that point and the packing ratio. This is indicated below. The explanations of the symbols in the equations are given in **Fig. 9**.

Compression process (*n* indicates, as is shown in Fig. 9, the initial part of the respective deformation processes during a sequence of processes, starts from 0, an even number indicates the initial part of a compression process, and an odd number indicates the initial part of an expansion process. *n*=0, 2, 4, … *n*=4 is sufficient for the calculation of mechanics in the particulate layer as a continuum.)

$$\sigma_{xx} = \left[1.2 \times 10^7 \left(\frac{\rho_b}{\rho_p} \right)_n - 5.0 \times 10^6 \right] \left(\varepsilon_{xx} - \varepsilon_{xx(n)} \right)^2 \\ + \left[1.5 \times 10^5 \left(\frac{\rho_b}{\rho_p} \right)_n - 7.0 \times 10^4 \right] \left(\varepsilon_{xx} - \varepsilon_{xx(n)} \right) \\ \text{where} \left(\varepsilon_{xx} - \varepsilon_{xx(n)} \right) \le 0.035$$
(6)

• Expansion process (*n*=1, 3, 5, … *n*=5 is sufficient for the calculation of mechanics in the particulate layer as a continuum.)

$$\sigma_{xx} = \left[1.2 \times 10^7 \left(\frac{\rho_b}{\rho_p}\right)_{n-1} - 5.0 \times 10^6\right] \\ \times \left[\left(\varepsilon_{xx(n)} - \varepsilon_{xx(n-1)}\right) -1.05 \left(\varepsilon_{xx(n)} - \varepsilon_{xx}\right) \frac{\left(\frac{\rho_b}{\rho_p}\right)_n}{\left(\frac{\rho_b}{\rho_p}\right)_{n-1}}\right]^2 + \left[1.5 \times 10^5 \left(\frac{\rho_b}{\rho_p}\right)_{n-1} - 7.0 \times 10^4\right] \\ \times \left[\left(\varepsilon_{xxn} - \varepsilon_{xx(n-1)}\right) -1.05 \left(\varepsilon_{xx(n)} - \varepsilon_{xx}\right) \frac{\left(\frac{\rho_b}{\rho_p}\right)_n}{\left(\frac{\rho_b}{\rho_p}\right)_{n-1}}\right] \\ \text{where } \left(\varepsilon_{xx(n)} - \varepsilon_{xx}\right) \leq 0.035$$
(7)



These equations represent all data to within $\pm 10\%$. From these equations, it can be seen that the normal stress in the compression process is expressed as a function of the normal strain, the initial normal strain of the process and the initial packing ratio. Taking the deformations after the series of compression or expansion from start deformation to yield occurence as one deformation cycle, the initial packing ratio is defined as the packing ratio at the time when the stress starts having effect from the zero state. This has been indicated in Fig. 9 as $(\rho_b/\rho_p)_0$, $(\rho_b/\rho_p)_2$, and $(\rho_b/\rho_p)_4$. As can be understood from Eqn. (7), the normal stress in the expansion process requires, in addition to the case of the compression process, the packing ratio at the time when the deformation process changes from compression to expansion. This has been indicated in **Fig. 9** as $(\rho_{\rm b}/\rho_{\rm p})_1$, $(\rho_{\rm b}/\rho_{\rm p})_1$ $(\rho_{\rm p})_{3}$, and $(\rho_{\rm b}/\rho_{\rm p})_{5}$. σ_{yy} and σ_{zz} are obtained using similar equations from the respective normal strain.

From the above equations, it can be seen that the normal stress of a particulate layer can be expressed as a second order function of strain. The normal stress of particulate layer has a larger dependence on strain than the usual linear relationship.

The gradient of the curve becomes higher when the packing ratio of the particulate layer becomes higher. These equations indicate quantitatively that it becomes difficult to deform as the packing state becomes dense. In addition, Eqn. (6) and Eqn. (7), show that the normal stress of a particulate layer is expressed as the product of the strain and the packing ratio. There is a nonlinear effect between these physical quantities, indicating that the nonlinearity becomes larger if both of these change simultaneously.

Eqn. (6) and Eqn. (7) which represent the constitution relationship include the packing ratio, then these equations also express the relationship of state. The packing ratio can be computed from the continuity equation, etc.,

4.2 Shear stress

Fig. 10 shows the computed results of the instantaneous velocity vector of particles when a cell is sheared. **Fig. 11** shows the similar computed results when sheared at the same speed in the opposite direction after plastic deformation. In either case, the behavior of the particles in the sheared plane can be understood. This indicates that the sheared plane of a particulate layer is not horizontal but is quite crooked.

Fig. 12 shows the computed results of the rela-



Fig. 9. Schematics of stress-strain curve using Eqs. (6) and (7)



Fig. 10. Particle velocity vector diagrams (σ_{zz} =990Pa, Y=2.3~2.5mm, t =0.032s)



Fig. 11. Particle velocity vector diagrams (σ_{zz} =990Pa, Y=2.3 \sim 2.5mm, t =0.037s)









Fig. 13. Relation between shear stress and strain (σ_{zz} =990Pa)



Fig. 14. Relation between shear stress and strain (σ_{zz} =2180Pa)

tionship between the shear stress and shear strain when a particulate matter is deformed. It is possible to divide this result into an elasto-plastic region and a highly plastic (flow) region, which is the flowing state and expressed as a function of the deformation velocity, that is, of the velocity gradient. Its formulation has already been done by a large number of researchers including the present authors⁸. Therefore, the most important problem at present is to correctly formulate the relationship between the stress and strain in the elasto-plastic region.

Fig. 13 and 14 show the computed results of the shear stress and shear strain in the elasto-plastic region when two types of normal load are applied. These are equivalent to σ_{zz} = 990Pa and 2180Pa when converted to stress (the intermediate data between these two of $\sigma_{zz} = 1650$ Pa is omitted). The numbers in the figures indicate the packing ratios of the particles in those states. As is clear from these figures, a hysterisis is observed. The relationship between stress and strain is largely different from the case of normal stress. This indicates that the deformation of the particulate layer is different in the case of a normal stress than a shear. Since friction is a large factor for the shear stress in a particulate layer, as can be understood from these figures, σ_{zz} has the largest effect on the shear stress. Compared to that, the packing ratio does not have such a large effect.

The values of shear stress normalized by σ_{zz} are shown in **Fig. 15**. As shown in the figure, it is almost possible to express valous normalized value for different σ_{zz} on the same curve. This is because the friction between particles plays an important role in the shear stress of a particulate layer. Based on the above fact, we attempted to express the dimensionless values of shear stress using a simple numerical equation. This equation is shown below. The explanations of the symbols in the equation are shown in **Fig. 16**.

• Shear loading process (*n*=0, 2, 4, … *n*=4 is sufficient for the calculation of mechanism the particulate layer as a continuum.)

$$\left(\frac{\tau_{zx}}{\sigma_{zz}}\right) = \sqrt{\left[230\left(\frac{\rho_b}{\rho_p}\right)_n - 0.59 + 4.4\right]} \left(\gamma_{zx} - \gamma_{zx(n)}\right)$$
where $\left(\gamma_{zx} - \gamma_{zx(n)}\right) \le 0.025.$ (8)

• Shear unloading process (*n*=1, 3, 5, … *n*=5 is sufficient for the calculation of mechanicsin the particulate layer as a continuum.)

$$\begin{pmatrix} \tau_{zx} \\ \sigma_{zz} \end{pmatrix} = \begin{pmatrix} \tau_{zx} \\ \sigma_{zz} \end{pmatrix}_n - \left[870 \left\{ \begin{pmatrix} \rho_b \\ \rho_p \end{pmatrix}_{n-1} -0.59 \right\} + 54 \right] \left(\gamma_{zx(n)} - \gamma_{zx} \right)$$
where $(\gamma_{zx(n)} - \gamma_{zx}) \le 0.025.$ (9)

 τ_{xy} and τ_{yz} are obtained using similar equations from the respective shear strain. These equations represent all the computed data to within $\pm 10\%$. The packing ratios of the particulate layers of these results were from 0.59 to 0.61. As is clear from the above equations, the stress changes by a large amount due to changes in the density of particulate matters. The shear stress is proportional to the 0.5 power of the strain during the shear loading process, and is linearly proportional in the shear unloading process. This indicates that the particulate layer easily deforms for a shear loading process, but does not for a shear unloading process and does not return to the original state. The process of unloading shear stress is similar to the loading process due to normal stress. This may be because when the load is released, friction does not become a major mechanism



Fig. 15. Relations between shear stress and strain normalized by σ_{zz}

Fig. 16. Schematics of stress-strain curve using Eqs. (8) and (9)

as during applying the load. During the shearing process, plastic deformation occurs easily even in small deformations that are the large deformations taking place during much smaller than flow state. Even if the same level of deformation is present in normal stress, a small difference in hysterisis is present and it returns almost to the original state. This difference is considered to be caused by the friction of the particulate layer occurring between particles.

When the equations expressing the stress are compared between normal and shear stresses, the normal stress becomes a second order equation of the strain, and the order is higher than the 0.5 or 1.0 power in the case of shear stress. As is also evident from the results shown in the figures, it is also indicated quantitatively that a particulate layer is easily deformed by shear stress.

5. Conclusions

In a general and simple field, using DEM, we obtained the relationship between the stress, strain, and packing ratio of particulate layers. The following concluding remarks were found from the results.

- (1) The normal stress can be expressed as a function of normal strain and packing density.
- (2) Hysterisis is present in the constitution relationship of particulate layers. This is because of changes in the internal state.
- (3) A particulate layer is more easily deformed by shear stress than by normal stress. The obtained constitution relationship expresses this quantitatively.
- (4) The constitution relationship was summarized in the form of numerical equations, and made them usable in practical calculations. These are shown in Eqs. (6) to (9). The normal stress is a second order function of strain, the shear stress is a function of a power of 0.5 of the strain during loading and 1.0 of the strain during unloading.
- (5) The shear stress can be expressed in a unified manner by making dimensionless using the normal stress. This is because friction plays an important role in shearing process.

Now, we intend to clarify the constitution relationship for particulate matters of fine particles or of adhered powders, etc., and make calculations possible for the behavior of more widely used particulate materials.

Nomenclature

$D_{\rm p}$: particle diameter	[m]
$E_{\rm p}, E_{\rm w}$: modulus of elasticity for particle and v	wall
	[Pa]
F: force	[N]
g : gravitational acceleration	$[m/s^2]$
i, j, k: numbers of computational cell in the x	, <i>y</i> and <i>z</i>
directions	[-]
$m_{\rm w}$: mass of wall [=8000 $\pi \rho_{\rm p} D^3_{\rm p}/6$]	[-]
N: number of particles	[-]
n: number of load and unload processes	[-]
P: pressure	[Pa]
t: time	[s]
Δt : time step	[s]
$V_{\rm s}$: shear velocity	[m/s]
u_1, u_2 : velocities on surfaces (1) and (2) of the	compu-
tational cell	[m/s]
x, y, z: coordinate	[m]
$\Delta x, \Delta y, \Delta z$: computational call sizes	[m]

Greek letters

ε : normal strain	[–]
γ : shear strain	[-]
$\mu_{\rm P}, \mu_{\rm w}$: friction coefficients of particle and wall	[-]
v: Poisson ratio	[-]
$ \rho_{\rm p} $: particle density [kg	g/m ³]
$ \rho_{\rm b} $: bulk density [kg	g/m³]
σ : normal stress	[Pa]
τ : shear stress	[Pa]

Subscripts

i, j: combinations of directions [-]]
--------------------------------------	---

x, y, z : directions	[-]
0: initial state	[-]

Superscripts

m, n: particle number	[-]
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Application of Penetration Method to Evaluation of Non-uniformity of Particle Bed Structure

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Abstract

Based on the fluid penetration, an evaluation method of the non-uniformity of a particle bed structure was developed. The newly developed apparatus has a cubic sample box that can be set at any direction. Pressure drops through the packed bed in the same direction as the packing direction and the cross direction of that were measured in the apparatus. It was found that the fluid penetration resistance in gravitational direction (=packing direction) was higher than that in cross direction to gravity. The differences between them depend on the particle size and shape.

In order to represent the differences as the apparent alignment of packed bed structure, the experiments using the model packed bed constructed by uniform circular bars having a diameter of 4mm were conducted. Through the experiments, correlation between aligned angle and the ratio of specific surface area of the cross direction to that in the gravitational direction was obtained. By means of the correlation, the non-uniformity of the packed bed structure can be evaluated as the apparent aligned angle.

Keywords: Penetration method, Particle bed, Particle bed structure, Pressure drop

1. Introduction

Packed particle beds are used in many processes, for combustion control or as catalyst beds or as particle bed filters. In combustion control applications in particular, they have been used for fixed bed combustion in refuse incinerators, coal power generator boilers and blast furnaces. Incidentally, because of growing needs for higher combustion efficiency and cleaner combustion processes to satisfy environmental and energy-related requirements, a highly sophisticated control for fixed bed combustion must be realized. In diverse research conducted to date, a packed particle bed is assumed to be a homogeneous porous body¹). However, it is clear from much research on heat transmission² that the size and shape of particles in a packed particle bed considerably affect

* Corresponding author TEL 086-251-8084 E-mail: gotoh@cc.okayama-u.ac.jp the behaviors in terms of the transfer of heat and/or mass. Therefore, for effective research into combustion on packed beds with relatively large particles, such as those of RDF (Refuse Derived Fuel) and coal, it is important to evaluate a packed particle bed, with the fuel particle size and particle shape taken into consideration.

When the propagation velocity of combustion plane is measured in a packed particle bed combustion process of counter flow operation, a powder material of a smalle size, either spherical particles or crushed particles (non-sphere particles), features a greater propagation velocity if the superficial air velocity remains unchanged; and crushed particles rather than spherical particles shows a greater propagation velocity for a given size³⁾. The effect of the fuel particle shape and air velocity on the combustion plane propagation velocity can be evaluated, based on an effective mass transfer coefficient calculated by using an equivalent sphere size determined by the air-permeability method as a representative size.⁴⁾ This seems to be because the equivalent sphere size determined by the air-permeability method is a value that reflects contact efficiency; this assumption in turn means that the equivalent sphere size and spe-

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cific surface area determined by this method reflect, as has been claimed to date, the data for the passage the fluid passes in an actual particle bed.

Thus, the air-permeability method appears to be useful, not only in measuring the fluid drag with a packed powder material (which is also possible with a conventional method) but equally in evaluating an air flow passage through a packed bed. Therefore, presuming the air-permeability method to be useful for an air flow passage in a packed particle bed, the authors have attempted to express an air flow passage structure for a millimeter-order-thick packed particle bed, based on the anisotropic pattern in fluid drag; more specifically, we attempted to define nonuniformity in a packed particle structure. For example, let us consider a particle bed, such as that shown in Fig. 1 (not fully packed). When viewed from the top, the pattern with the particles in this structure is relatively random; while viewed from the side, the pattern is significantly non-uniform. In other words, there are tightly or Loosely packed regions in this structure. The pressure drop on the air flow in the cross direction through this type of packed particle bed relative to the gravity Δ Pc appears to be smaller compared with the pressure drop Δ Pp on the air flow parallel with the gravity through the same particle bed. Therefore, the authors considered that we were able to evaluate the three-dimensional non-uniformity of a packed particle bed structure by measuring pressure drops in two orthogonal directions on a packed particle bed and comparing the values thus obtained.

For this purpose, the authors fabricated a prototype fluid permeability experimental apparatus capable of measuring bidirectional fluid drags on a packed particle bed by varying the insertion direction of a packing cell, wherein the packing cell is a cubic body filled with a particle material. To be able to define an apparent orientation direction, as an index for evaluating non-uniformity in the packed particle bed, based on the obtained fluid drags in two directions, the authors performed a series of experiments with models, thereby studying the interrelation between the orientation direction of the packed particles and the fluid drag.

2. Experimental Apparatus and Method

The present experimental apparatus of fluid permeability is schematically illustrated in **Fig. 2**. The packed particle cell (test cell) was a cubic body, the side length being 100 mm in the clear. The frame of the test cell consisted of aluminum angle pieces, and

Fig. 1 Concept of non-uniformity measurement.

two opposing faces made of acrylic panels to ensure the mechanical strength of the apparatus while the remaining four faces were made of metal mesh, with an opening size approximately 0.5 mm. One mesh face could be opened and closed to allow the particles to be loaded into the apparatus. As shown in the diagram, the cell was situated in the apparatus such that its mesh face capable of opening/closing was at the top and its acrylic panels were located toward the flow passage walls. It was possible in this setup to measure the fluid drag-induced pressure drop Δ Pc in the cross direction relative to the packing direction of the particles. In contrast, the cell was turned by 90 degrees and situated in the apparatus such that the mesh face capable of opening/closing was situated toward the air inlet and the acrylic panels were located toward the flow passage walls; in this setup it was possible to measure the fluid drag-induced pressure drop Δ Pp in the parallel direction relative to the direction of packing the particles.

In each of the upstream and downstream sides of the cell, a layer packed with spherical glass beads was inserted to regulate the air flow. The pressure drop on the test cell was measured with a manometer connecting to the pressure taps placed between the packed glass beads layers and the test cell. The compressed air was supplied by a compressor, and desiccated by a dryer, its flow rate was adjusted with a pressure control valve and a mass flow controller, and then it was introduced into the test section.

The powder specimen used was a granulated spherical particle product of millimeter-order (GAC

Fig. 2 Experimental apparatus.

from Hokutan Sangyo) derived from the same primary particle material (active carbon particles, Feret diameter; 1-30 μ m). The spherical particles were classified with a sieve into three spherical particle groups (S, M, and L), each group having a unique particle size range. Additionally, the granulated spherical particles were further crushed and the resultant product was classified with a sieve into three nonspherical crushed particle groups (NS, NM, and NL). Also, two additional powder specimens were used, each having a more non-isotropic shape compared with crushed particles and consisting of a material almost equivalent to that of the granulated spherical particle product. These specimens were the PAC, which is a particle product with particles having been formed into columns through a granulation product and the YAC, whose particles are flake-shaped. The individual columns in the PAC each measured approximately 4 mm in diameter and 6-8 mm in Length; while the individual flakes in the YAC measured 1.5-2 mm in thickness, and the flat surtace in each flake measured approximately $6 \times 8 \text{ mm}^2$. Typical shapes of these particle groups are shown in Fig. 3, and the particle size ranges of the spherical particle and nonspherical crushed particle groups are summarized in Table 1.

The experimental conditions are summarized in **Table 2**. In filling particles into the test cell, an amount of powder was taken from the container with a shovel, allowed to drop into the test cell via gravity, and the powder in the test cell was not tapped. Consequently, the packing fraction with the packed particles fell within the range 0.5 to 0.6. Incidentally, even when the test cell with packed particles was turned through 90 degrees for the pressure drop

Fig. 3 Tested particles.

 Table 1
 Size range of spherical and non-spherical tested particles

	(mm)
Sample name	Size range
Spherical particles	
S particle	$2.8 \sim \!\! 4.0$
M particle	$4.0 \sim \! 5.6$
L particle	$5.6\sim 6.7$
Non-spherical particles	
NS particle	$1.0 \sim 2.0$
NM particle	$2.0\sim 2.8$
NL particle	$2.8 \sim \!\! 4.0$

Table 2 Experimental condition	ns	
Tested particles		
Material	Activated carbon (granula	r particle)
Density	860	(kg/m^3)
Porosity (BET)	0.22	(-)
Operating conditions		
Packing fraction ϕ	$0.50 \sim 0.60$	(-)
Airflow rate Q	$1.18{\times}10^{4}{}{\sim}1.65{\times}10^{3}$	(m ³ /s)
Superficial air velocity u	$0.012 \sim 0.165$	(m/s)
Temperature	22±5	(°C)
Humidity	30±10	(%)

Fig. 4 Results of pressure drop measurements.

measurement, no reorientation of the particles was observed. Furthermore, since the powder specimen used in the experiment was a granulated product, its void fraction measured with the adsorption method (BET) stood at 0.2; which suggests that the specimen was a porous material. However, because this void fraction is low compared with that of the particle bed $(1-\varphi)$, it appears that no air penetrated the interior of the individual particles in the specimen.

The pressure drop ΔP was measured for the superficial air velocity within the range of u=0.012 to 0.165 m/s. This superficial air velocity range corresponds to the particle Reynolds number being in the range 3 to 50 in the case of spherical particles M (Dp=(4.0+5.6)/2=4.8 mm), for example. The particle Reynolds number is defined by

$$\operatorname{Re}_{p} = \frac{\rho u D_{p}}{\mu} \tag{1}$$

3. Experimental Results and Discussion

As examples of the results, the pressure drop measurements for the crushed particle products NS, NM and NL are shown in **Fig. 4**. The plotted pressure drop values ΔP were obtained by deducting the pressure drop value unique to the experimental apparatus (pressure drop through the test cell, which was not yet filled with a particle product) from the total pressure drop measurements.

The pressure drop ΔP of each particle type was nearly proportional to the superficial air velocity *u*. With the same particle type, the pressure drops in the direction parallel to gravity (p) are apparently greater than those in the cross direction (c) relative to the gravity. Based on these pressure drop values, we calculated the equivalent sphere diameters Dpe by using the Ergun Equation⁵⁾.

$$\Delta P = 150 \frac{(1-\varepsilon)^2 \ \mu \ u}{\varepsilon^3 D_{pe}^2} + 1.75 \frac{(1-\varepsilon) \ \rho \ u^2}{\varepsilon^3 \ D_{pe}}$$
(2)

Also, the authors calculated the specific surface area Sv, determined from the interrelation between the calculated equivalent diameter Dpe and specific surface area (Sv=6/Dpe). As is clear in Eq. (2), the equivalent diameter Dpe is smaller as the pressure drop increases. Incidentally, as the reciprocal of the equivalent diameter Dpe, the specific surface area Sv is greater with a greater pressure drop. Now, we attempt to engage in discussion using the specific surface area Sv, whose magnitude corresponds to that of the pressure drop.

The calculated specific surface areas Sv relative to the superficial air velocities u are illustrated in **Fig. 5**. It is found that except for the results for NL at lower air velocities, where the measured pressure drop is low, the specific surface area Sv remains almost constant, regardless of the superficial air velocity, meaning that the results in **Fig. 5** can be expressed with the Ergun Equation. Based on this finding, the present experimental apparatus can be considered a sound design, which is capable of measuring the pressure drop with a packed particle bed (the objective of the Ergun Equation is to determine such a pressure drop).

The specific surface area values Sv, which remained constant regardless of the superficial air

velocity, with the respective powder specimens are summarized in **Table 3**. For reference, **Table 3** also lists the equivalent diameters *Dpe*. When considering the difference between the data for the parallel direction (p) and that for the cross direction (c) of a given particle group in this table, the specific surface area in the parallel direction Svp is almest the same as the specific surface area in the cross direction Svcwith a spherical particle of any particle size and it is thus apparent that there is virtually no difference in pressure drop due to the difference in air penetration direction. In contrast with any non-spherical crushed particle product, the specific surface area in the cross direction Svc is smaller than that in the parallel direction Svp.

Here, we determined the specific surface area

ratios *Svc/Svp* as representative values standing for the difference in specific surface area between the parallel and cross directions. Following evaluation in terms of the specific surface area ratio, the specific surface area in the cross direction with a non-spherical crushed particle product is apparently 13% to 15% smaller. Among non-spherical particle products, the PAC particle product (like a spherical particle product), which comprises column-formed particles with relatively uniform shapes, features a specific surface area ratio of approximately 1; while the YAC, which comprises flake-type particles, is characterized by a specific surface area ratio in the cross direction that is almost 30% smaller compared with a similar ratio in the direction parallel with gravity.

In the present experiment, measuring operations

	D_{pc} (m)	D_{pep} (m)	S_{vc} (m ⁻¹)	S_{vp} (m ⁻¹)	S_{vc}/S_{vp} (-)
Sphere					
L	0.00534	0.00533	1123	1127	0.997
Μ	0.00363	0.00350	1655	1713	0.967
S	0.00321	0.00312	1871	1925	0.972
Non-sphere					
NL	0.00264	0.00224	2270	2677	0.848
NM	0.00155	0.00135	3880	4443	0.873
NS	0.00100	0.00087	6007	6924	0.868
PAC	0.00169	0.00163	3542	3692	0.960
YAC	0.00230	0.00180	2607	3331	0.783

Fig. 5 Calculated results of specific surface area.


were performed on each of the packed particle beds with varied air penetration directions. Therefore, the variation in the specific surface area for a given packed particle bed between the air penetration directions appears attributable to the variation in void structure on the packed particle bed. More specifically, the void structure on a packed bed comprising spherical particles is the same, regardless of the air penetration direction through the packed particle bed (almost random in any direction). In contrast, with the void structure on a packed bed comprising nonspherical particles, the air passages formed through the voids between particles viewed in the parallel direction are relatively small. While the packed bed is viewed in the cross direction, there are regions with more tightly packed particles and regions with more loosely packed particles, thereby the air typically flows through more loosely packed regions where the air drag is low. Such difference between the parallel and cross directions seems attributable to the fact that since powder was uniformly packed in each layer, the particles are arranged at random when the packed particle bed is viewed in a parallel direction relative to gravity; and that because no compacting efforts, including tapping, were attempted after filling with powder and since reorientation seldom occurs with non-spherical particles being allowed to fall under gravity, tightly or Loosely packed regions are present on the resultant packed particle bed when viewed in the cross direction.

To sum up, the authors believe that by using the two-directional air-permeability method, the threedimensional non-uniformity of the void structure of a packed particle bed can be numerically evaluated. For this purpose, the authors attempted to evaluate this non-uniformity in terms of the apparent packing structure. Let us consider a packed bed, whose particles are oriented in a particular direction, wherein like with the previously mentioned particle bed, consisting of non-spherical particles, the packed particle bed provides hard-to-penetrate air passages when viewed in the parallel direction and a void structure that allows easy penetration by air when viewed in the cross direction. Therefore, we performed a series of experiments, using a model packed bed consisting of rods, in an attempt to evaluate the three-dimensional non-uniformity of the packed particle bed as represented by a specific surface area ration Svc/Svp as an equivalent apparent aligned angle.

For the model cell packed with rods, pieces of dia. 4 mm drinking straws, each filled with putty, which had been 100 mm (a length that coincides with the



a) top view



b) Side view Fig. 6 Model packed bed made by uniform rods.

inside measurement of one side with the test cell), these were filled into the test cell such that almost all were oriented in a particular direction as shown in **Fig. 6**. The resultant aligned angle θ was determined by taking photos of the straw pieces, measuring the angles of the same, and then obtaining the average for these angles. With the group of rods in **Fig. 6**, aligned angles of $\theta = 9.7$ degrees when the air was blown from above; and $\theta = 80.3$ degrees when the air was blown from the left were revealed. Incidentally, portions with an aligned angle of 0 degrees (parallel with the air penetration) and those with an aligned angle of 90 degrees (cross to the air penetration) were regularly arranged in a staggered pattern.

Pressure drop measurements were obtained with varied penetration air velocity, and substituted in the Ergun Equation (Eq. (2)) to determine specific surface areas, with the latter plotted in **Fig. 7**. The Ergun Equation is intended for spheres, and may not be fully suitable for rod-shaped objects as used in the present experiment. Based on **Fig. 7**, in the low flow velocity range of u<0.1 m/s in particular, it is apparent that at specific angles ($\theta=0$ to 25.0 degrees, and 80.3 degrees and 90 degrees), the specific surface area Sv decreases as the flow velocity increases; while at other angles ($\theta = 65.0$ degrees and 69.2





Fig. 7 Equivalent diameter of model bed calculated by Ergun equation.

degrees), the specific area once decreases and then increases as the flow velocity increases: namely there is no clear-cut correlation between the variation in specific surface area and the increase in flow velocity at a given aligned angle. This may be because the interaction between the wakes generated by the rods varies depending on the flow velocity. However, because the flows in the groups of rods are very complicated[®], the true reason for such variation remains unclear.

Since the authors believe that for cases where the Ergun Equation applies, the specific surface area Sv should remain constant regardless of air flow velocity, we believe the use of the Ergun Equation for low air flow velocity will be problematic. Incidentally, at a higher air flow velocity range, the specific surface area calculated by this equation tends to gradually approach a specific value, the authors considered this equation to be useful for a higher air flow velocity range, and adopted the resultant asymptotic values as representative specific surface area values Sv for various aligned angles.

Taking the specific surface area at a standard aligned angle θ as the *Svp* and that in the cross angle (90- θ) as the Svc, the specific surface area ratios *Svc/Svp* were determined and plotted relative to the aligned angle θ , and the result of plotting is shown in **Fig. 8**. Since in this plotting, the effect of the apparent aligned angle of 45 degrees is the same for both the packing (parallel) direction and cross direction, this aligned angle represents a random packing

mode, wherein the corresponding specific surface area ratio *Svc/Svp* is 1.

As can be understood from **Fig. 8**, the specific surface area ratio *Svc/Svp* of the model packed particle bed simply decreases as the aligned angle increases and is plotted as a near-straight line on a semilogarithmic graph. Based on this data, the authors attempted to develop an experimental formula, thereby the equation below was obtained with a correlation function of R^2 =0.999:

$$S_{vc}/S_{vn} = 3.53 \exp(-0.028\theta)$$
 (3)

or,

$$\theta = 45.0 - \ln \left(\frac{S_{vc}}{S_{vp}} \right)^{\frac{1}{0.028}}$$
(4)

The specimen NL, for example, which is a nonspherical crushed particle, has a specific surface area ratio Svc/Svp of 0.848. Based on the results of experiments on this model paeked bea, this packed particle bed has an air flow passage structure that is equivalent to a group of rods apparently oriented by 51 degrees to the horizontal direction relative to the packing direction (vertical direction) or a group of rods shifted by 6 degrees to the horizontal direction, relative to the random packing direction (=45 degrees). Thus, by determining the ratio of the specific surface area in the packing direction (parallel direction) to that in the cross direction through experiments on a model packed bed, it is possible to evaluate the three-dimensional non-uniformity of a packed particle structure as the equivalent apparent aligned





Fig. 8 Relation between aligned angle and specific surface area ratio.

angle.

4. Conclusion

The fluid-permeability method, in which a fluid is allowed to pass through a packed particle bed to determine the specific surface area from the measured pressure drop, is characterized by its ability to reflect the voids between particles that provide passages for the fluid. By measuring the bidirectional pressure drop of the penetrating fluid utilizing this feature, the authors attempted to evaluate non-uniformity in the packed particles.

The authors performed a series of experiments with a packed bed that comprised millimeter-order particles, thereby learning that by allowing air to flow through the same packed particle bed while mutually crossing two directions and measuring the pressure drop in each direction, the non-uniformity of the packed particle structure could be numerically evaluated. It seems possible to express the non-uniformity of the packed particle structure as the equivalent apparent aligned angle by comparing the experimental results obtained from model particle bed.

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Nomenclatures

D_p	particle diameter	[m]
D^{pe}	equivalent diameter	[m]
Q	airflow rate	$[m^{3}/s]$
R	correlation coefficient	[-]
S_{ν}	specific surface area	$[m^{-1}]$
u	superficial air velocity	[m/s]
ΔP	pressure drop	[Pa]
3	void fraction	[-]
ϕ	packing fraction	[-]
μ	viscosity of air	[Pa·s]
ρ	density of air	[kg/m ³]
θ	alignment angle of particle bed	[deg]

Súbscript

- *c* cross direction to gravity
- *p* parallel direction to gravity

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Author's short biography



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Dr. Kuniaki Gotoh graduated from Hiroshima University in 1986, and from the graduate school of Hiroshima University in 1988. He obtained the Doctor degree of Engineering from Kyoto University in 1995. He was appointed Associate Professor of Mechanical Engineering Department of Yamaguchi University in 1997. Presently he is Professor of Applied Chemistry Department of Okayama University since 2003.

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Dr. Tatsuo Nishimura graduated fro Yamaguchi University in 1975, and from the graduate school of Toyama University in 1977. He obtained the Doctor degree from Hiroshima University in 1981. He was Associate Professor of Toyama University since 1988 until 1990. He was appointed Associate Professor of Yamaguchi University in 1990 and Professor of Mechanical Engineering Department in 1993.



The 41st Symposium on Powder Technology

The 41st Symposium on Powder technology was held on September 11, 2007 at Senri Hankyu Hotel in Osaka under the sponsorship of the Hosokawa Powder Technology Foundation and with the support of Hosokawa Micron Corporation. The symposium was very successful as usual with the attendance of 144 including 24 academic people. The main subject was "Nanoparticle Technology: Development of New Markets and Entry into them".

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Dr. Kikuo Okuyama, Professor of Hiroshima University, was selected as the winner of the 15th KONA Award, which is sponsored by Hosokawa Powder Technology Foundation and given to the scientists or groups who have achieved distinguished research works in the field of particle science and technology.

Dr. Okuyama is Professor in the Department of Chemical Engineering, and vice dean in the Graduate School of Engineering at Hiroshima University. He received BS (1971) and MS (1973) degrees in chemical engineering from Kanazawa University, and he received Doctor of Engineering (1978) in chemical engineering at University of Osaka Prefecture. His research has touched many aspects of aerosol science and technology, from fundamental investigations into the dynamic behavior of aerosols to the development of advanced aerosol measurement equipment with a recent focus on materials synthesis using aerosol techniques. Professor Okuyama has engaged in a number of national projects concerning particle contamination during semiconductor processing, materials synthesis by aerosol routes, and investigations of atmospheric aerosols. Professor Okuyama has received numerous honors and awards, including the Fuchs Memorial Award of the International Aerosol Research Assembly in 2002.

On January 29, 2007, Mr. Masuo Hosokawa, President of the Foundation, handed the 15th KONA Award to Professor Okuyama at the ceremony of presentation held at Senri Hankyu Hotel in Osaka.





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GENERAL INFORMATION

HISTORY OF THE JOURNAL

In the history of KONA 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 non-profit 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 authorized 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-Oceania, American and European. The policy and system have not changed after the Hosokawa Foundation has taken over from the CPT. The CPT is active still today and collaborates with the Hosokawa Foundation.

AIMS AND SCOPE

KONA publishes papers in a broad field of powder science and technology, ranging from fundamental principles to practical applications. The papers discussing technological experiences and critical reviews of existing knowledge in special areas are also 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 except the translated papers which are selected by the Editorial Committees.

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- 3)Seborg, D. E. (1969): Ph.D. Dissertation, Princeton Univ., N.J., U.S.A.
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