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# KONA POWDER AND PARTICLE

NO. 11(1993)

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Magnetic domain structure in (a)as-cast and (b)sintered Nd-Fe-B permanent magnetic alloys by optical Kerr effect.



# KONA POWDER AND PARTICLE

KONA, issued annually since 1983 by the Council of Powder Technology, Japan, is a referred journal publishing the articles on powder sciences and technology, and is distributed to the interested persons and institutions throughout the world.

### About the Cover of Journal "KONA"

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



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# Letter from the editor



It is my privilege to inform you all the readers of KONA that Professor Genji Jimbo, the former editor-in-chief of this journal, has retired from Nagoya University on March, 1993.

After nine years with Tokyo University, Professor Jimbo joined the faculty of engineering, Nagoya University in 1967. From 1989 to 1993, he has played an active role as the president of the Society of Powder Techology, Japan. During this period, he has organized the second World Congress Particle Technology (Kyoto, 1990) and the sixth International Symposium on Agglomeration (Nagoya, 1993) both as the chairperson.

A creditable achievement made by Professor Jimbo in his studies should be highly evaluated in that it has improved the studies in powder and particle technology field in Japan up to the world standard.

Unfortunately, it is my regret to tell you that his dearest wife has passed away this August by a traffic accident in South England on their travelling abroad commemorating his retirement. He is, however, now recovered from the heavy blow and is very active as the director of Chubu Powtech Plaza Laboratory<sup>\*</sup>.

Thank you for your attention.

Kai Miyanam

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### **KONA**

### GENERAL INFORMATION

### HISTORY OF THE JOURNAL

The Council of Power Technology (CPT), Japan, has been established on 1969 as a non-profit organization to enhance the activities of research and development on powder sciences and technology in Japan. Under the sponsorship of Hosokawa Micron Corporation. In 1983, the CPT has decided to issue an international journal, named "KONA", which publishes the excellent articles appeared in Japanese Journals concerning with powder sciences and technology, translated into English, throughout the world. After the seventh volume issued on 1989, the CPT has changed its policy to internationalize the "KONA" from the 8th issue (1990) on by incorporating the monographs originally written in English from the authors throughout the world.

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KONA Journal is to publish the papers in a broad field of powder sciences and technology, ranging from fundamental principles to practical applications. The papers discussing technological experiences and critical reviews of existing knowledge in specialized areas will be welcome.

These papers will be published only when they are judged, by the Editor, to be suitable for the progress of powder sciences and technology, and are approved by each Block Editorial Committee. The paper submitted to the Editorial Secretariat should not have been previously published except the translated papers which would be selected by the Block Editorial Committees.

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# KONA Powder and Particle No. 11 (1993)

### Contents

### <Review>

- Selective tribocharging of particles for separation
- Particle sizing in the submicron range by dynamic light scattering
- High-performance structual ceramics: Powders and components
- Rigid ceramic filters for hot gas cleaning
- Discrete particle simulation of gas-solid flows (From dilute to dense flows)
- Size enlargement of pharmaceutical powders by wet agglomeration and drying techniques
- A critical review of thickner design methods
- E-SPART Analizer: Its performance and applications to powder and particle technology processes

### <Original Research Paper>

- Experimental study of horizontal plug flow of cohesionless bulk solids
- Rheological investigation of suspensions and ceramic pastes: Characterization of extrusion properties
- The use of standpipes for increasing limiting gravitational flowrate from mass flow bins
- Interparticle friction in granular ceramic materials
- Solution approaches to the dynaic, population balance modeling of grinding with transport
- An effective sem-based image analysis system for quantitative mineralogy

### <Translated Research Paper>

- Numerical analysis of movement of balls in vibration mill in relation with its grinding rate
- The experimental stress-strain rate relationship of granular materials
- Dispersion of aggregate particles by acceleration in air stream
- Initial collection efficiency of electret filter and its durability for solid and liquid particle
- Study of static pressures on granular materials in a silo using the distinct element method
- Dry submicron classification by a small blow down cyclone
- Analysis of the Powder composite process by a mechanical method

R. Ciccu, M. Ghiani and G. Ferrara	5
R. Finsy	17
A. Kerber	33
J.P.K. Seville	41
1. ISUI	57
H. Leuenberger	69
F. Concha, and A. Barrientos	79

K. Daoud, A. Ould Dris, P. Guigon and ..... 119 J.F. Large

*M.K. Mazumder* ..... 105

W. Gleißle, J. Graczyk and H. Buggisch ..... 125

Z.H. Gu, P.C. Arnold and A. G. McLean ..... 139

N.W. Page, M. Yousuff and C.J. Wauchope .. 147 M.C. Williams, T.P. Meloy, and ..... 157 M. Tarshan

- R.P. King, and C.L. Schneider ..... 165
- T. Yokoyama, K. Tamura, H. Usui and..... 179 G. limbo
- S. Yuu and S. Kamimura ..... 191
- Y. Kousaka, Y. Endo, T. Horiuchi and ...... 199 T. Niida Y. Otani, H. Emi and J. Mori ...... 207
- K. linoya, T. Fuyuki, Y. Yamada, ..... 223
- H. Hisakuni and E. Sue
- M. Naito, M. Yoshikawa, T. Tanaka and ..... 229 A. Kondo



### Explanation of the Cover Photograph Optical Kerr Micrograph of Nd-Fe-B Sintered Magnets



Nd-Fe-B permanent magnets having a record-high energy product about 400kJ/m<sup>3</sup> have been produced by the following process using powder metallurgy method: (1) melting of the Nd-Fe-B alloy to obtain an ingot (photo (a)), (2) pulverizing, (3) compacting in a magnetic field to align the powders, (4) sintering and (5) annealing. Photo. (a) shows that the ingot is composed of  $Nd_2Fe_{14}B(T_1)$ ,  $Nd_{1.1}Fe_4B_4(T_2)$  and Nd-rich phase.  $T_1$  is the main magnetic phase identified by the striped magnetic domain patterns and  $T_2$  is non-magnetic B-rich phase. Two kinds of liquids are formed during sintering process: one is the ternary eutecic liquid by the reaction of  $L \rightleftharpoons T_1 + T_2 + Nd$ -rich phase and the other is the pseudo-binary eutectic liquid by the reaction of  $L \rightleftharpoons T_1 + T_2$ . This phenomena makes a liquid phase sintering possible, which enables higher densification and contributes toward curing faults and removing impurity phase in the surface of powders.

Photo. (b) shows that the sintered specimen is composed of  $T_1$  phase identified by the striped magnetic domain patterns and the minority phases of  $T_2$  and Nd-rich phase. This Nd-rich phase mainly exists in cluster at triple points of grain boundaries.  $T_2$  phase exists in a cluster near the grain of Nd-rich phase. The presence of the thin intergranular layer of the Nd-rich phase is essential to increase the coercivity of this magnets, because the thin non-magnetic layer disconnects exchange paths between  $T_1$  grains.



## Review Selective Tribocharging of Particles for Separation †

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Department of Chemical Engin., Environment and Raw Materials Unversity of Trieste $^{\ast 2}$ 

### Abstract

Selective tribocharging is a suitable way for separating mineral constituents from heterogeneous mixtures using an electrostatic field. Though contact charging mechanisms have been studied intensively, understanding is far from clear and complete, due to the variability of material properties and to the influence of ambient conditions, which are often difficult to control.

After outlining the scientific fundamentals of contact electrification, the paper illustrates and discusses some significant cases of selective charging of minerals under different experimental conditions, pointing out the effect of operational variables.

Separators of practical interest are briefly described, the performance of which is assessed on the basis of beneficiation results obtained for a variety of ores and coal both on a laboratory and industrial scale.

### 1. Introduction

Electric separation is a process by which a ground solid matter can be divided into two or more fractions according to the different electric properties of the various components.

Dielectrophoresis is based upon the difference in dielectric constant and consists in the displacement of uncharged particles into a medium of intermediate dielectric constant under the action of a strongly divergent static field. In contrast, separation by electrophoresis takes place when charged particles are subjected to the action of an electric field and, therefore, selective charging of mineral particles represents the fundamental step for the success of the operation (1). This latter method is the most interesting for practical application.

Charging can be obtained either by induction/conduction, ionic bombardment or contact charging as well as by a possible combination. Correspondingly, three distinct types of separation equipment can be conceived, namely the electrostatic, electrodynamic, and triboelectric separators (2).

Separators using a purely static field were first developed, although high-tension electrodynamic sep-

KONA No.11 (1993)

arators have been most widely applied. Recently, interest is being directed towards the development of triboelectric separators but, despite the efforts, the method has not yet achieved a great level of popularity: actually industrial application is restricted to few instances, such as the separation of salt minerals (3-6) and the beneficiation of nepheline and muscovite ores (7).

The main reason for such a limited diffusion of tribocharging techniques lies in a scant understanding of the scientific aspects underlying contact electrification, due to the great complexity of the charging mechanisms involved and to the high sensitivity of the process to the environmental conditions.

In spite of this, triboelectric separators are characterized by some interesting features, allowing some of the handicaps of conductance-based separators (limited throughput capacity, deterioration in efficiency towards the fine size range) to be overcome.

The contribution to the research in the field provided by the Mining and Mineral Engineering Department of the University of Cagliari over the last 20 years is substantiated in the theoretical and experimental study of tribocharging phenomena and in the application of the basic results to the design and development of suitable separators, whose technical efficiency and economic profitability has been

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<sup>†</sup> Received May 13th, 1993



demonstrated at both the laboratory and pilot plant stage.

### 2. Scientific Fundamentals

Selective charging prior to separation in a static field can be attained by exploiting the different energy properties of the mineral grains in the surface layer.

In fact, charging is the result of one or more processes of charge carrier migration within the mineral particles themselves and between the particle and the environment (8, 9).

Most minerals behave as semiconductors. Their energy structure can be described by a band model where an empty conduction band is separated from a completely filled valence band by a forbidden gap hosting localized donor or acceptor levels. The main consequences are:

- conductance increases with temperature;
- contact charging against a metal or semiconductor surface can be produced by electron transfer according to the respective work function or electrochemical potential;
- charge is partially released across the contact area;
- after disengagement, residual charge is redistributed on the mineral surface according to its surface conductivity;
- thermoelectric effects may be important.

Amorphous or highly resistive substances (organic phosphate, coal macerals, pure crystals of insulator minerals, for instance) are charged by other mechanisms (ion exchanges, material removal, piezoelectric effects, dust coating, charge displacement due to temperature gradients, surface contamination, hot spot formation). High-resistivity minerals become intrinsic semiconductors at high heating temperatures. In the case of insulators, final charge remains concentrated near the contact points and leakage is controlled by corona or thermoionic effects.

Practically, the various minerals show a different behaviour, from that of metals on the one extreme to that of insulator solids on the other. Therefore a distinct consideration should be given to the different groups of substances into which minerals can be classified.

### 2.1 Separation charging of metals and metallike minerals

In the absence of sliding between the two contacting bodies, the mechanism of charge transfer consists in a flow of electrons from the substance having a lower work function to the other, giving rise to a steady double layer across the interface until equilibrium state is reached. On disconnection, the charge can partially leak back by electron tunnelling.

The amount of the final charge therefore depends on the separation rate: the faster the disengagement, the higher the final charge retained.

In the presence of sliding, additional triboelectrification mechanisms can also take place such as charging by transfer of matter from softer to harder material, or by thermoelectric effects (Seebeck potential).

### 2.2 Charging of semiconductors

When a semiconductor approaches a metal below a critical gap, electrons start to transfer by means of the tunnelling effect. As true contact is achieved, a double layer builds up at a rate determined by the relaxation time, eventually establishing a contact potential. The ensuing electromotive force causes both contacting bodies to charge up because of electron flow across the contact area; the final charge depending on the capacity of the system.

Charging kinetics is controlled by the time constant RC.

Accordingly, two distinct charging phases can be envisaged: the first, coming from the double layer, generally gives a minor contribution owing to the small area involved; the second, due to the subsequent charging of the capacitance between the two contacting bodies, can be much more important. When a saturation charge has been transferred, the potential difference is eliminated, thus preventing the charge from leaking.

### 2.3 Charging of insulators

Electrons do not participate in the charging of insulators except at high temperatures at which all crystalline solids tend to behave as intrinsic semiconductors. At normal temperatures, a good insulator cannot be charged by the same mechanism as natural semiconductors, due to its wide energy gap which prevents electron transfer.

In principle, the only possible contact charging of insulators at normal conditions is therefore by transfer of some adventitious ions collected from the surroundings as compensatory charges of dangling bonds at the surface. The transfer of these chemisorbed ions from one body to the other is controlled by the respective affinities and/or by the relative abundance.

Hydrogen and hydroxyl ions are the responsible



charge carriers in most cases.

Insulators can be classified into two classes:

- Electrophylic which can charge up relatively easily, or
- Electrophobic which are highly reluctant to charging even after very long contact duration.

In electrophilic insulators, contact charging is produced by redistribution of free-to-move or weakly bound ions onto the surface of contacting bodies. Charge is small if ion affinities are very close or if there is a dearth of available ions.

By applying a sufficiently large external field in the appropriate direction, the polarity of the charge can be reversed. This superimposing process of charging is merely a consequence of electrostatic induction. Some surface conductivity is necessary for this to occur.

Contact charging of otherwise electrophobic insulators can only result from electrophylic alkaline contamination (which generally produces positive charging) or acid contamination (favouring negative charging).

Electrolytic phenomena in the presence of adsorbed moisture may be important.

In the case of a sliding contact, electrophobic insulators are charged by other mechanisms such as material transfer and hot spot formation. Adherent sliding contact involving rough surfaces under relatively high pressure between the surfaces is the necessary prerequisite.

Under load, surface asperities are crushed or flattened by plastic deformation and minute quantities of material will be transferred from one surface to the other. Fragments removed may carry an electric charge, which, however, is not likely to be very large.

Hot-spot formation is favoured by a combination of high strength and low thermal conductivity of the materials involved, large area of true contact points and adherent rubbing under high speed and pressure.

Continued rubbing may change the nature of one of the surfaces. In some instances, frictional contact may even reverse the polarity associated with charging in the absence of sliding.

### 2.4 Charging of dissimilar materials

Charging process involving dissimilar materials is more complicated than in the case of similar substances.

For metal/semiconductor pairs, the main mechanism is again based upon the transfer of electrons, according to the band model.

When one of the partners is an insulator, it is

this latter that prevails. In fact, although electrons are available on the metal or semiconductor side, they cannot be transferred to the insulator as this is unable to accommodate them except in some occasional recipient sites (electron traps).

In fact, it has been experimentally demonstrated that electrophobicity is an intrinsic characteristic of a given material, irrespective of the nature of the contacting body (9).

### 3. Laboratory technique

### Measurement of electrophysical parameters

From the standpoint of the solid state physics, the surface energy structure of minerals can be described by means of some representative parameters (10-12): the electron Work Function  $\phi$  [eV], which is the energy required to remove an electron from the Fermi level to the "vacuum" level; the width of the forbidden energy gap  $E_g$  [eV]; the concentration of electrons and holes n and p [cm<sup>-3</sup>] and their respective mobility  $\mu_n$  and  $\mu_p$  [cm<sup>3</sup>/s].

The Fermi level may be taken as characterizing, in terms of average behaviour, an energy structure that may be very complex. It represents the mean energy of the electrons involved in the interphase exchanges that occur in electric or electrochemical phenomena.

However, the resulting effect of a charging process is hardly affected by the Work Function alone.

In fact, if the concentration or the mobility of the charge carriers is too low, the exchanges will be limited and the contribution from the crystal bulk will be small. From this standpoint emerges the importance of the concentration and mobility of the charge carriers of either type, and of the concentration ratio p/n, which determines the rate of displacement of the Fermi level as a function of temperature.

The extent of the forbidden band is particularly important in contact charging, since it represents the maximum shift of the Fermi level attainable through external actions capable of modifying the carrier concentration ratio p/n. Hence a mineral characterized by a very narrow forbidden band is generally barely sensitive to various external actions.

The position of the Fermi level can be determined in two different ways:

The first consists in the measurement of the contact potential difference between the mineral speci-



men and a gold reference electrode according to the modified Kelvin method. The capacitance of the condenser formed by the two is periodically varied by rotation or vibration, thus producing a displacement current which is amplified and counterbalanced by means of a known external voltage (8, 13).

The second method consists in the determination of the Fermi level  $E_f$  with respect to the upper limit of the valence band, once  $E_g$  is known, from the measurement of the thermoelectric potential (Seebeck coefficient)  $\alpha$  (mV/°C) as a function of temperature (13, 14).

The first method is more suitable for studying the charge transfer process between two different bodies, whereas the second is preferable when the effect of different actions on the same mineral is to be investigated. This latter is more versatile since it can be also applied to mineral samples in the form of compressed dust.

The width of the forbidden band  $E_g$  can be determined by measuring the electrical conductivity as a function of temperature, taking the gradient of the curve in the intrinsic field into account.

The charge carrier concentration ratio p/n can be calculated once the values of  $E_g$  and  $E_f$  are experimentally known, since the product np is, at a given temperature, an invariant of each semiconductor dependent only on the forbidden gap width.

### Measurement of electric charge

The charging mechanism can be elucidated through the direct measurement of electric charge on single grains, after sliding on vibrating chutes. Vibration frequency and amplitude can be varied so as to reproduce the different kinds of rubbing, from gentle sliding to high-velocity impingements (13).

Rubbing promotes closer mating involving a larger contact area. If the normal load is large enough, it helps in eliminating particle contamination and breaking-up of oxide layers.

Charging can also be obtained by friction on the inner wall of microcyclones made of different materials (13).

Individual charges are measured with a Faraday well connected to a high-input impedence electrometer. The charging device and the instrumentation used are shown in **Fig. 1**.

### 4. Experimental studies

Relationship between work function and triboelectric charging



Fig. 1 Experimental set-up for the measurement of tribocharge on individual particles.

Work Function data for different minerals and metals obtained with the Kelvin method on shaped specimens fitted into the rotating condenser device are given in **Table 1**. The data refer to particular mineral samples and may be different according to origin and crystal lattice conditions. For instance, values ranging from 4.24 to 4.46 eV have been found for various occurrences of fluorspar.

It appears that the W.F. of minerals is affected by moisture, decreasing as the ambient humidity increases.

different minerals and metals.						
		Average particle charge [pC]				
Mineral	Work Function	NC 1 1	Contract	Gold (4.71 eV)		
	[eV]	(4.30  eV)	(4.51 eV)			
Fluorspar	4.32	-4.10	+ 5.50	+ 4.50		
Calcite	4.41	-6.30	+ 3.50	+ 4.60		
Quartz	4.39	-2.50	+ 2.00	+ 5.60		

-2.60

-0.24

-0.18

-0.36

+ 5.80

-0.35

-0.04

-0.05

Barite

Galena

Pyrites

Sphalerite

4.31

4.50

4.57

4.58

Table.1 Work Function and average particle charge for different minerals and metals.

Contact charges of a large number of particles, 1.2 to 2.4 mm in size, have been measured and statistically processed for different mineral-metal pairs. Charge frequency distribution generally follows the normal model, although a log-normal trend is sometimes found.

Average charges for various minerals are reported again in **Table 1**.

Fig. 2 shows the average particle charge of various minerals upon contact with different metals plotted against the difference in the respective Work Functions.

+ 6.10

-0.44

-0.37

+ 0.01





Fig. 2 Average particle charge of minerals against the difference in Work Function.

It emerges that:

- polarity is in very good agreement with prediction based on Work Function;
- charge is not proportional to the difference in Work Function owing to the great variability of charge carrier concentration and mobility among mineral substances; moreover leakage rate is different depending on conductivity;
- many other factors (particle shape, effects of comminution, lattice defects, surface contamination and so on) may influence particle charging resulting in a considerable dispersion of statistical charge distribution.

In tests using air microcyclones, results are similar but charge distribution follows more closely the normal model, owing to stronger contacts involving a larger particle surface.

### Modification of mineral energy structure

In triboelectric charging, conditions most favourable to selectivity can be met by resorting to suitable external actions such as: adsorption of reagents, heat treatment, X or  $\gamma$  radioisotope irradiation, neutron or ion bombardment, doping by solid diffusion, and so on (14).

Some interesting instances are illustrated in Fig. 3.

The effect of heating on the position of the Fermi level for some selected minerals is shown in **Fig. 3**, under variable experimental conditions (wet or dry grinding, X or  $\gamma$  irradiation). The following aspects are worth consideration:



Fig. 3 Position of the Fermi level as a function of temperature for fluorspar, barite and calcite. (1) Dry grinding; (2) Wet grinding (3) After X irradiation.

- at increasing temperature, the Fermi level shifts towards the centre of the forbidden band, upwards in p-type and downwards in n-type semiconductors;
- fluorspar and calcite behave as n-type semiconductors if wet-ground, turning into p-type if dry-ground. On the other hand, the behaviour of p-type barite is not affected by comminution, although its Fermi level is somewhat lower in the case of wet grinding.
- X and  $\gamma$  irradiation produce a downwards displacement of the Fermi level of fluorspar, barite and calcite with respect to that of wet-ground untreated minerals; moreover, fluorite and calcite turn from n-type into p-type.

The behaviour of the same minerals in a static field has been found to be in very good agreement with the indications of the charging study, as confirmed by the results of a test aimed at disclosing the influence of temperature shown in **Fig. 4**.

Each mineral, ground and screened into the size





Fig. 4 Mass fraction deflected towards the negative electrode of the tribocyclone separator as a function of feed heating temperature. (1) Fluorspar; (2) Barite; (3) Calcite; (4) Quartz.

class  $-500 + 150 \ \mu$ m, was separately charged using a stainless-steel cyclone after heating in a gas-fired rotating kiln and then fed into a free-fall electrostatic chamber.

The mass fraction deflected towards the negative electrode increases with temperature for p-type barite, dependent on the fact that the Fermi level is raised by heating and, consequently, positive charging is favoured. On the other hand, for n-type fluorspar and calcite, the effect of temperature is the opposite, since in this case the Fermi level is lowered at higher temperatures.

The practical importance of these results is evident: whereas at room temperature, separation of barite from fluorspar and calcite appears to be very difficult, it becomes less so after heating to 120 - 150 °C. This conclusion is supported by the successful results of separation tests (14).

The presence of maximum or minimum points in the curves of **Fig. 4** clearly results from thermoelectric effects produced by the abrupt particle cooling into the cyclone: migration of majority carriers (electrons in n-type minerals and holes in p-type minerals) towards the particle surface takes place due to the negative thermal gradient. While the main charging process becomes less and less important as temperature increases, this new superimposing effect, acting in the opposite direction, prevails in or near the intrinsic field.

# Tribocharging of heterogeneous particles by mutual friction

In typical triboelectric separators fed with a stream of ground mineral particles, two kinds of contact can take place: collision between particles themselves and/or impingement against a target surface. A necessary prerequisite for successful separation is that charging be consistent, i.e. each mineral component takes the same polarity in both the above cases. This condition is met if the properties of the target surface lie between those of the species to be separated.

Often, inter-particle charging is the most important.

This fact has been evidenced by ad hoc charging tests involving pairs of minerals, one of which plays the role of the rubbing medium applied to a vibrating plate. With this kind of experiment, all minerals can be arranged into triboelectric series under carefully controlled conditions.

To this end, the cases of phosphate and of coal appear very interesting as illustrated later on.

### Tribocharging of amorphous minerals

Concerning phosphate, individual charges of phosphorite, calcite and quartz particles sorted out of an African ore have been measured using a Faraday well, after sliding on a vibrating metal chute heated with an infrared lamp.

In order to reproduce the conditions for particleparticle charging, a layer of ground ore was glued onto a metal plate, forming the rubbing surface against which individual particles were charged (15).

The main findings are the following:

- On the stainless steel surface, all components take a negative polarity; the charge increases with temperature for phosphorite, decreases for calcite (which starts reversing its polarity at 140°C), whereas it remains almost constant for quartz. A higher charge is obtained after a prolonged contact time.
- On the ore-lined surface, calcite and quartz are both positively charged, whereas phosphorite particles take a negative charge at moderate temperatures and small charges of either polarity above 100°C. Unfortunately, the charging behaviour due to contacts involving mineral pairs could not be assessed.

Results are shown in **Fig 5**. It appears that tribocharging of gangue componenents is mainly affected by the contact with phosphate particles, which causes





Fig. 5 Average particle charge of different constituents of a phosphate ore as a function of temperature. 1-Phosphorite; 2-Calcite; 3-Quartz

their polarity to reverse compared to that of stainless steel. On the other hand, phosphate charging is strongly sensitive to temperature, while the contact with the gangue minerals is of no advantage or even detrimental.

Therefore, heating looks potentially beneficial for the separation of phosphate from calcite, since it eventually produces well differentiated charges upon contact with both the target surface and the other mineral components.

The relative abundance of the various mineral species in the ore is also of importance concerning their respective charging behaviour in triboelectric separators. In fact, tribocharging of particles of the less abundant components (generally the gangue particles in the case of phosphate ores), having a high probability of collision with those of the main constituent (the phosphate phase), will be strongly influenced by the contact with this latter.

Contrary to this, charging of phosphate particles will be less influenced by particle-particle collision, since for them the highest probability of contact is indeed against the target surface.

As confirmed by the experimental evidence, feed heating temperature plays a major role in tribocharging and often represents a decisive factor for separation efficiency.

In the beneficiation of phosphate ores using triboelectric separators, although the mechanism has not been thorougly clarified, different superimposing effects are likely to take place simultaneously such as charge migration between the contacting bodies and thermoelectric phenomena, while charge leakage is reduced due to the gradual elimination of adsorbed moisture.

In any case, pre-heating produces a sharper separation of phosphate particles from the gangue minerals, in agreement with the charging experiments on individual components sliding onto a stainless steel vibrating plate at varying temperature.

Accordingly, upgrading of phosphate becomes feasible above 110°C, as shown in **Fig. 6** for the case of an Algerian ore with carbonate gangue.

As regards coal, the electric charge of the different components commonly found in a run-of-mine (macerals, limestone, shale, pyrite, calcite, quartz) has been measured upon contact with rubbing media of a different nature: metals (stainless steel, copper, aluminum, brass, nickel, cadmium), plastic matter (PVC, polypropylene, perspex, teflon); glass doped with various metal ions; ceramic materials obtained by firing steatite and refractory clay. The main results obtained can be summarized as follows (16, 17):

### a) Charging on metals

For coal particles:

- charge polarity is always negative except for hot (200°C) stainless steel and copper;
- higher charges are obtained with copper, stainless steel and aluminum, in that order;
- charge always decreases with increasing temperature, irrespective of the metal;
- higher charges are achieved under vacuo (discharge is reduced);
- charges are often significantly higher for high-rank than low-rank coals;

For mineral particles:

- pyrite always takes a negative charge, practically independently of temperature, one order of magnitude lower than coal due to its high conductivity;
- shale also takes a negative charge, which, however, strongly increases with temperature (conductivity decreases as moisture is removed);
- contradictory results have been obtained for calcite;
- for limestone, the thermoelectric effect is masked by the concurrent process of electron transfer from the metal.
- b) Charging on fired-steatite ceramic
- coal is positively charged one order of magnitude more than on metals;





Fig. 6 Results of triboelectric separation for an Algerian phosphate ore. 1 - Recovery; 2 - Concentrate grade; 3 - Loss in the reject

- pyrite, calcite and shale also take a positive charge.
- c) Charging on glass
- all components show a very similar behaviour concerning both charge and polarity (negative);
- charging efficiency is gradually reduced with contact time (surface saturation);
- heating up to 100°C does not produce any significant effect.
- d) Charging on plastics
- on some plastic materials, coal particles are strongly charged;
- calcite and pyrite sometimes take well differentiated charges (strong positive); with respect to coal (small, either polarity);
- saturation phenomena appear after a relatively short charging time.

e) Charging on different surfaces in series

- Final particle charge is determined by the last contact surface. Positive charges are diminished or even reversed if the surfaces are arranged in order of decreasing electronegativity (attitude to acquire negative charges) and vice-versa.
- f) Mutual charging

Charging tests have been carried out on grains of the different mineral components (coal, limestone, shale), hand-sorted from a sample of a sub-bituminous coal.

In order to reproduce the effect of particle-particle frictional electrification, single grains of the different components were separately subjected to rubbing against each other.

It has been found that coal particles are positively charged in the presence of carbonate gangue, and negatively charged in the presence of quartz and silicate minerals. Separation can be successful in both cases but becomes impractical when the two kinds of gangue are present at the same time.

The possible presence of thermoelectric effects was studied by heating to 80°C either the grain or the surface or both and comparing the results with those obtained at room temperature.

The results can be summarized as follows:

- Charging of like materials is not affected by heating except for limestone. Coal and shale both take negative charges against themselves, moderate in the first case and very small in the second, whereas the charge of limestone against itself considerably increases by heating the rubbing surface.
- In the case of unlike partners, particle charges generally increase according to the different heating conditions: c/C, h/C, c/H, h/H in that order (c = cold and h = hot refer to particle, C and H to the rubbing surface).
- On reversing the rubber/rubbing order, polarity is respected for the coal-shale and limestoneshale pairs: for all heating conditions, coal and limestone are positively charged on shale and vice-versa. Actually, shale has a much stronger affinity to hydroxyl ions than coal and limestone. For the coal-limestone pair, reciprocity holds only when the rubbing surface is cold: coal is positively charged against limestone and limestone is negatively charged against coal. However the charge of limestone particles is reversed to positive when the coal surface is heated, while coal against a hot limestone surface maintains a positive polarity. Thermoelectric charging by displacement of electrons or negative ions towards the interior of the particle is likely to occur for limestone. A higher charge corresponds to the c/H heating condition giving the greater temperature gradient. This explain the anomalous outcome of limestone/limestone contact on varying heating conditions.



- The various coal macerals have different charging features. Those of the vitrinite group, more hydrophobic, are positively charged on contact against the macerals of the fusinite group, which are more hydrophylic.

### Other factors influencing tribocharging results

The presence of an external field, temperature and humidity of the environment, frictional energy, time of contact, surrounding gas pressure and rubbing surface conditions, though often neglected or underestimated, are to be considered as key factors in tribocharging.

The results of a research study carried out on coal clearly confirms the above statement, as summarized here below.

a) Charging in the presence of an external field

Contact charging can substantially be modified by the action of a static field as the consequence of induction/conduction.

As it was experimentally shown, the charge increases almost proportionally with the voltage applied to the stainless steel rubbing surface.

The conductor pyrite is strongly affected, whereas the gradient is lower for the other non-conductor components. A certain rectifying behaviour can be observed for the pyrite/metal contact: electrons seem to flow more easily from the metal to the mineral than in the opposite direction (pyrite can thus be considered as "reversible negative").

For coal and limestone particles, the negative triboelectric charge at zero voltage (surface grounded) is maintained over the entire voltage range if the applied voltage is negative (triboelectric and induction/conduction processes are concurrent); it disappears if voltage is positive (16).

For non-conductor materials (coal and limestone), the effect of voltage takes over only beyond a certain threshold, while for pyrite it becomes immediately effective.

### b) Charging as a function of time

The effect of time on triboelectric charging has been studied for coal and limestone particles. Charges versus rubbing time are represented by curves in **Fig. 7** for two different levels of vibration power.

The following aspects are worth noting:

- for coal, the charge increases with time reaching a peak point after 20 s experiment duration and



Fig. 7 Average particle charge as a function of rubbing time. 1-Coal, gentle sliding; 2-Coal, hard rubbing 3-Limestone, gentle sliding; 4-Limestone, hard rubbing

then decreases down to a steady level after 60 s. For limestone, the effect is less pronounced;

- higher charge is produced in the case of gentle sliding than in the case of hard rubbing;
- charges are considerably greater for coal than for limestone.

This can be explained by assuming that:

- The surface becomes dirty. Actually, as time elapses, the rubbing surface is progressively covered by an invisible layer of dust causing a gradual deterioration of its charging capacity (see later: Rubbing surface conditions).
- The temperature plays an unfavourable role. The particle is increasingly heated by friction whereas the metal surface temperature remains steady due to its larger mass and better heat dispersion ability. The differential temperature (particle hotter than metal) is a negative factor as far as coal charging is concerned, as was already discussed. For limestone, the effect of heating is almost negligible. It should be borne in mind that coal is softer and more resistant to heat transfer than limestone; therefore dust is easily released due to abrasion and hot spots are more rapidly formed.

### c) Charging as a function of energy

In principle, a higher charge should be expected as the vibration power is increased.

However, experimental results are somewhat contradictory in this respect. In fact, for a given experiment duration, the charge is higher in the case of gentle driving than in the case of powerful shaking



of the charging device, as shown in the curves of Fig. 7.

A possible explanation can be found in light of the following considerations:

- Charging kinetics. Due to the high resistivity of both coal and limestone, it takes a relatively long time for saturation charge to be achieved. If the allowed time for effective contact is too short, saturation is never reached.
- Temperature effects. As pointed out earlier, differential temperature between a particle/metal contact caused by stronger contact energy is detrimental to coal and limestone charging on a stainless steel surface.
- The presence of other unfavourable phenomena such as material transfer and even a modification in the solid nature (for coal incipient pyrolisis upon impingement against a hot surface was observed).
- d) Rubbing surface conditions

Contamination by moisture, hydrocarbon patches and foreign dust can be important, even offsetting the main charging process. It has been found that:

- Dust blasting of stainless steel produces major charging modification with respect to the clean surface. Charge polarity of both coal and limestone is reversed from negative to positive in the case of a shale-blasted surface, whereas it remains the same in the case of limestone-blasting. Finally, in the case of coal-blasting, while the coal and shale polarity is not affected, that of limestone is gradually reversed on c/H heating condition. In all cases, charges are generally smaller except for hot shale-blasted surfaces.
- Cleaning with distilled water restores the charging ability of surfaces which is progressively deteriorated by dirt.
- e) Temperature and humidity of environment

Temperature and humidity of the surroundings are always factors of utmost importance in triboelectric charging, especially in the case of hydrophilic minerals.

### Tribocharging of soluble minerals

In salt ore beneficiation, selective tribocharging prior to separation becomes feasible by resorting to suitable dry chemical reagents under carefully controlled temperature and humidity of the ambient air before and after particle surface conditioning. The process consists of the following subsequent phases (18):

- a) addition of the reagent for controlling the electric charge, ensuring its even distribution throughout the feed;
- b) dry conditioning of the material under controlled air temperature and humidity;
- c) selective tribocharging of the particles to be separated, accomplished by vigorous stirring of the mixture under controlled humidity;
- d) direct feeding of the material into the electrostatic separator.

The influence of air temperature and humidity during the preliminary conditioning stage is summarized in **Fig. 8 and 9** for a kainite-halite ore, ground to below 0.5 mm, containing 11.5% K<sub>2</sub>O.

A careful setting of both variables is a decisive factor for the separation results. In particular, during the conditioning stage, the relative humidity should be kept as low as possible (5% or less), while the optimum temperature ranges between 55 and  $65^{\circ}$ C Fig. 8.

During the tribocharging stage, air conditions must be kept in the range between 50 and 60% relative humidity for attaining a satisfactory recovery associated with the desired concentrate grade (**Fig. 9**).

### 6. Conclusions

Triboelectrification can be produced by two distinct processes: contact charging and frictional electrification, dependent on the kind of rubbing. Contact charging (smooth sliding) is due simply to the exchange of electrons or ions between different



Fig. 8 K<sub>2</sub>O recovery versus conditioning temperatures for different concentrate grades (K<sub>2</sub>O %)





Fig. 9 K<sub>2</sub>O recovery versus relative humidity of air during the charging phase at varying concentrate grades (K<sub>2</sub>O %)

substances, whereas frictional charging (hard rubbing) is due to substantially different mechanisms such as material transfer and hot-spot formation.

The tribocharge strongly depends on the nature of the contacting bodies and varies according to the different experimental conditions such as: temperature of the solids involved and moisture adsorbed on their surface; temperature and humidity of ambient air; kind, energy and time of contact; presence of an electrostatic field; influence of modifying actions (mechanical stress, contamination, irradiation, bombardment by atomic particles).

If all these factors are properly controlled, selective charging can be achieved, thus rendering triboelectric separation viable for ore and coal beneficiation.

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Author's short biography



### Raimondo Ciccu

Raimondo Ciccu graduated in Mining Engineering at the University of Cagliari in 1965. Shortly after he joined the National Research Council covering the position of Senior researcher until 1973. From 1974 to 1981 he covered the position of Chief Sector at the Sardinian Mining Body and meanwhile he acted as Managing Director of a major mining Company in Italy. In 1982 he joined the University of Cagliari as Associate Professor and from 1983 as Full Professor of Surface Mining and Land Reclamation. The fields of interest range from excavation and cutting technology to various subjects of mineral processing like electrostatic separation, comminution, gravity separation and flotation. He is Author of about 200 scientific and technical papers, most of them discussed in International Conferences.

### Marcello Ghiani

Marcello Ghiani graduated in Mining Engineering at the University of Cagliari in 1958 and developed his entire Academic career at the same University. In 1966 he was abilitated as lecturer in the field mineral processing. In 1975 he won a national call for a position of Full Professor and presently holds the chair of Mineral Processing. He carries on a scientific activity within the frame of the research programs of the Department of Mining and Minerals Engineering and of the Mineral Science Study Centre of the National Research Council at the University of Cagliari. He participated in various national and international conferences giving numerous contributions.

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Gianfranco Ferrara obtained his degree in Mining Engineering in 1954 at the University of Cagliari (Italy). At the same University he was appointed Research Assistant in 1955 and Assistant Professor in 1960. In 1971 was appointed to his present position of Professor of Mineral Processing at the University of Trieste, where since 1979, has been Chairman of the Mineral Engineering Division.

Member of the Steering Committee of the IMPCs, International Mineral Processing Congresses, as Italian delegate.

To date has produced some hundred publications concerning mineral processing research, characterization of particulate solids, behaviour of particles in the transport phenomena in fluids, mechanical, hydraulic and pneumatic classification of solids, dense medium separation processes in centrifugal field, rheology of dense suspensions, electrostatic separation, modelling and simulation of the separation processes of minerals and particulate solids.



### Review

### Particle Sizing in the Submicron Range by Dynamic Light Scattering †

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### Abstract

The application of dynamic light scattering for the determination of particle size distributions in the submicron range is reviewed. First, the basic principles and assumptions used in this application are presented. The practical performances are illustrated with results obtained from round-robin studies. A short comparison with particle sizing by static light scattering is included. Finally, new developments for on-line or in-situ characterization of concentrated and opaque dispersions are briefly presented.

### 1. Introduction

In the last two decades, dynamic light scattering (DLS) techniques were applied in an increasing number of applications $^{1-8)}$ . In this contribution, we will focus on the application of DLS-also referred to as quasi-elastic light scattering (QELS), or photon correlation spectroscopy (PCS)-for the determination of particle sizes. Although the technique was not at all developed for the determination of particle sizes-it was actually meant as a research tool for probing dynamics of polymers and colloidal systems, and as a way of studying critical phenomena and the statistical nature of light-it became the main application of DLS. The increasing success of PCS for particle sizing is based on the fact that it provides absolute estimations in very short measuring times without elaborate sample preparation procedures, and that easy-to-use commercial equipment is available.

In this paper, the basic principles of the application of DLS for particle sizing will be briefly reviewed. The practical performances will be illustrated with case studies. Finally, a brief summary of new developments is presented.

### 2. Basic Principles

### 2.1 Spectral analysis

In a typical experiment the particles are illuminated with a collimated beam, called the incident beam, and part of the radiation scattered under an angle  $\theta$  with respect to the incident beam is registered with an ultra-sensitive detector, very often a photomultiplier tube (**Fig. 1**).



Fig.1 Basic light scattering geometry

In a DLS experiment, the dynamic information of the scatterers can be deduced from the spectrum, i.e. from the "amount" of light as a function of wavelength  $\lambda$  or frequency v or circular frequency  $\omega = 2\pi v$ . The incident light is a monochromatic laser source, i.e. a light source with a single wavelength or circular frequency  $\omega_0$ . The spectrum S  $(\omega)$  of the incident light therefore has a single peak at  $\omega = \omega_0$  (Fig. 2). The first question that arises is what is the spectrum of scattered light? The answer is that when a monochromatic beam with frequency  $\omega_0$  and incident wave vector k  $_i$  (with modulus  $k_i = 2\pi m_1 / \lambda_0$ ,  $\lambda_0$  is the wavelength in vacuo and  $m_1$  is the refractive index of the propagation medium) shines on a particle in motion, it emits scattered radiation in all directions. A fixed observer will register a slightly different frequency  $\omega = \omega_0 + \omega_0$  $\Delta \omega$ , whereby the frequency shift  $\Delta \omega$  is nothing

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Fig. 2 Spectrum of scattered light

more than an (optical) Doppler shift (**Fig. 2**). The frequency shift depends on the velocity  $\vec{v}$  of the particle and the angle of observation

$$\Delta \omega = \overrightarrow{q} \cdot \overrightarrow{v} \tag{1}$$

In Eq. (1),  $\vec{q} = \vec{k}_s - \vec{k}_i$  is the so called scattering vector with modulus  $q = 4 \pi m_1 \sin (\theta/2)/\lambda_0$ .

In the application of particle sizing, the particles do not all move with the same velocity along the same direction. On the contrary, the investigated particles, which are usually smaller than about  $1\mu$ m, are in constant thermal or random Brownian motion. Typical for such a motion is that the particles often change their direction of motion and their speed. Intuitively, one can then predict that the spectrum of scattered light will be a superposition of different positive (particles moving towards the detector) and negative (particles moving away from the detector) frequency shifts  $\Delta\omega$ . Therefore, the spectrum of light scattered by particles in Brownian motion looks like a bell-shape curve (**Fig. 3**). The average displacements for a



Fig.3 Spectrum of light scattered by particles in Brownian motion

Brownian motion can be quantified by the particles (translational) diffusion coefficient D. It can be shown that this quantity is related to the half width at half height  $\Delta \omega_{1/2}$  of the bell-shaped spectral curve by

In order to obtain reliable values of the particles' diffusion coefficient, accurate measurements of the spectrum are required. In the early experiments,  $S(\omega)$  was determined with spectrum analysers. The accuracy of DLS experiments was significantly enhanced by the use of digital correlators instead of spectrum analysers.

### 2.2 Intensity autocorrelation

Typical DLS measurements are performed in the time domain. Information theory tells that the dynamic properties of the studied scatterers can be obtained equally well from the Fourier transform of the spectrum. The latter is the autocorrelation function  $G_2(\tau)$  of the scattered intensity I(t), and is an average value of the product of the intensity registered at an arbitrary time t, I(t), multiplied by the intensity registered at a time delay  $\tau$  later I(t +  $\tau$ ):

$$G_2(\tau) = \langle I(t) \cdot I(t + \tau) \rangle$$
(3)

The brackets denote an average which is performed practically by forming the product in (3) for a great number of times t.

### 2.3 Some basic equations

For a dispersion of monodisperse particles in Brownian motion, the intensity autocorrelation function  $G_2(\tau)$  is modelled by

$$G_2(\tau) = A + Bexp(-2\Gamma\tau)$$
(4)

In Eq. (4), A and B can be considered as instrumental factors with B < A. The ratio  $B/A \le 1$  or (B/A-1) is often designated as the intercept, as a % merit or as a signal to noise ratio. The decay rate  $\Gamma$  is linked to the translational diffusion coefficient D by

$$\Gamma = Dq^2 \tag{5}$$

Note that the diffusion coefficient is determined and not the particle size. The latter quantity can only be determined by relating the diffusion coefficient to the particle size. Unfortunately, there is no general relation that applies in all situations. The frequently used Stokes-Einstein expression for the diffusion coefficient  $D_0$ 



$$D_0 = \frac{kT}{3\pi\eta d} \tag{6}$$

where k is Boltzmann's constant, T the absolute temperature,  $\eta$  the viscosity of the suspension liquid and d the particle diameter, has only limited validity: it applies only for non-interacting spherically shaped particles. The effect of particle interactions on the diffusion coefficient will be discussed in section 3.3. Polydispersity is presented in section 3.4.

### **3. SOME APPLICATIONS**

### 3.1 Sample concentration

### 3.1.1 Dispersion

In order to characterize particles with PCS, the first task that arises is to prepare a suitable sample. Although this is easy compared to the sample preparation procedures required for, e.g. Transmission Electron Microscopy (TEM), it demands due caution. Especially the particle characteristics (dimensions, interactions) should not be modified by the dispersion procedure. Much can be said about this requirement: it may involve the whole field of colloid chemistry to which the interested reader is referred. Practically, one has to choose the right solvent and/or dispersing agent and to ensure that no coagulation or physical or chemical change of the dispersed phase occurs.

### 3.1.2 Single scattering – multiple scattering

The particles must scatter independently. This requirement implies that effects of multiple scattering are to be avoided. Multiple scattering is the phenomenon whereby light scattered at an angle  $\theta_1$  by a first particle, is scattered a second (or even a third or fourth) time at an angle  $\theta_2$  by another particle.



Since  $\theta_1$  and  $\theta_2$  can take any value, the scattering vector magnitude q of the light inpinging on the detector is no longer fixed. As a result, the diffusion coefficient and particle size can no longer be deter-

mined unambiguously from the decay rate of the autocorrelation function (Eq. 5). Obviously, multiple scattering effects are expected to become more important at relatively high particle concentration. The net effect as a function of increasing concentration is as follows:

- a. The instrumental factor B/A decreases<sup>9</sup>. This factor is dependent on the degree of constructive interference of the light waves inpinging on the detector area. The largest value is obtained when all scattered rays have the same scattering vector  $\vec{q}$ , that is the same scattering angle  $\theta$  and only single scattering. In the event of multiple scattering, the scattered waves with different  $\theta$  values interfere destructively, resulting in a decrease of the instrumental (coherence) factor B/A.
- b. At higher concentrations, however, mostly only multiple scattered light reaches the detector. In this case, the particle size estimated by PCS becomes smaller. This is due to the fact that the autocorrelation function  $G_2(\tau)$  decays faster for a multiple scattered signal than for a single scattered one<sup>10</sup>.

Thus multiple scattering limits the application of the technique to very dilute dispersions. In section 4, some tricks that allow measurements in concentrated dispersions, whereby multiple scattering effects are circumvented, are presented.

### 3.1.3 Number fluctuations

At low concentrations, another complication can occur. In the derivation of Eq. (4), it is assumed that the registered fluctuations in the scattered intensity arise only from a change in position of the particles inside the measuring or scattering volume. If the particle number concentration becomes low, additional intensity fluctuations are caused by particles moving in and out of the measuring volume<sup>11)</sup>. These effects become significant when the average number of particles N in the scattering volume does not satisfy the condition N<sup>2</sup> » N. In practice, it is assumed that for N larger than about 1000, this condition is fulfilled. For a given concentration of dispersed material and a fixed scattering volume V, N decreases with particle size and can be estimated by

$$N = 6\phi V/\pi d_{PCS}^3$$
(7)

In Eq. (7),  $\phi$  is the volume fraction of the dispersed phase related to the concentration in weight per unit volume c and the particle density  $\rho$  by  $c = \rho\phi$ .



Eq (7) predicts that, for a volume fraction f of 10-4 (at higher volume fraction, multiple scattering may bias the measurements) and for a typical value of the scattering volume V of 10<sup>-6</sup> cm<sup>3</sup>, effects of number fluctuation are to be expected for particle diameters above about 500 nm. In a round-robin comparison, a monodisperse latex with TEM diameter of 804 nm was studied by different laboratories<sup>9)</sup>. At a concentration of  $2 \times 10^{-4}$  g/cm<sup>3</sup> or a volume fraction of about  $2 \times 10^{-4}$ , the PCS diameters ranged from 1082 to 1372 nm. This overestimation can be explained as follows. Number fluctuations lead to an additional time decaying term in the measured intensity autocorrelation function. Since the characteristic decay time of this additional term is usually much slower than the decay attributed to the Brownian motion of the particles<sup>11)</sup>, the average particle size, proportional to the average decay time, will be overestimated when neglecting the effect of number fluctuations.

Another complication that arises for larger particles is sedimentation. Micron-sized particles will sediment during the PCS experiment if their difference in density is large enough. The sedimentation rate  $v_s$  can be estimated using Stokes law by

$$v_{\rm s} = d^2_{\rm PCS} \Delta \varrho g / 18\eta \tag{8}$$

where  $\Delta \rho$  is the difference in density between the dispersed phase and the dispersion medium, and g is the gravitational acceleration. Eq. (8) predicts that a  $1\mu m$  diameter particle sediments at a rate of  $1\mu$ m/s in water for a density difference  $\Delta \varrho$ of about 2. Since a typical vertical linear dimension of the measuring volume is about  $100\mu m$ , it means that it takes no more than 2 min for such a particle to sediment through the measuring volume. Particularly in a polydisperse sample, the larger (micron sized) particles may sediment while the smaller ones (d <  $0.5\mu m$ ) do not. As a result, the average PCS diameter decreases as a function of the measuring time. Therefore, it is advisable to check the sample at the end of a PCS experiment to see whether or not a sediment did deposit at the bottom of the test tube.

From the discussion in sections 3.1.2 and 3.1.3, it appears that the concentration of dispersed material must not be too high in order to avoid complications from multiple scattering and not too low to avoid bias from number fluctuation. As a rule of thumb, a volume fraction of dispersed material in the range  $10^{-4}$  to  $10^{-5}$  fulfils the requirements for particle sizes below about 500 nm. For larger particles, it is not always possible to find a concentration that is neither too low nor too high. For sizes above  $1\mu$ m, a concentration suitable for PCS determinations can only be found in exceptional cases, and even then one must keep in mind that biasing due to sedimentation may occur.

### 3.2 Narrow size distributions

One of the strong points of PCS is that it allows determination of particle sizes on an absolute basis, i.e. without calibration, in only a few minutes. For narrow size distributions, it is difficult to imagine a faster, more repeatable and more accurate technique for sizes below about 500 nm. Both the repeatability and the accuracy are typically better than  $\pm 2\%$ . As a result, some commercially available standards, certified in the past by TEM measurements, are nowadays increasingly certified by PCS measurements. Especially since PCS determinations do not require calibration, it occurred that improper labelling caused by calibration errors in TEM determinations were revealed by PCS measurements<sup>12)</sup>. Typical examples of narrow size distributions that were characterized very successfully by PCS are polystyrene latex dispersion, microemulsions, and liposomes, to name just a few, and there is still a continuing need to measure such systems with particle sizes in the submicron range.

### 3.3 Particle interaction

As mentioned, one of the basic assumptions is that the particles must scatter independently. Besides multiple scattering, there is a second complication that leads to dependent scattering, namely particle interaction  $^{13-14)}$ .

The effect of particle interaction is proportional to the average interparticle distance and hence to particle concentration, much like the effect of multiple scattering.

Hence the question arises: which one of the two effects comes first with increasing concentration. The answer is dependent on particle size. Since single particle scattering power increases dramatically with particle size, multiple scattering effects will occur first for the larger particle sizes. For a fixed volume fraction, the average interparticle distance decreases with particle size. Hence the effect of interaction will be less pronounced for the larger sizes. On the other hand, smaller particles, typically with diameters below 100 nm, scatter much less light so that dispersions with low-volume fractions  $(10^{-4} - 10^{-5})$  very



often do not scatter enough for reliable PCS measurements. In these cases, particle concentration can be increased to volume fractions up to 0.1 without effects of multiple scattering. However, at these concentrations, particle interaction effects now arise. Particle interaction affects the diffusion coefficient. For small particles at high concentration (average interparticle distance small compared to the inverse scattering vector magnitude q<sup>-1</sup>, the collective diffusion coefficient D<sub>C</sub> of an ensemble of interacting particles is determined by PCS<sup>15-16</sup>).

Qualitatively, the effect of interactions can be summarized as follows. Repulsive interactions such as hard sphere, electrostatic or steric interactions lead to an increase of  $D_C$  with concentration, whereas for attractive, Van der Waals type interactions, D<sub>c</sub> decreases with concentration. In these circumstances, particle sizes can in principle only be determined from extrapolations to infinite dilution of measurements of the collective diffusion coefficient  $D_C$  as a function of particle concentration. The particle size is estimated from the extrapolated diffusion coefficient D<sub>0</sub> with the Stokes-Einstein equation. If, at finite concentration, an apparent particle diameter is calculated from the collective diffusion coefficient D<sub>C</sub>, this apparent diameter will be underestimated for repulsive interactions and overestimated for attractive interactions.

### 3.4 Polydispersity analysis

Since PCS was so successful for a fast determination of average particle sizes, much effort has been spent – especially for narrow sized distributions – on the determination of particle size distribution. It turned out, however, that the inversion of intensity autocorrelation functions for particle size distributions is considerably more difficult 17-35).

In the application of particle sizing in polydisperse systems, it is assumed that all dispersed particles are homogeneous spheres. The only difference between individual particles is their size or diameter.

### **3.4.1** Autocorrelation function

The extension of Eq. (4) to non-interacting homogeneous spherical particles is as follows. The intensity autocorrelation function  $G_2(\tau)$  is related to the modulus of the field autocorrelation function  $g_1(\tau)$ by a Siegert relation (if the number of particles N in the measuring volume V is large enough) :

$$G_2(\tau) = A + Bg_1^2(\tau)$$
 (9)

For non-interacting monodis perse spherical particles,  $g_1(\tau)$  is an exponentially decaying function:

$$g_1(\tau) = \exp(-\Gamma\tau) \tag{10}$$

Substitution of Eq. (10) in Eq. (9) yields then Eq. (4). Since the decay rate  $\Gamma$  is inversely proportional to the particle diameter (see eqs. 5 and 6), there are different decay rates  $\Gamma_i$  inversely proportional to the different particle diameters  $d_i$  in the case of non-interacting homogeneous spherical particles with different sizes. Hence Eq. (10) can be written as a sum of exponentials:

$$g_{1}(\tau) = \sum_{i=1}^{n} c_{i} \exp\left(-\Gamma_{i}\tau\right)$$
(11a)

In Eq. (11a), the coefficient  $c_i$  represents the normalized intensity weight of the particles with diffusion coefficient  $D_i = \Gamma_i/q^2$ . The continuous form of Eq. (11a) is

$$g_{1}(\tau) = \int_{0}^{\infty} C(\Gamma) \exp(-\Gamma\tau) d\Gamma$$
 (11b)

where  $C(\Gamma)$  represents the normalized intensityweighed distribution of decay rates.

Typical polydispersity data analysis generally involves two steps. In the first, the modulus of the field autocorrelation function  $g_1(\tau)$  is estimated from the experimentally measured autocorrelation function  $G_2(\tau)$ . In the second step, Eq. (11a) or Eq. (11b) is inverted for the distribution of decay rates. One of the limitations of the resolution comes from the extremely ill-conditioned nature (in the mathematical sense) of this Laplace inversion. Practically, very small differences in  $g_1(\tau)$  may result in quite different particle size distributions after inversion or in other words quite different types of particle size distributions correspond within typical experimental accuracy with the same autocorrelation function<sup>36-37)</sup>. Therefore, not only accurate data are required, but the necessary care has to be exercised on both steps in the data analysis procedure. Many efforts have been spent on the second step, i.e. the Laplace inversion. However, less attention was paid to the first one. We will now discuss both steps in more detail.

# 3.4.2 Estimation of the field autocorrelation function

Firstly, it should be noted that experimental data are always "contaminated" by noise and experi-



mental uncertainties, so that Eq. (9) should be written as

$$G_2(\tau) = A + Bg_1^2(\tau) + \mathcal{E}(\tau)$$
 (12)

where  $\delta(\tau)$  is the (unknown) experimental uncertainty. In order to extract the field autocorrelation function under normalized,  $g_1(\tau)$ , or unnormalized form,  $G_1(\tau) = B^{1/2}g_1(\tau)$ , the baseline A has to be evaluated. Two experimental strategies are used to this end:

- 1. Since for large time delays,  $G_2(\tau)$  decays to its background value A, the baseline is approached by a measurement of  $G_2(\tau)$  for large delay times.
- 2. The baseline can be estimated from the timeaveraged intensity which is monitored by separate counters in the instrumentation.

The unnormalized field autocorrelation function  $G_1(\tau)$  is calculated as

$$G_1(\tau) = \sqrt{G_2(\tau) - A}$$
(13a)

or the normalized field autocorrelation function is given by

$$g_1(\tau) = \sqrt{[G_2(\tau) - A]/A}$$
 (13b)

The experimental uncertainties in both  $G_2(\tau)$  and A lead to complications, however. For larger values of the time delay, the experimental estimates for  $[G_2(\tau) - A]$  are sometimes negative so that it is not possible to extract the square root. In order to circumvent this problem several strategies are used:

- 1. Measurements with  $[G_2(\tau) A] < 0$  are discarded
- 2. If  $[G_2(\tau) A] < 0$ ,  $G_1(\tau)$  is made equal to zero 3. If  $[G_2(\tau) - A] < 0$ ,  $G_1(\tau)$  is estimated as  $-\sqrt{|G_2(\tau) - A|}$

The first two strategies lead to a biased estimation of  $G_1(\tau)$ . Although the third strategy seems intuitively reasonable, it has not been shown that this does not bias the estimates of  $G_1(\tau)$ . Secondly, although the error in baseline A may be of a random nature, the errors introduced upon normalization (Eq. 13b) are systematic ones because all data points are divided by the same (erroneous) estimated value of the baseline<sup>36</sup>. These normalization errors increase as the values of the field autocorrelation function  $g_1(\tau)$  decrease, i.e. with increasing delay time  $\tau$  and can be approximated by<sup>37</sup>

$$\Delta g_{1}(\tau) = -\frac{1}{2} \left[ \frac{1}{g_{1}(\tau)} + g_{1}(\tau) \right] \frac{\Delta A}{A}$$
(14)

where  $\Delta A$  is the estimated error on the baseline.

### 3.4.3 Inversion for the intensity-weighed particle size distribution

The next step is the inversion of the Laplace transform (Eq. 11b) for the distribution function  $C(\Gamma)$ , or the inversion of the sum of exponentials (Eq. 11a) for the set decay rates  $\{G_i, i = 1, ..., n\}$  and intensity weights  $\{ci, i = 1, ..., n\}$ .

There are essentially two kinds of methods used for the inversion: methods that do not require any prior knowledge about the distribution and methods that do require prior knowledge. The majority of the different methods used belongs to the second kind. The most frequently used methods are the following.

### 3.4.4.1 Methods that require no prior knowledge

i. The cumulants method<sup>17)</sup>

This is probably the most widely used method. The idea behind this method is that for monodisperse samples,  $G_1(\tau)$  is a mono-exponential decaying function so that  $\ln G_1(\tau)$  is a straight line with constant slope proportional to the decay rate or inversely proportional to the particle size. For polydisperse samples,  $G_1(\tau)$  is a multi-exponential. As a result, In  $G_1(\tau)$  is no longer a linear function of  $\tau$ : for relatively large values of  $\tau$ , differences from the initial slope of  $\ln G_1(\tau)$  can be observed. The departure from the initial slope is used as a measure of polydispersity. In practice, this method is mostly used to obtain average particle sizes from an average decay rate  $\Gamma$  and a polydispersity index defined as  $K_{2}/\langle \overline{\Gamma} \rangle^{2}$ . The average particle size d<sub>PCS</sub> obtained from  $\overline{\Gamma}$  is a harmonic intensity average<sup>38)</sup>:

$$\frac{1}{d_{PCS}} = \frac{\sum c_i/d_i}{\sum c_i} \text{ or } d_{PCS} = \sum_i \frac{c_i}{\sum_i} \frac{c_i}{d_i}$$
(15)

For particles which are small compared to the wavelength of light, the intensity scattered by a particle of diameter  $d_i$  is proportional to the volume squared or the sixth power of particle size. In this case

$$d_{pcs} = d_{6, 5} = \frac{\sum_{i}^{1} n_{i} d_{i}^{6}}{\sum_{i}^{1} n_{i} d_{i}^{5}}$$
(16)

where n<sub>i</sub> is the number of particles with diameter



 $d_i$ . Note that even then,  $d_{pcs}$  is not a z-average which would be the d7.6 average diameter. However, in the more common case where the particle size is comparable to the wavelength of light, d<sub>pcs</sub> is not given by Eq. (16), i.e. as  $d_{6, 5}$ , but is usually smaller. The kind of average for d<sub>ncs</sub> depends in most practical cases on the size range of the distribution and particle refractive index. For polydisperse samples,  $d_{pcs}$  is in all cases significantly larger than the number or geometric average diameter that is usually determined by TEM. Whereby one should be aware that only minor amounts of relatively large particles will strongly determine the value of  $d_{pcs}$ , while they have little effect on the number average diameter<sup>38)</sup>. Therefore, the necessary care should be taken when comparing PCS and TEM results for polydisperse samples.

ii. The singular value analysis and reconstruction method  $(SVR)^{34-35)}$ 

This is one of the methods dealing with the illconditioned nature of the problem. The particularly attractive feature is that the first step in this procedure gives, without any prior knowledge, an answer to the question of how many exponential decay rates can be recovered from noisy data.

The main limitation of the method is that it can only be applied to data sampled at equidistant time delays.

### 3.4.4.2 Methods requiring prior knowledge

A large number of this kinds of method has been reported<sup>18-32)</sup>. A review of the state of the art up to about 1984 has been published<sup>33)</sup>. Of all the methods described in<sup>33)</sup>, the non-negatively constrained leastsquares method (NNLS)<sup>21)</sup> and the regularization method of Provencher (Contin)<sup>22-23)</sup> are the ones most often used. More recently, it has been reported that the maximum entropy method (MEM) also allows reliable reconstructions of particle size distributions<sup>27), 30)</sup>. We will therefore limit this brief review essentially to these three methods.

### The prior knowledge

The common feature of these methods is that they require the following prior knowledge<sup>39)</sup>:

1. In order to extract the field autocorrelation function  $G_1(\tau)$ ,  $g_1(\tau)$  or  $G_1^2(\tau)$  from the experimental data for the intensity autocorrelation function  $G_2(\tau)$ , the knowledge of the baseline is required. More often than not, constant baseline values determined separately are used.

Corrections for normalization errors can be

made 37).

- 2. The weighing of the data. Here, the necessary prior information about the experimental errors in determining the intensity autocorrelation function is lacking. Hence only empirical weighings are used. Most commonly it is assumed that the experimental errors are uncorrelated. Following the fact that in many counting processes the data follow Poisson statistics, it is often assumed that the weights are inversely proportional to the square root of data points.
- 3. The range of particle sizes (or decay rates) where solutions for the inversion of  $g^{1}(\tau)$  for the distribution is expected. This range must be discretized. The setting of the intervals and the number of grid-points N in the interval have to be provided by the user based on (subjective) experience, trial and error or prior knowledge about the answer. Note that preprocessing with the non-a priori methods (cumulants and/or SVR) can be used as a guide to set the range. For the discretization of the range of particle sizes. samplings according to geometric series are preferred to equally spaced samplings. This choice, sometimes designated as exponential sampling, is based on the Pike-Ostrowski eigenvalue analysis of the Laplace transform<sup>20</sup>.

Once baseline, weighing of the data, range of particle sizes and its discretization have been obtained, the following set of simultaneous equations is obtained for a set of M data:

$$g_{1}(\tau_{j}) = \sum_{i=1}^{N} c_{i} \exp(-\Gamma_{i}\tau_{j}) + \varepsilon_{j}$$
  
(j = 1, 2, 3,..., M) (17)

In other words, in the first term of the r.h.s. of Eq. (17), the set decay rates  $\{\Gamma_i\}$  have been fixed and the remaining unknowns are the intensity weights  $c_i$ , including the weighing resulting from the discretization. Since in general, the set of equations is overdetermined (M > N), the computation of the set  $\{c_i = i = 1 \dots N\}$  can in principle be performed with a linear least-squares procedure. However, owing to the ill-conditioned nature of the problem and the fact that no reliable prior information about the noise terms  $\mathcal{E}_j$  is available, a simple least-squares algorithm often yields strongly biased and even non-physical answers for the distribution, e.g. the set intensity weights  $c_i$  should be a set of positive numbers, whereas often negative values for some



intensity weights are obtained with simple leastsquares fitting procedures. Adding to the confusion is the fact that the results obtained are unstable in the sense that they are sometimes strongly dependent on the range of particle sizes set and the number of grid-points N, i.e. on the prior choice of the set of decay rates  $\{\Gamma_i\}$ . In order to deal with these problems and in order to come to a selection of the "best answers" out of all possible answers fitting the data set, different strategies are used. We shall briefly review how this selection procedure is carried out by NNLS, Contin and MEM. The procedures are schematically represented in **Fig. 5**.



Fig. 5 Venn-diagram representation of several methods of data analysis.

- A All possible sets of solutions (an infinite number)
- B All possible sets of solutions (also an infinite number)
- fitting the data within one standard deviation on average C All possible sets of non-negatively constrained solutions
- (NNLS) D Contin preferred solution (NNLS + parsimony principle)
- E Maximum Entropy most probable solution

### NNLS<sup>21)</sup>

A first criterion for selecting solutions out of all possible answers fitting the data is to use the prior knowledge that distribution functions are represented by positive numbers. This is the basis for the nonnegative constrained least-squares fitting methods whereby only solutions with  $c_i > 0$ ,  $\forall$  i are retained. Mostly, the NNLS routine published in the book of Lawson and Hanson<sup>40</sup> is used. Several commercially available software packages are based on the NNLS method. Although the positive constraint on the intensity weights is an important improvement compared to unconstrained least-squares fitting, the final results are still dependent on the range of particle sizes set and the number of grid-points N. Therefore, even more prior information that allows further selection of the possible answers is needed. This is achieved in two different ways by Contin and MEM.

### Contin<sup>22-23)</sup>

In addition to the positive constraints, Contin uses the prior knowledge that the simplest solution, i.e. the one that reveals the least amount of new information or detail for the distribution function, is to be preferred (parsimony principle). Both constraints, i.e. non-negativity and parsimony, are achieved by constrained regularization.

Nevertheless, in practical cases the main weak points are the prior choices of the baseline and the range of particle sizes: the final results are very sensitive to small differences in baseline estimates and not always independent of the range of particle sizes.

### MEM<sup>27). 31)</sup>

In the maximum entropy method, the "best solution" is estimated as the most probable solution. The most probable solution is the set of intensity weights  $\{c_i\}^*$  that maximizes the Shannon-Jaynes-Skilling entropy function

$$S = \sum_{i=1}^{N} [c_i - c_i^0 - c_i \ln (c_i / c_i^0)]$$
(18)

In Eq. (18), the set  $\{c_i^0\}$  is the measure of the prior information of the distribution. Without detailed prior information, it is assumed that the intensity weights of all particle sizes are equal over the range of sizes set, i.e. all values of  $c_i^0$  are made equal. The maximization of the entropy function also satisfies the positivity constraints. It is also claimed that the maximum entropy solution is a smooth distribution<sup>27)</sup>. The main weak points are essentially the same as those of Contin: the final results are very sensitive to estimates of baselines and are not always independent of the range of particle sizes and the number of gridpoints N.

### 3.4.4.3 Analysis of multiangle measurements<sup>34), 41-42)</sup>

Since the scattering power of submicrometer and micrometer size particles is strongly dependent on the scattering angle and particle size, it may happen that the fraction of particles of a certain size class in a polydisperse specimen is hardly detectable at a given angle, whereas it dominates the scattering at another angle. Hence a survey of the autocorrelation functions over several angles may give more information on the size distribution than any single-angle analysis does. This point is illustrated by analysis



of measurements on binary mixtures of 250 nm and 520 nm diameter lattices at several scattering angles including an angle for which the scattering of the larger 520 nm particle is hardly detectable<sup>41)</sup>. Since the angular dependence of particle scattering power is used as a constraint, the method can only be used if the particle shape and refractive index are known.

Simultaneous analysis of multi-angle PCS data that do not require prior knowledge of the angular dependence of the scattering power on particle size is also possible by the singular value analysis and reconstruction method<sup>35)</sup>. In general, however, our experience is that simultaneous analysis of multiangle PCS data only slightly improves the resolution in particle size, and that one is still limited by the ill-conditioning of the inversion of multiexponential PCS data. In order to benefit fully from the angular dependence of particle scattering power, the simultaneous analysis of multi-angle static light scattering data (SLS) is preferable, owing to the better conditioning of the inversion of SLS data<sup>43-48</sup>.

### 3.4.4.4 Information content

With the a-priori methods of section 3.4.4.2, typically a set of 40 - 50 values of the particle size distribution are computed. However, due to the ill-conditioned nature of the inversion of the Laplace transform, this is not a set of 40 - 50independent parameters. Therefore, it is important to know how many truly independent parameters or pieces of information there are in a solution. Several estimations for the number of independent parameters are used in the different methods: essentially, the number of degrees of freedom in Contin and the parameter "good" in classical MEM. Typical values for these parameters range from about 2 to 5. These values compare fairly well with the number of parameters that is determined using the non-a priori SVR method. This illustrates that the number of independent parameters that can be extracted reliably from PCS data is limited even for advanced inversion methods. The fact that the number of independent parameters is low implies that mainly average particle sizes and distribution widths can be determined, but that the detailed shape of the distribution cannot or hardly be determined reliably.

### 3.4.4.5 Distributions by weight and number

The primary information obtained from PCS data constitutes intensity distributions whereby the re-

lative amount of each particle size is weighted by the intensity scattered by all the particles of the considered size<sup>38)</sup>, i.e. the intensity-weighted coefficients  $c_i$  in Eq. (11a) are proportional to  $n_i i_i$ , where  $i_i$  is the intensity scattered by one single particle of size class i and n<sub>i</sub> is the number of particles in that size class. The intensity-weighted distributions can be converted into distributions by weight and by number provided prior knowledge of the particle size and mass on the one hand, and particle scattering power on the other hand, is available. In the absence of prior information about particle shape, it is assumed that the particles are spherical objects, mostly homogeneous spheres. In this case, the relationship between the particle diameter and scattering power depends on the ratio particle diameter d to wavelength  $\lambda_0$  of light, the ratio of the refractive index of the particles m2 to the refractive index of the dispersion medium  $m_1$ , the scattering angle  $\theta$ and the state of polarisation of the incident light, mostly orthogonal to the incident and scattered direction (vertical polarization). The detailed functional dependence is given by the Mie scattering equations for spheres<sup>49)</sup>. As a result, distributions by number or weight can only be obtained if the refractive index of the particle is known. Without this knowledge, a relationship between particle size and scattering power is available only in the limiting case for particles which are small compared with the wavelength of light (Rayleigh and Rayleigh-Gans-Debye limits).

It should be noted that the parameters for the computed weight and number distributions are less accurate than those describing the intensity distributions, owing to the propagation of errors by the transformation of intensity to weight or number distributions.

### 3.5 Polydispersity analysis. Practice

Most methods of data inversion have been developed and tested with synthetic data and/or with samples for which the size distribution, i.e. the expected answer for the inversion problem, was known a-priori. Practical performances of PCS for the determination of particle size distribution for samples with a-priori unknown size distributions were investigated in several round-robin studies by the Belgian Particle Technology Group (BPTG)<sup>9), 50-51)</sup>.

The aim of these round robins was to take a snapshot of the results obtained by routine procedures by different users (industrial and academic research groups and manufacturers) with mostly commercially



available equipment and software. In a first study, several commercial monodisperse latex dispersions with particle diameters in the range 30 nm to about  $2\mu m$  were investigated<sup>9)</sup>. The results confirm the fact that the best accuracy and repeatability was obtained in the deep submicron size range, i.e. the size range below roughly 0.5µm. For the large sizes, the accuracy and repeatability suffered from complications due to number fluctuations (see section 3.1.3). In another study it was investigated in how much detail a particle size distribution can be characterized by PCS in a relatively short measuring time (typically by six repeated measurements of 5 min duration)<sup>51)</sup>. In particular, the ability of PCS to discriminate between monomodal and bimodal distributions of several industrial samples was studied. Four samples were distributed to eight laboratories. The first two samples were monomodal but not monodisperse. Samples 3 and 4 were mixtures of the first two in weight ratios of 1:1 and 1:3. This information was only communicated to the participants after five of them had returned their results. All participants returned results for the average size d<sub>PCS</sub> and the polydispersity index  $K_2/\langle \overline{\Gamma} \rangle^2$  as obtained by a cumulants analysis. The results are summarized in Fig. 6. The larger spread of average diameters for sample 1, compared to sample 2, is due to the fact that for this particle size, large in terms of PCS determinations, the average number of particles in the measuring volume is rather small (see section 3.1.3). From the values of the second cumulants it can be concluded that none of the samples are monodisperse and that the size distributions of samples 3 and 4 (i.e. of the mixtures of samples 1 and 2) are broader compared to those of samples 1 and 2. However, the results of a cumulant analysis do not allow discrimination between mono- and multimodal distributions. Note that the reproducibility of the determinations of the normalized second cumulants is about an order of magnitude poorer than the reproducibility of the average diameter.

The other analysis methods used in this study basically allowed multimodal distributions to be resolved. In the main, four inversion methods were used. Most participants reported results obtained with commercially available Non-Negative Least-Squares (NNLS) methods. Three participants used the Contin software package, and one participant also used the Maximum Entropy (MEM) and the Singular Value analysis and Reconstruction (SVR) methods. In a first step, each participant was asked to report



Fig.6 Single angle (90°) PCS harmonic intensity-weighed average particle diameters and normalized second cumulants (poly-dispersity indices, PI) for samples 1 to 4 as reported by the different contributors.

the number of modes of the size distribution as obtained from an analysis of single-angle PCS experiments. The results are summarized in **Fig. 7**. The results for the intensity weighted distribution are in agreement for samples 1 and 2: all participants agree on mono-modal particle size distributions, i.e. for the two samples with the smaller normalized second cumulants. For samples 3 and 4, the results for the intensity-weighted distributions are no longer



in agreement. Note that the results for the last two samples, i.e. for the mixtures of samples 1 and 2, reported by the three contributors (labs 1, 7 and 8) who had prior knowledge that the distributions were bi-modal, are also in disagreement. Even the results reported by different participants but obtained with the same software package disagree for samples 3 and 4.

The collective simultaneous analysis of data sets obtained at different scattering angles led to the conclusion that samples 1 and 2 were monomodal, whereas samples 3 and 4 were bimodal. However, this collective multi-angle analysis appeared to be only a slight, and certainly not a spectacular, improvement.

This case study illustrates that due to the ill-conditioning of the (Laplace) data inversion, the amount of information that can be extracted reliably from measurements of a relatively short time duration is limited. More precisely, the mean and the variance of a distribution, as obtained by a cumulants analysis, is quite repeatable but even the overall shape (monomodal or bimodal) is not reproduced reliably. On the other hand, if the shape of the distribution is to be determined more reliably, extremely accurate PCS measurements, i.e. measurements of typically 10 hours or even more are required. This point was illustrated by H. Ruf with experimental data of high statistical accuracy obtained from a sample of phospholipid vesicles<sup>37</sup>). The shape of the monomodal distribution for this sample could be retrieved by a Contin data analysis, however, only if correction for the normalization errors (see section 3.4.3) was taken into account. Without such a correction, even these highly accurate data yielded an additional spurious peak by inversion.

### 3.6 A comparison with static light scattering

The time-averaged scattering power of submicron and micronsized particles is strongly dependent on scattering angle and particle size. This property was



Fig.7 Number of modes of the particle size distribution of samples 1 to 4 as determined by PCS in different laboratories (1 to 8)



already exploited successfully for the characterization of larger particles (diameters larger than a few micrometre) by forward light scattering, sometimes also referred to as Fraunhofer diffraction<sup>52)</sup>. This method can be extended for smaller submicron particles taking into account the inverse relation between particle size and scattering angle. The dependence of scattering power of submicron particles at large scattering angles, e.g. in the angular range 10 to 150°, contains enough information for a general interpretation procedure<sup>43-48)</sup>.

As an example, the angular dependence of scattering power of the four samples studied by the BPTG<sup>51)</sup> is shown in Fig. 8. The distributions obtained by inversion of these data revealed that samples 1 and 2 were monomodal and samples 3 and 4 bimodal. The better performance compared to PCS comes mainly from the higher information content of the variation of particle scattering power as a function of the scattering angle. This can be illustrated by the angular variation of scattering power of the four samples shown in figure 8. For sample 1 with the larger, particle size, four minima are obtained in the investigated angular range, whereas for sample 2 (with the smaller particle size), only one minimum is found. The scattering curves of samples 3 and 4 contain the characteristic features (e.g. the angular positions of the minima) of the scattering curves of both samples 1 and 2, and can be recovered by linear superposition of the curves of samples 1 and 2 in a ratio of 1:1 for sample 3, and 1:3 for sample 4. From this observation, the author concluded that sample 3 was a 1 : 1 weight mixture of samples 1 and 2, and sample 4 a 1 : 3 mixture by weight of the first two samples, without having the prior knowledge of the composition of samples 3 and 4.

### 4. Recent and Future Developments

Since PCS allows fast determinations of average size and distribution width, the applications for quality control are still increasing. One of the aims thereby is to arrive at preferably portable "PCS sensors" that allow on-line or even in-situ measurements in concentrated dispersions. Promising is the downsizing of the different instrumentation components. There is a trend to replace the He-Ne lasers by smaller solid state lasers<sup>53</sup>. The use of monomode fibers allows construction of particularly simple PCS systems<sup>54-56</sup>. Avalanche photodiodes have been proposed as a replacement for photo-



Fig.8 Variation of sample scattering power as a function of scat tering angle

multiplicator tubes<sup>57-58)</sup>. In addition to their small size, an interesting feature of avalanche photodiodes is their higher quantum efficiency compared to photomultiplicators. Correlators are continually downsized.

On the other hand, great efforts are spent to allow measurements in highly concentrated and opaque samples. In order to extract single particle pro-



perties from measurements on concentrated dispersions, two main problems have to be solved, i.e. the effects of multiple scattering (see section 3.1.2) and of particle interaction (see section 3.3).

The effect of multiple scattering can be reduced very substantially by the use of cross-correlation techniques<sup>56-61)</sup>. In this technique, one illuminates a sample with two antiparallel laser beams of the same wavelength, positions two detectors on opposite sides of the sample at 90° angles so that scattering vectors  $\vec{q}$  and  $-\vec{q}$  are defined, and then studies the cross correlations in intensity fluctuations. Although multiple scattered signals reach both detectors, they do not contribute to the crosscorrelation of the signals. The reason is that the observed scattered electric fields add coherently only for single scattered events, while for multiple scattering events the different scattered fields interfere destructively. A variant of this cross-correlation technique that allows varying the scattering angle by using two laser beams at different wavelength has been reported by Drewel et al.<sup>62)</sup>. From a practical point of view, the present problem with cross-correlation is the extreme care required in alignment of the instrument (both detectors must register signals coming from the same scatterers). As a result, it is not yet used for routine measurements but only in off-line research applications.

Another, much simpler, way to avoid complications of multiple scattering is to collect the backscattered signal (i.e.  $\theta = 180^{\circ}$ ) with a monomode optical fibre<sup>63-66)</sup>. This technique, whereby the incident beam is launched through the same optical fibre is particularly promising since it allows in-situ measurements in concentrated and opaque dispersions. There are, of course, a few problems that still have to be solved. Firstly, with the fibre optic backscatter system, not only light scattered by dispersed particles is collected, but also incident light reflected by the probes tip. This problem can be solved by working with carefully cleaned slanted optode probes<sup>66)</sup> or by taking the interference between back scattered and reflected incident light into account in the data analysis<sup>67)</sup>. For instance, with the latter technique, not only the certified particle diameter of some monodisperse samples were recovered, but even closely spaced bimodal mixtures of them were resolved<sup>67)</sup>.

The other complication for characterization of very concentrated dispersions (i.e. at a volume fraction above roughly 0.01) are particle interactions. From

a theoretical point of view, much progress has been made in understanding the behaviour of concentrated systems. An excellent review was given by P. Pusey<sup>14)</sup> recently. Due to the complexity of this matter and to the variability of particle interactions in different practical systems, no general strategy for accounting for particle interaction has been developed yet. This does not exclude that for particular quality control applications, particle interactions can be taken into account in the data analysis of measurements on very concentrated dispersions.

### 5. Conclusions

Originating some twenty years ago from a research tool in a form only suitable for experts, PCS has become a routine analytical instrument for the determination of particle sizes. Like all other techniques, it has its strong and its weak points. The major strong point is that it is difficult to imagine a faster technique for sizing submicron particles: average particle sizes and distribution width can be determined in a few minutes without elaborate sample preparation procedures. The price to be paid for this advantage is the low resolution. Reasonably accurate resolution of the shape of the particle size distribution requires extremely accurate measurements over a period of 10 hours and more and careful and critical data analysis including interaction with a highly qualified operator. Nevertheless, since in many quality control applications only an average size is sufficient, PCS is very often an excellent choice. The recent trend for this analytical application is the development of measuring systems that allow the control of production processes by online and in-situ measurements, preferably in highly concentrated dispersions.

One has to bear in mind that some of the commercially available PCS equipment also allows the measurement of the time-averaged scattered intensity as a function of the scattering angle, and that the inversion of such data for particle size distribution yields more reliable particle size distributions.

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### Symbols and Abbreviations

А	Baseline or background term of the in-				
	tensity autocorrelation function				
В	Instrumental factor				
BPTG	Belgian Particle Technology Group				
с	Concentration in weight per unit volume				
C;	Normalized intensity weight corresponding				
1	to a particle diameter d,				
$c_{\pm}^{0}$	Prior information about c				
с(Г)	Normalized distribution function of decay				
- <- /	rates (intensity weighed)				
d. d.	Spherical particle diameter				
d	Average diameter as determined by PCS				
D. D.	Translational diffusion coefficient				
$\mathbf{D}_{\mathbf{n}}^{\prime}$	Stokes-Einstein diffusion coefficient				
$\mathbf{D}_{\mathbf{C}}$	Collective diffusion coefficient				
DLS	Dynamic Light Scattering				
g	Gravitational acceleration				
$g_1(\tau)$	Modulus of the normalized field auto-				
81(1)	correlation function				
$G_1(\tau)$	Modulus of the unnormalized field auto-				
-100	correlation function				
$G_2(\tau)$	Intensity autocorrelation function				
2	(unnormalized)				
i,	Intensity scattered by a single particle of				
1	size class i				
I(t)	Scattered intensity as a function of time t				
k	Boltzmann constant				
$\vec{\mathbf{k}_{i}}$	Incident wave vector				
$\vec{\mathbf{k}}_{c}$	Scattered wave vector				
K <sub>2</sub>	Second moment or cumulant				
$m_1^2$	Refractive index of the dispersion medium				
m <sub>2</sub>	Particle refractive index				
M	Number of data points				
MEM	Maximum Entropy Method				
n,	Number of spherical particles with diameter				
1	di				
Ν	Number of particles in the scattering volume				
	Number of grid-points in NNLS, Contin				
	and MEM				
NNLS	Non-Negatively constrained Least Square				
	method				
PCS	Photon Correlation Spectroscopy				
q	Modulus of the scattering vector				
QELS	Quasi-Elastic Light Scattering				
$S(\omega)$	Spectrum of scattered light				
SVR	Singular Value and Reconstruction method				
Т	Absolute temperature				
TEM	Transmission Electron Microscopy				
$\overrightarrow{v}$	Particle velocity				
v <sub>S</sub>	Stokes sedimentation rate				

- V Scattering volume
- $\Gamma,\,\Gamma_{i}$   $\ \ Decay rates of the field autocorrelation function$
- $\overline{\Gamma}$  Intensity averaged decay rate
- $\mathcal{E}(\tau), \mathcal{E}_{j}$  Experimental uncertainties in the intensity autocorrelation function  $\theta$  Scattering angle
- 9 Scattering angle
- $\eta$  viscosity of the dispersion medium
- $\lambda_0$  Wavelength in vacuo of the incident light v Frequency
- *ρ* Particle density
- $\phi$  Volume fraction of dispersed material
- $\omega$  Circular frequency
- $\Delta \omega$  Doppler frequency shift

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### Author's short biography

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Robert Finsy received his M.A. in Physical Chemistry from the Vrije Universiteit Brussel (Belgium). For his Ph. D. thesis, devoted to dielectric relaxation and far-infrared spectroscopy studies of simple liquids, he worked in the groups of Professor I. Prigogine at the Free University of Brussels and Dr. Chantry at the National Physical Laboratories in Teddington, England. His Ph D. work was awarded with the Duddell Premium by the Institution of Electrical Engineers (IEE, London, England). His current major research work has been in the field of colloid chemistry, especially the characterization of colloidal systems by physico-chemical methods such as dynamic light scattering. The author is Professor of Physical Chemistry at the Vrije Universiteit Brussel, Belgium.



### High-Performance Structural Ceramics: Powders and Components †

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### Abstract

High-performance ceramics have attracted much interest during the last decade, but a broad market introduction has not taken place so far due to the inherent disadvantages of ceramic components in applications with high mechanical loadings. The high brittleness and the low reliability as compared to metals, as well as the high production costs are severe obstacles in an area like the automotive engine. Typical defects of ceramic components may be introduced by the powders themselves, but in a like manner, sources of defects also lie in the forming and the densification of the components. The production technologies used for high-performance ceramics are mostly the same that are applied in traditional ceramics. It is demonstrated exemplarily for the materials silicon carbide, zirconia, alumina and silicon nitride, exactly what the main sources of defects are and how they could be avoided. From this, the desired powder properties can be derived. It is expected that improvements in powder processing and forming technologies will improve the reliability of ceramic components and lower the costs, thus leading to the remarkable market growth which has been predicted for more than ten years.

### 1. Introduction

Components in high-performance ceramics are exclusively made from synthetic powders in order to avoid the deviations in properties typical for natural raw materials. The field of high-performance ceramics can be subdivided into two main areas of application:

- structural ceramics and
- electronic ceramics

Structural applications are characterized by high mechanical, thermal and abrasive loading, whereas electronic applications make use of the electrical properties of ceramic materials, which can be either active or passive functions. **Table 1** shows the materials which are used in high-performance ceramics with their main field of applications. The materials alumina ( $Al_2O_3$ ), silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), and zirconia (ZrO<sub>2</sub>) to a lesser extent are the candidates with the highest potential in the future. Today, electronic ceramics have reached a much higher market penetration than structural ceramics. The reason for this lies in the low reliability of structural components which is not only due to unsuitable design, but also due to real existing

Table 1: Powders for high-performance ceramics

Material		Application		
		Structural Ceramics	Electronic active	Electronic passive
Aluminiur	n - nitride - oxide - silicates	×		× ×
	(Mullite)	×		
	- titanate	×		
Barium	- titanate		×	
Lead	- (Lanthan-) zirconium- titanate (PZT/PLZT)		x	
Boron	- carbide	×		
Silicon	-carbide	×		×
	-nitride	×		
Titanium	-boride	×		
Zirconium	-dioxide	×	×	

imperfections in the whole manufacturing process of powders and components. The presented article concentrates on structural ceramics and possible improvements with respect to technical performance and costs.

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### 2. Properties of ceramics and related problems

In comparison with the conventional construction materials such as metals and polymers, ceramics show some considerable advantages:

- low density compared to metals
- high hardness
- high thermal and chemical stability
- strength at very high temperatures

On the other hand, severe disadvantages have to be considered:

- low strength at ambient temperature
- high brittleness
- high costs (for powders and components)

The low reliability of ceramics is caused by the brittle fracture behaviour and a wide range of strength values, expressed by a low Weibull modulus. Whereas the brittleness is an intrinsic property of a certain material, the distribution of strength values is correlated directly to the distribution of flaw sizes, as postulated by Griffith [1] in his theory of rupture. This correlation is shown in **Fig. 1**, where the



Fig. 1 Mechanical poperties of ceramics

strength values are plotted versus the critical flaw size with the fracture toughness  $K_{IC}$  (reverse of brittleness) as a parameter. The values for ceramics vary between 2 and 12 MPa m<sup>1/2</sup>, whereas a high-toughness-steel reaches up to 200 MPa m<sup>1/2</sup>, which clearly demonstrates the brittleness of ceramics. In order to achieve a required strength level in a given material, only a maximum critical defect size can be tolerated. This can exemplarily be explained for  $Al_2O_3$  and  $ZrO_2$ ; if a minimum strength level of 500 MPa is required, the tolerable flow size in an alumina ceramic component is 32  $\mu$ m ( $K_{IC} = 3.5$  MPa m<sup>1/2</sup>), whereas in zirconia ( $K_{IC} = 10$  MPa m<sup>1/2</sup>) the defect size might be as large as 250  $\mu$ m.

The above-mentioned example clearly indicates that only two ways of improving the reliability of ceramic components are possible: 1. increasing the fracture toughness and/or 2. increasing the Weibull modulus by reducing the flaw sizes or rather the width of the flaw size distribution.

Possible improvements of the fracture toughness by incorporating a second phase into the matrix material, as described by Nihara [2] for the wellknown nano composite ceramics, for example, shall not be discussed in detail in this paper. Improving the strength of ceramic components requires a reduction of flaw sizes. Most of the observed defects can be explained in well-defined terms and are subdivided into three different populations as indicated in Fig. 2. The relative frequency of defects is shown as a function of the defect size. Although the size ranges of the different flaw populations strongly overlap, this schematic view allows conclusions to be drawn about the origin of the respective defect. The kind of defect, the process step in which the defect occurs and the reasons are summarized in Table 2. The underlinings show that powder synthesis and preparation make a considerable contribution to the entirety of defects.



Fig. 2 Typical defects in ceramics

# 3. Manufacturing of ceramic components as source of defects

In order to better understand the existing problems of structural ceramics, it is necessary to examine the different steps of ceramic processing which are shown in **Fig. 3**. The process as a whole is quite similar to the manufacturing of traditional ceramics such as tableware, tiles or sanitary ware, except the powder production. Today, the submicron powders  $Al_2O_3$ , SiC,  $Si_3N_4$  and  $ZrO_2$  are mostly produced by


Table 2 Typical defects of ceramics

Kind of defect	Processing step	Origin of defect		
■surface defects	finishing	mechanical loading too high		
	green machining shape forming	forming tools with defects		
■contaminations	powder synthesis powder preparation shape forming	open systems insufficient cleaning		
■non- homogeneities	powder syntheses	insufficient energy input		
-chemical	powder preparation	homogenizing		
-density	powder preparation shape forming sintering process	hard agglomerates bad flowing properties temperature gradient		
■broad distribu- tion of crystal-	powder synthesis	oversized grains in the powder		
lite sizes	powder preparation	non-homogenous distribution of sintering aids		
	sintering process	sintering temperature too high		
Powder Production	Comminution Particle growth <	Precipitation Crystallization Gas-phase reaction		
Powder Preparation	Deagglomeration Mixing (organic an Granulation	nd inorganic additives)		
Forming	Dry pressing (axia Slip casting (with, Extrusion Injection moulding Green machining	al, isostatic) without pressure)		
Densification	Pressureless sinte Gas pressure sinte Hot pressing Hot isostatic press	ering ering sing		

Fig. 3 Ceramic processing steps

Finishing

comminution of coarser materials which are primarily made for abrasive, refractory or metallurgical applications. Particle growth methods such as precipitation followed by crystallization or gas-phase reactions are used to a lesser extent for high purity aluminas and  $ZrO_2$ -TZP-powders, and the latter in an experi-

mental stage for  $Si_3N_4$  and SiC. But also with those so-called more advanced processes for powder synthesis, the problems in powder processing remain the same. Complete deglomeration and homogeneous mixing of the inorganic and organic additives are of utmost importance. The main sources of defects, which cannot be corrected in the subsequent processing steps, lie in the powder production and preparation.

In the following, some examples of the link between flaw type and processing step are accentuated from the summarizing description of table 2. Surface defects may originate during finishing, green machining or by the forming tools directly. External contaminations are not possible after the forming process has been finished, but they can easily occur during the powder production and preparation. Inhomogeneities in density can be introduced in the forming and the densification process, but they can also be attributed to an inadequate powder preparation process. Chemical non-homogeneities are due only to incomplete mixing and homogenizing, which might be caused by insufficient mixing intensity and time or indestructible aggregates in the powder. The existence of large grains in the microstructure of the densified ceramic material is mainly due to unsuitable powder qualities and/or a densification process which is not optimally adjusted in terms of temperature and time.

## 4. Typical defects and possible solutions

This section focuses on the effect of powder production and preparation on the final microstructure. The experimental work has been conducted on the materials silicon carbide, zirconia, alumina and silicon nitride.

### 4.1 Silicon carbide

Two submicron SiC powders (Fig. 4) have been mixed with the sintering aids boron carbide, carbon and the organic additives. After axial pressing at 200 MPa, the materials were densified under identical conditions (2130°C in argon atmosphere) to reach a final density of > 97% of the theoretical density. Powder A, with a narrow particle size distribution, results in a fine grained microstructure, whereas powder B, which contains 5% of larger grains between 2 and  $6\mu$ m, leads to a microstructure with exaggerated grain growth. Some large crystallites of approximately 150 $\mu$ m in size will substantially reduce the strength of such a component.



Besides the coarse particles, detectable by the usual methods and shown in curve B of **Fig. 4**, the powders usually contain very small quantities of oversized grains which are not accessible to an optical measuring method. Using instead ultrasonic wet screening with round sieve openings of 5  $\mu$ m reveals that the very small amount of 0.06 wt. % of large single crystals or hard agglomerates are



Fig. 4 Exaggerated grain growth in sintered SiC

present also in the powder A. Fig. 5 shows an SEM picture of the residue on a  $5\mu$ m sieve. The influence of this kind of oversized grain on the reliability of SiC ceramics is demonstrated in Fig. 6, where the strength distributions of components obtained by two different powders are shown. In case 1, a commercially available SiC powder leads to a mean strength value of 380 MPa with a Weibull modulus of 5. If the oversized grains >  $2\mu$ m are eliminated, the strength can be improved to 570 MPa and the Weibull modulus to 15, clearly demonstrating the scope of possible improvement.

As mentioned earlier in this paper, SiC powders have to be mixed with sintering additives in order to successfully allow pressureless sintering. The mixing process is difficult, because materials with



Fig. 5 Oversized grains in SiC powder



Fig. 6 Influence of oversized grains on the strength distribution of SiC ceramics



extremely different physical/chemical properties such as density, specific surface area and wettability must be homogenized. Additionally, the quantities to be homogenized may differ by orders of magnitude. The result of a poor mixing process can be seen in **Fig. 7**, where an agglomerate consisting of mainly carbon and boron carbide with a diameter of  $150\mu$ m results in a very porous area of the microstructure, thus acting as the fracture origin. Chemical homogeneity can be reached by intensive mixing or milling. Adjusting the surface chemical properties of the single components in the mixture is also of great importance.



Fig. 7 Chemical non-homogeneity in sintered SiC

## 4.2 Zirconia

Two commercially available co-precipitated ZrO<sub>2</sub> powders with 3 mol percent yttria each and a primary crystallite size of 40 nm have been pressed under identical conditions. The pore size distributions of the green compacts were measured by a mercury porosimeter and the sintering behaviour was characterized by densification in a dilatometer. The results are presented in Fig. 8 [3]. The powder L has a very narrow, monomodal pore size distribution with a mean value of slightly above 10 nm (upper left part). The corresponding curve of the sintering rate (upper right part) during heating also shows a monomodal shape and the shrinkage is finalized at 1600°C. In contrast to this, powder C has a bimodal pore size distribution due to hard agglomerates of the primary crystals (lower left part). The corresponding sintering curve (lower right part) shows that the smaller pores of 10 nm are eliminated at the same temperature found for powder L, but that the larger pores in the case of powder C require a much higher temperature of nearly 1800°C for full densification. As a result of the high sintering temperature, additional grain growth occurs with the negative effect on the strength behaviour already mentioned in the case of SiC.



Fig. 8 Correlation pore radius/sintering rate for  $\rm ZrO_2\text{-}TZP$  powders

## 4.3 Alumina

A low-soda alumina powder with a specific surface area of 8 m2/g was mixed with the organic additives, spray dried, isostatically pressed at 100 MPa and sintered. The results of this processing are shown in figure 9, parts a), b) and c). Part a) gives an impression of the powder after spray granulation, b) shows a cross-section of the green body and c) of the sintered material. Large pores up to more than  $100\mu m$  can be found. The reasons for this can either be hard granules which are not deformed or destroyed during the pressing step or collapsed hollow granules. Optimizing the organic additives and the conditions for spray granulation leads to the result shown in part d) of Fig 9. The density could be increased from 3.91 g/cm<sup>3</sup> to 3.97  $g/cm^3$  and the maximum pore sizes are smaller than  $10\mu m$ . In this case, the two main sources of pores, hollow granules and large triple points in the green compact, can be avoided by increased solids content of the slurry prior to spray drying and by adjusting the blend of organics in order to improve the deformation behaviour of the granules under compressive load.

## 4.4 Silicon nitride

In the case of  $Si_3N_4$ , technical problems shall not be in the foreground of our considerations, but the





Fig. 9 Alumina ceramics, a) spray granules, b) cross-section of green body, c) cross-section of sintered Al2O3, d) optimized

emphasis will be put on economical and cost aspects of the powder production. The qualities of commercially available  $Si_3N_4$  powders are very good, and the performance of components made from them is satisfactory even under severe mechanical conditions. But a breakthrough of  $Si_3N_4$ -components has not yet happened, because the costs are too high [4]. Besides the machining costs for finishing, the powder price plays an important role. Generally, it can be stated that the powder price should not be higher than 30 US\$ per kg.

The possible methods of synthesis for  $Si_3N_4$  are well known from literature [5]. The most common processes are reviewed in this paper, mainly considering costs and quality.

The diimide process results in a high-quality powder, but the costs for the raw materials and the process itself are very high, especially if we take into account that the byproduct ammonium chloride is produced in quantities which are 4 times higher than the product silicon nitride.

Gas-phase processes require high costs for raw materials, the process and safety installations.

The direct nitridation of silicon which is used for the largest powder quantities today causes high costs for environmental protection. In order to obtain the required quality of powders, milling and subsequent chemical treatment are necessary.

The carbothermal synthesis, developed by the Alusuisse-Lonza company, offers the chance to overcome the above listed problems. Starting from silica, carbon and nitrogen, a new process technology has been developed which yields high-quality and lowcost powders [6]. In addition, the process is ecologically beneficial. As compared to the diimide process and gas-phase reactions, the raw material costs are 4 times lower, in comparison to direct nitridation, the factor is 2. **Fig. 10** shows a photograph of the powder according to the newly developed process and a microstructure which can be achieved with this powder.



Fig. 10 Silicon nitride, left: carbothermal (CT) powder, right: microstructure of sintered  $Si_3N_4$  from CT powder

In literature [4], it is mentioned that an ideal powder price of 10 US \$/kg should be aimed at, but even the carbothermal process on a large industrial scale cannot reach this target.

#### 5. Desired powder properties

As indicated in the examples above, it is possible to overcome or at least to reduce the typical defects in ceramics by optimizing the powder production and preparation processes. From the experimental work with silicon carbide, zirconia, alumina and silicon nitride, the following conclusions regarding powder properties can be drawn: a narrow particle size distribution with d90 < 2d50 and d50 < 0.5 to  $1.0\mu$ m guarantees a good sintering activity and



lower sintering temperatures in order to achieve the required density.

A powder free of oversized grains (e.g.  $> 2\mu$ m) avoids excessive grain growth under regular sintering conditions. The absence of hard agglomerates facilitates the step of powder preparation and allows sintering at lower temperatures, thus resulting in a fine grained microstructure with the well-known positive effect on the mechanical properties of the finished component. A good deformation behaviour of powder granules depends on the composition of organic additives and helps to avoid the formation of large pores during the densification step. Intensive mixing/milling of powders and additives is of great importance in order to destroy hard aggregates and to ensure homogeneous distribution of all the additives.

As demonstrated for silicon nitride, the powder costs can be considerably reduced, if factors such as environmental compatibility and raw material costs are considered accordingly.

## 6. Conclusions

In order to realize the predicted growth rates in structural ceramics, technical and economical improvements for ceramic powders and components are necessary. One possible solution lies in an integration of the two separate steps of powder production and preparation. This will ensure better qualities of the ready-to-use sintering mixes and lower the costs considerably. Different types of

## Author's short biography

feedstock such as spray granules for dry pressing or slip casting and compounds for injection moulding or extrusion, will gain an increasing market share instead of powders without additives.

The economic and technical benefits will promote the market growth for structural ceramic components.

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## Rigid Ceramic Filters for Hot Gas Cleaning †

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## Abstract

Rigid ceramic filters have emerged in the last decade as the most promising technology for particulate removal from process gases at temperatures up to 1000°C. Granular and fibrous forms of media have been developed and both are commonly employed in the form of cylindrical "candles" which are periodically cleaned by application of a reverse gas pulse. Research has focused on this cleaning process, which governs the long-term performance of the filter. The problem is two-fold: to develop an expression for the intrinsic dust cake "detachment stress" from knowledge of the dust particle properties and cake structure, and to model the propagation of the cleaning pulse which is applied to remove it. The results of this research are summarized and experimental methods for investigation of filter cleaning briefly described. The implications for design and further development of ceramic filters are discussed.

## 1. Introduction

The development of technologies for particulate removal from gases at high temperatures has been extraordinarily rapid over the last decade, following the pioneering work of the UK/US/German collaborative project at the Grimethorpe Pressurised Fluidised Bed Combustion Facility in the late seventies and early eighties. The long-term needs of the power generators may have driven this early development but the focus has now shifted to the chemical and process industries. Environmental legislation now being rapidly implemented in most industrialised countries means that their needs are anything but long-term! Furthermore, their filtration requirements are at least as challenging as the high-pressure, high-temperature filtration problems which stimulated the earlier development of the technology.

**Table 1** gives some examples of applications for hot gas cleaning and their operating requirements<sup>1</sup>). The first group comprises three distinct types of system for electrical power generation from coal, all of which have their own requirements for gas cleaning at high temperatures. In Pressurised Fluidised Bed Combustion (PFBC), for example, coal is burned in a pressurised fluidised bed, raising steam within in-bed tubes. The gases from the com-

bustor enter a turbine at typically 10-20 bars and 1100 to 1150 K in order to generate further power and drive the compressor on the air inlet. These gases must be thoroughly cleaned in order to avoid turbine blade damage, and there is a strong thermodynamic advantage in doing this at the operating temperature rather than first cooling the gases, passing them through a conventional gas-cleaning device, and then reheating them. As an alternative, longer term approach to power generation from coal, the fuel is partially or completely gasified and the gases used to fire a turbine (Gasification Combined Cycle). Because turbine entry temperatures are even higher than for PFBC, high generation efficiencies can be achieved, but only at the expense of more thorough gas cleaning, which may include removal of alkali salts derived from the coal<sup>2</sup>). For cycles in which the coal is devolatilised or partially gasified, the economics are again in favour of cleaning the gases hot<sup>3)</sup>.

In the chemical and process industries and in incineration, the need for gas cleaning is being driven increasingly by the requirements of environmental legislation, which has been directed specifically at particulates, acid gases, heavy metal compounds, hydrogen chloride and organic chlorides such as dioxins and furans. The reasons for interest in cleaning gases hot rather than cold are many and various. They include a desire to remain well above acid dew points, improved thermodynamic efficiency, especially where downstream heat recovery is em-

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Application	Operating T/P	Gas Environment	Filter Device Requirements
Power Generation • Pressurised Fluidized Bed Combustion	800°C/10 bar	Oxidising with Alkali	• Turbine Protection ; Meet Environmental Standards
Integrated Gasification Combined Cycle	600 to 800°C 10 to 30 bar	Reducing with Alkali, H <sub>2</sub> S	• Turbine Protection, Meet Environmental Standards, Protect Sulphur Capture Beds
Conventional	<700°C, 1 bar	Oxidising	• Meet Environmental Standards; Low $\Delta P$
Chemical Process • metal refining • calcination/drying • catalytic cracking • precious metal recovery	300 to 750°C 1 to 3 bar	Varied, can be severe	• Enhance Product Recovery; Reduce Environmental Emissions; Resource Recovery; Energy Recovery
Incineration • Hazardous Wastes • Municipal Waste • Kiln/Furnaces	up to 1000°C 1 bar	Oxidising, containing reactive chemical species	<ul> <li>Reduce Environmental Emissions</li> <li>Improve Incineration Process</li> <li>Protect Downstream Equipment</li> </ul>

Table 1. Summary of potential high-temperature gas filter applications and operating requirements (Lippert<sup>1)</sup>)

ployed, and an improvement in the versatility of the overall process. In cases where the alternative is to cool process gases by dilution with ambient air, there may also be simple economic advantages to filtering the gases hot, because the total power requirement resulting from the filter pressure drop and throughput is actually reduced by so doing<sup>4</sup>. The ability to clean process gases hot also allows the simultaneous removal of gaseous components by "dry scrubbing". A further possible advantage concerns the reformation of chlorinated organics, which is thought to be catalysed by elements of the particulates in the process gases as they are cooled<sup>5</sup>); removal of such particulate catalysts should therefore prevent emissions of these damaging compounds.

Table 2 summarizes the performance of the par-

Table 2.	Summary o	of hot gas	particulate 1	removal	technology	(adapted from	Lippert <sup>1)</sup>	)
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Device	Collection Efficiency	Operating Pressure Drop (mbar)	Flow Capacity (am <sup>3</sup> /s/m <sup>2</sup> )	Energy Requirements
Cyclones				
Conventional	Low (>90%)	Moderate to High 75 to 275	Very High	Low
Enhanced	>90%	Moderate to High	Very High	Moderate to High
Granular Filters	Good (>99%)	Moderate 60 to 100	High 0.15 to 0.2	High
Electrostatic-				
Precipitator	Good (>99%)	Very Low 3 to 6	Low to Moderate .01 to .03	Moderate to High
Ceramic Bags	Good (>99%)	Low 10 to 35	Low to Moderate .01 to .03	Low
<b>Rigid Barrier Filters</b>				
Ceramic Candle	Excellent (>99.5%)	Moderate to High 50 to 250	Moderate to High .03 to .07	Moderate
Cross-Flow     (Westinghouse)	Excellent (>99.5%)	Low to Moderate 25 to 75	Moderate to High .03 to .07	Low to Moderate
• Ceramic Tube (ASAHI)	Excellent (>99.5%)	Moderate 80 to 125	Moderate to High .03 to .05	Moderate



ticulate collection devices which are under consideration for hot gas cleaning applications. In many applications, it is conventional to carry out the preliminary coarse particle capture in one or two stages of cyclones. However, cyclones have been found to be ineffective for collection of particles much below about 7  $\mu$ m so that it is conventional to apply a so-called tertiary gas cleaning stage, which at near-ambient temperatures is frequently a fabric or "bag" filter. There is still debate about the necessity for tertiary gas cleaning and the newest generation of PFBC plants designed by ABB Carbon has only two stages of cyclones to protect the turbine. At the time of writing it is unclear whether this strategy has been successful.

Of the available tertiary cleaning methods, rigid ceramic barrier filters are the most promising and the most highly developed, although advances continue to be made in the development of high temperature fabrics for bag filters<sup>6)</sup>, and there are likely to be specific applications for granular bed filters<sup>7)</sup>. and electrostatic precipitators<sup>8)</sup>. It is the intention here to review the recent advances in understanding of the behaviour of rigid ceramic filters. For a wider view of hot gas cleaning in general the reader is referred to the comprehensive review by Gilbert/Commonwealth<sup>9)</sup> and the proceedings of the two International Conferences on Gas Cleaning at High Temperatures<sup>10, 11)</sup>.

## 2. Types of Ceramic Filtration Media

An effective high-temperature filtration medium must be resistant to chemical and thermal attack and sufficiently porous not to offer an unacceptably high resistance to flow, but not so porous as to allow appreciable particle ingress or "penetration" into the structure.

Some of the important properties of the most commonly available porous ceramics are compared in **Fig.**  $1^{12}$ . It is clear that the high strength and temperature-resistance of silicon carbide, which remains one of the most important filter materials, is to some extent balanced by its high intrinsic density and high relative cost. Weight is an important factor, not only because each individual filter element must be formed in such a way as to support its own weight, but also because in large filter installations the total weight of the filter elements can be a major factor in the design of the containment vessel.

Two qualitatively different types of filter medium



are now available, as shown in Fig. 2:

- (a) Granular media, usually of silicon carbide but sometimes also alumina or alumino-silicates. Generally, the granules are bonded with siliceous material and it is the nature of the bond which determines the ultimate conditions which can be withstood. The porosity or void fraction of these media is generally in the range 0.3 to 0.5.
- (b) Fibrous media, usually formed from alumina or alumino-silicate fibres, with a siliceous bond. The porosity of these media is considerably higher, in the range 0.8 to 0.9, but their strength is substantially lower than for the granular media. As supplied, the material may also contain an organic binder, such as starch, to confer handling strength to the filter element; this rapidly burns off on first use. (Other fibrous materials have been used at high temperatures<sup>13, 14)</sup>, such as glass, graphite and stainless steel, but with less satisfactory results.)

Given the large difference in void fraction between the two types of medium, it is not surprising that the resistance to flow of an unused ("virgin") filter element of fibrous ceramic is considerably less than that of a granular ceramic element of similar filtration performance. Improvements have been made, however, to the granular medium<sup>12</sup>) by adopting a layered construction, with a thin skin of mean pore size  $8-10\mu$ m being applied to a coarse support of pore size typically  $125-150\mu$ m. This effectively prevents penetration without incurring substantial penalty in increased pressure drop. A similar effect







Fig. 2 (a) Granular ceramic medium (Schumachter DIA – Schumalith F40) – showing fine surface layer
(b) Fibrous ceramic medium (Foseco ''Cerafil'')

can be obtained for both types of medium by spraying or painting on a surface coat of suitable material during manufacture, or by pre-coating the filter with a carefully selected dust.

Both types of filter medium are conventionally used in the form of long hollow cylindrical "candles", usually with one closed end and with the flow inwards during filtration so that dust is collected on the external surface.

## 3. General Features of Filtration Behaviour

A distinction can be drawn between two main types of filtration behaviour: "depth" filtration and "surface" or "barrier" filtration. In depth filtration, collection of particles from the gas occurs throughout the filter medium. In surface filtration, the medium acts as a barrier to the solids so that a dust "cake" is built up on the up-stream surface, with no penetration into the medium itself. In practice, filtration behaviour depends on the properties of both the dust and the medium: not only the relative size of the pores in the medium but also the surface properties (such as adhesion) of both. In general, gas cleaning using fibrous ceramic media and the finer grades of granular ceramic media approximates to surface filtration. Perfect surface filtration is rare and with a virgin "surface filter" it is usual for there to be a short period of penetration into the surface layers of the medium before cake formation begins. During this short period the filtration efficiency may be slightly lower than in steady operation.

Filtration efficiency is usually extremely close to 100% for ceramic filters unless the dust is substantially sub-micron or the grain/fibre size of the medium is large. Where either of these is the case, depth filtration is to be expected and the filtration efficiency can then be calculated using the same approach as for stationary granular bed filters<sup>7</sup>.

In general, ceramic filters, in common with most other surface filters, are operated cyclically. During filtration, dust builds up on the filter. After a prescribed time, or when the resistance to flow reaches a prescribed level, the medium is cleaned. The usual cleaning action is a reverse pulse of gas, applied to the clean side of the filter while it is on-line. This detaches the cake of deposited particles, which then falls into a collecting hopper at the base of the unit, and the cycle is restarted.

Fig. 3 shows schematically the behaviour of two hypothetical media over many cycles of filtration and cleaning, assuming that the gas flowrate remains constant during filtration. Medium 2 shows satisfactory performance: it "conditions" over relatively few cycles to give a stable "baseline" resistance, i.e. the resistance immediately following a cleaning pulse. Medium 1 shows unsatisfactory behaviour: the baseline resistance continues to rise over many cycles of filtration and cleaning and may fail to reach a steady equilibrium value. Because filters must operate over many cycles, it is the "conditioned" resistance rather than that of the virgin element which is of most concern. There are several possible reasons for the unsatisfactory behaviour of medium 1. The filtration velocity may be high enough to cause penetration of particles into the medium, which cannot be subsequently removed by the cleaning pulse; alternatively, the cleaning system may not be properly designed or operated to achieve the desired cleaning effect, or the adhesion of the cake may be high enough to prevent its removal.





Fig. 3 Filter conditioning behaviour (schematic) 1. Unsatisfactory 2. Satisfactory

These factors are considered further below.

The conditioning process itself is poorly understood. However, it involves the establishment of a thin "residual layer" of dust on the surface of the medium and there is evidence that this may have a smaller mean particle size than the challenging dust<sup>15, 16)</sup>. This layer has an anomalously high flow resistance compared with the remainder of the cake and is not removed at the end of the cleaning cycle. Once it has formed, it dominates the subsequent filtration and cleaning behaviour.

#### 4. Resistance to Flow

In general, the pressure drop through a planar porous medium can be represented as

$$-\frac{\mathrm{d}P}{\mathrm{d}z} = k_1 \mu U + k_2 \rho U^2 \tag{1}$$

where (-dP/dz) is the pressure gradient in the direction of flow and U is the superficial fluid velocity, i.e. the actual volumetric flowrate divided by the area available for flow. In the case of each of the media considered here, the Reynolds number  $(Up d_p/\mu)$  is much less than unity, so that the second term in equation (1) can be neglected and  $k_1$  can be replaced by the Kozeny expression<sup>17</sup>:

$$k_1 = K_k (1 - \varepsilon)^2 \varepsilon^{-3} S_0^2$$
(2)

where  $\varepsilon$  is the void fraction,  $S_0$  the specific surface area of the medium and  $K_k$  is the Kozeny parameter, which depends on the geometrical structure. Seville et al<sup>18</sup> investigated the resistance to flow of samples of ceramic media prepared from fibrous and granular constituents mixed in various proportions. Values of the Darcy's law resistance,  $k_1$ , varied from  $4 \times 10^{10}$ to  $5 \times 10^{11}$ m<sup>-2</sup> but the value of  $K_k$  remained approximately constant at 6.1 with a standard deviation of about 0.7, suggesting that equation (2) can be used to "design" a medium with the desired resistance characteristics. (It should be noted, however, that  $K_k$  is a strong function of  $\varepsilon$  for  $\varepsilon > 0.95^{17}$ .) Furthermore, the same study<sup>18)</sup> showed that for a given medium,  $k_1$  is, as expected, independent of temperature in the range 0-1000°C, confirming that thermal expansion is negligible. The only effect of temperature on the resistance of the medium is therefore through the gas viscosity.

Since Darcy's law applies, the flow resistance of an arbitrarily shaped filter element can be predicted by solution of Laplace's equation ( $\nabla^2 P = 0$ ) with appropriate boundary conditions, provided that the pressure drop across the filter is small compared with the system pressure so that the gas density can be regarded as constant.

As noted earlier, it is the conditioned rather than the virgin flow resistance which is of most importance in practical applications. This depends on the residual dust layer and is a great deal more difficult to predict. At present there is no substitute for experiment. As an example, Withers<sup>19)</sup> defines a normalised resistance to flow, R, as

$$R = \Delta P/\mu U \tag{3}$$

and quotes <u>differences</u> in R between the conditioned and the virgin state from  $0.4 - 1 \times 10^9 \text{m}^{-1}$  for combustor ash to  $5 \times 10^9$  for fumed silica. In principle, the flow resistance attributable to the filter cake could be predicted by application of equation (2), but in practice the void fraction is extremely system-specific so that cake resistances must again be obtained by experiment. Frequently, the cake resistance, as defined in equation (3), will be simply proportional to the "areal" dust loading<sup>20</sup> (the dust mass loading per unit area of filter surface) but this cannot be assumed since some filter cakes are compressible.

### 5. Mechanisms of Filter Cleaning

Effective cleaning is essential if the conditioning behaviour of the filter is to be acceptable; it is clearly important to be able to assess the magnitude of the required cleaning action. In some circumstances, over-cleaning may be as damaging as under-cleaning



since it may lead to resuspension of the dust, which will not then separate into the collection hopper.

#### 5.1 Cake Removal Stress

Several analyses of the problem of cake detachment from flexible fabric filters have been presented<sup>21-24)</sup>, but the common assumption in all of them is simply that the dust cake detaches from the filter medium when it experiences a tensile stress sufficient to overcome either the strength of the adhesive bond between the cake and the medium (or a residual dust laver) or the internal cohesion of the cake. In theory, as soon as the strength of this adhesive or cohesive bond is exceeded (by whatever cleaning mechanism) the cake detaches everywhere simultaneously. In practice, however, neither the adhesive/ cohesive cake strength nor the applied stress is entirely uniform across the filter surface so that "patchy" cleaning results, as shown in Fig. 4, i.e. cake is completely detached from some areas of the filter and completely retained in others. This sort of behaviour is to be distinguished from progressive removal of dust layers, which is not observed.

In a conventional bag filter it is usually assumed that the required tensile cleaning stress is set up primarily by the movement caused by the cleaning pulse or, in the case of mechanically-cleaned filters, the shaking action. Pulse cleaning displaces the fabric outwards. When it becomes taut, it decelerates sharply, normally at many times gravitational acceleration. The cake then experiences a tensile stress which depends on its areal density and on the deceleration. If the stress is sufficient, fracture occurs so that the cake is thrown clear of the medium.

Rigid media such as the ceramics considered here show no displacement on cleaning. The tensile stress is therefore entirely the result of the pressure drop imposed across the cake due to reverse-flow of cleaning gas, as shown below. [It is interesting to note that work on cleaning of flexible bag filters by reverse pulse<sup>25)</sup> shows that reverse flow of cleaning gas can also be an important mechanism for flexible media, particularly if the bag is long.]

# 5.2 Analysis of Cleaning by Reverse Flow or Pulse

Consider first the case of a filter medium on which a uniform cake has been laid down. A cleaning flow is now set up in the opposite direction to the filtration direction, as shown in **Fig. 5**. During reverse-flow cleaning a pressure difference will be set up across





Fig. 4 Patchy cleaning of fly ash from silicon carbide filter at high temperatures<sup>16</sup>)
(a) isolated patch detachment

(b) 'orange peel' resulting from repeated patch detachment

the filter, consisting of contributions from the cake and the medium.

$$\Delta P_{\rm T} = \Delta P_{\rm c} + \Delta P_{\rm m} \tag{4}$$

The gas viscosity is effectively constant and the cake and medium thicknesses can be incorporated into modified resistances,  $k_{\rm c}$  and  $k_{\rm m}$ , so that





Fig. 5 Pressure distribution in medium and cake during reverse  $\mathrm{flow}^{15)}$ 

$$\Delta P_{\rm m} = k_{\rm m} U \tag{5}$$

and:

$$\Delta P_{\rm c} = k_{\rm c} U \tag{6}$$

Combining equations (4), (5) and (6):

$$\Delta P_{\rm c} = \Delta P_{\rm T} \left[ \frac{\mathbf{k}_{\rm c}}{\mathbf{k}_{\rm c} + \mathbf{k}_{\rm m}} \right] \tag{7}$$

This is the pressure drop across the cake itself and also, as shown in **Fig. 5**, the tensile stress acting at the cake/medium interface. It is therefore this quantity which is of prime interest when investigating the cake removal characteristics of a given dust/medium combination.

Equation (7) was developed for a uniform cake. However, it is equally applicable to a partially cleaned filter<sup>26)</sup>. Because of its inhomogeneous resistance to flow, a patchily cleaned filter will show regions of preferential gas flow (**Fig. 6**). However, in the uncleaned areas the total pressure drop across the filter must still be distributed across the medium plus cake as shown in equation (7), provided that the flow is rectilinear; i.e. in the uncleaned areas the gas velocity is the same in the medium and in the cake. This approximation is valid provided that the undetached cake patches are large compared with the cake thickness.

From the analysis above it is clear that when comparing the cleaning behaviour of different dust/



Fig. 6 Patchily-cleaned filter during reverse flow<sup>15)</sup>

medium combinations it is  $\Delta P_c$ , the pressure drop across the cake alone, which should be considered and not  $\Delta P_T$ , the total pressure drop. Indeed, comparison of values for  $\Delta P_T$  necessary to detach the cake may be misleading, because they depend on the cake loading, whereas  $\Delta P_c$  should not. It is sometimes asserted that thick cakes are easier to clean from filter media than thin ones. The foregoing analysis shows why this appears to be so. For the total pressure drop across the cake to remain at its critical value for detachment, a thicker cake requires a smaller pressure gradient for removal and therefore less cleaning gas flow and less pressure drop across the medium itself.

The approach outlined above considers only steady reverse-flow cleaning, but it also applies to pulse cleaning, since the maximum stress to which the cake is subjected corresponds to the steady flow cleaning value from equation  $(7)^{15}$ . In many industrial applications, the pressure rise associated with the cleaning pulse is, in any case, so slow that the process is really better considered as steady reverse flow cleaning.

## 5.3 Cake Detachment Tests

Because such factors as the cohesion of the collected dust and the adhesion of the dust to the medium cannot be predicted *a priori*, it is essential to carry out experimental work to investigate the filter cleaning behaviour. Primarily because of variations in the surface characteristics of the filter



medium, the critical stress at which the cake detaches is not uniform across the surface of a filter so that detachment occurs progressively as the cleaning pressure is increased.

It is possible to determine the range of tensile stresses over which the cake detaches from the medium by progressively increasing  $\Delta P_T$ , and measuring the fractional cake removal at each value of  $\Delta P_T$  by collecting and weighing the dust removed from the filter. This is most conveniently carried out on a small flat "coupon" of filter medium, as described by Cheung et al.<sup>15,27</sup> Not only are the quantities of dust required for conditioning more manageable, but since the coupon is small it is comparatively easy to ensure that the imposed cleaning stress is uniform across it; this is not usually the case for a candle (see section 7). Results from the coupon test are plotted in the form of "percentage cake remaining" versus "applied stress" (see Fig. 7), where the applied stress is the appropriate value of  $\Delta P_c$  for each point, calculated from equation (7). (Values of  $k_c$  and  $k_m$  are obtained from pressure drop measurements before the test and after complete cake removal). This "cake detachment curve" provides the information needed for rational selection of cleaning pressure. For fabrics, the cake detachment stress has been determined by "jerk tests", in which progressively larger accelerations are applied and the proportion of cake detached is measured at each acceleration level<sup>21-24)</sup>. For obvious reasons, the steady-flow cleaning test described above is more suitable than a "jerk test" for characterising the performance of a hot filter.

Cheung et al<sup>27)</sup> describe a coupon test rig used for hot test work at the British Coal Research Establishment, Stoke Orchard. This rig allows dust-laden gas to be sampled hot and passed directly from a combustor or gasifier to the test coupon, which is mounted within an electrically-heated sleeve. Thus the sample gases are kept at the process temperature until they are exhausted from the test section. The sample gas flow is then cooled, metered, and drawn through a sampling pump to control the face velocity through the filter. The base of the heated test section comprises a removable dust pot, to collect the particles detached at each cleaning step for removal and weighing.

A typical set of reverse-flow cake detachment curves is presented in Fig. 7, for dust cakes of limestone (mass median diameter  $1.9\mu m$ ) on coupons of a fibrous ceramic filter<sup>28)</sup>. This shows a dependence of cake detachment stress on cake mass areal loading,



Cake removal stress,  ${}_{\Delta}P_{c}$  , for limestone on fibrous Fig. 7 ceramic<sup>28)</sup> showing effect of cake areal loading

W<sub>A</sub> = areal loading  $(g/m^2)$  $\mathbf{P}_{pp}$ 

peak pulse pressure during conditioning period

= cleaning pulse duration t<sub>pp</sub>

= no. of conditioning cycles before cake removal experiment carried out

and the detachment curves have a long "tail", the stress required for 100% cake removal being an order of magnitude greater than that for 50% removal. Both of these features are typical for cake removal from rigid ceramic filter coupons. It may be noted that the values of cake removal stress are at least an order of magnitude larger than those measured for similar dusts on flexible fabrics<sup>21-24)</sup>. Given that the cake usually fails where it adheres to a residual dust layer, the difference does not simply result from stronger adhesion of dust particles to rigid media, but may be the result of the tensioning of the fabric which occurs in flexible media, which cracks and weakens the cake, lowering the strength of the bonds which must be broken to detach it. Koch<sup>20)</sup> carried out cake detachment tests at ambient temperature using both the reverse flow method and centrifugal acceleration. A comparison of the two methods is given in Fig. 8, showing that the cake removal stress as measured by acceleration is consistently lower than that derived from reverse flow experiments, and less strongly dependent on cake areal loading. The results of the two methods show signs of convergence at high cake loadings (>1000 g/m<sup>2</sup>). The difference between the methods was explained in terms of cake "hinging" during reverse flow, whereby patches of cake remain loosely attached to the filter surface after cleaning, even though their apparent detachment stress has been exceeded. They are not then included in the measured detached dust fraction. No such effect can occur in the centrifugal acceleration test, which is therefore recommended







Reverse flow (mean of several measurements)

Acceleration (experimental points)

as a true measure of the adhesion of cake to medium. However, since in practice cake removal occurs due to reverse flow, this method remains the most appropriate for estimation of the cleaning flow requirement.

#### 5.4 Prediction of the Cake Detachment Stress

At present it is not possible to predict *a priori* the stresses which must be imposed to clean the filter medium. One approach is to sum the interparticle forces at each of the contact points across the failure surface, taking due account of their directions, as in the classic agglomerate strength model due to Rumpf<sup>29)</sup>. This leads to an expression for the limit stress,  $\sigma$ , for a cake of monosized particles, as follows<sup>30)</sup>:

$$\sigma = \pi \frac{1-\varepsilon}{\varepsilon} \frac{\gamma}{d_p}$$
(8)

where  $\gamma$  is the surface energy of the particles and  $d_p$  is their diameter. Recent work by Aguiar and Coury<sup>31)</sup> for detachment of phosphate rock dust from polyester fabric has shown roughly the dependence on  $\mathcal{E}$  and  $d_p$  predicted by equation (8), albeit for a fitted value of  $\gamma$ . This approach, however, assumes simultaneous failure of all particle-particle contacts across the failure surface. In practice, fracture of agglomerates usually occurs by crack propagation from zones of weakness or flaws<sup>32)</sup>; cracks propagate when the energy stored in elastic deformation - in this case by elastic distortion of particles in contact - is released to provide the

energy needed to separate particles across the failure surface. It has been demonstrated that compressed particle compacts resembling filter cakes do store elastic energy in this way<sup>33</sup>, and attempts have been made to relate the macroscopic fracture mechanics of agglomerate failure to the single-particle bond energies<sup>33, 34</sup>, albeit with limited success.

The widespread evidence of patchy cleaning of rigid and flexible filter media suggests that detachment does not occur simultaneously over the filter surface, as implied by equation (8), but that the cake "blisters" at points of weakness, and that the blisters grow to a limiting size before breaking and either detaching completely or remaining hinged to the surface. Koch<sup>20)</sup> has shown that the patch size increases linearly with the cake areal loading, again for limestone dust on a fibrous medium, suggesting that the patch size is determined by the cake thickness, rather than by any intrinsic inhomogeneity in the cake or the medium (although such inhomogeneities undoubtedly exist). Work continues on a fracture mechanics-based analysis of patch detachment<sup>35)</sup>.

## 6. Comparison of Filter Behaviour

A variety of test data is now becoming available on the performance of rigid ceramic filters at ambient and elevated temperatures. Sources include the media manufacturers and a number of organisations which are active in evaluating the technology, notably the Coal Research Establishment in the UK and Westinghouse in the USA.

**Fig. 9** shows the conditioning behaviour under similar conditions of two granular media. What is noticeable here is the poor behaviour of the homogeneous coarse granular medium when compared with the two-layer medium, which has a fine surface membrane to prevent dust penetration into the structure. The homogeneous coarse medium shows strong signs of penetration into the structure and therefore depth filtration.

**Fig. 10** illustrates the strong effect of face velocity variation on conditioning behaviour for a fibrous medium: the filter shows almost no rise in residual pressure loss over successive cycles at 3 and 5 cm/s but catastrophic behaviour at 8 cm/s. Even when the dust shows unacceptable penetration into the medium at the desired face velocity, it is often possible to achieve satisfactory operation by applying a pre-conditioning layer of appropriate material<sup>36</sup> which was the solution found in the particular case





Fig. 9 Conditioning curves for two types of granular media:<sup>48,49</sup>) A – homogeneous coarse granular medium B – granular medium with fine surface membrane (Test dust: fly ash; face velocity: 5.5 cm/s; temperature 20°C – ΔP values extrapolated to 850°C)

## illustrated in Fig. 10.

At present there is no a priori method for predicting whether unacceptable penetration will occur and small test filters are increasingly used on site to obtain information on conditioning behaviour.

Fig. 11 compares the cake detachment stresses for three filter media filtering fly ash from ambienttemperature air at 13 cm/s. The behaviour of the coarse granular medium is again poor when compared with the other media on this basis. The medium with a fine surface coating and the fibrous medium are both rather easier to clean than the homogeneous coarse medium. The shape of the detachment curve for the coarse granular medium again suggests depth filtration and therefore ineffective cleaning. In this case, electron microscopy confirmed localised penetration.

In general, depth filtration is more likely for

- (a) large granule or fibre sizes;
- (b) high face velocities;
- (c) low dust cohesivity

The reason for (a) is clear; the argument behind (b) and (c) is as follows. As dust particles approach the filter they come into contact with particles of the medium itself or of the deposited cake. If the



Fig. 10 Filter pressure drop history - zirconium oxide dust (fibrous ceramic medium)<sup>36)</sup>

particles approaching the filter have high kinetic energy (large diameter or approach velocity or both), they will possess enough energy to avoid capture at first contact<sup>37)</sup> and will be able to penetrate deeper into the cake/medium structure. This behaviour will be even more likely if they possess low cohesivity. Even if depth filtration does not occur, a high face velocity may give rise to other undesirable effects such as the formation of a dust cake with a higher specific resistance<sup>38)</sup>.

## 7. Filter Geometry

As mentioned earlier, ceramic media have usually been used in the form of cylindrical "candles", with the dusty gas flow passing from the outside in. These are comparatively easy to manufacture but show certain disadvantages, especially where face velocities are high and pressure drop on the clean side of the candle becomes excessive (see later). In addition, cleaning, especially of long candles, may be difficult. The actual pressure at any point in the candle during cleaning will typically be a small fraction





Detachment Stress  $\sigma_{c}$  (kPa)

- Fig. 11 Cake detachment stresses various media<sup>27)</sup>
  - 1. granular medium with fine surface membrane
  - 2. coarse granular medium
  - $\label{eq:coarse granular medium showing strong penetration$
  - 4. fibrous medium

(Test dust: fly ash; face velocity: 13 cm/s; temperature  $20\,^\circ\text{C})$ 

of that in the pulse reservoir, and the cleaning pressure across the cake may easily vary by a factor of two or more along the length of the candle<sup>15, 39</sup>. This should be considered when scaling up from coupon cake detachment tests.

## 7.1 Candle Geometry

Candle dimensions differ between manufacturers, but typical dimensions are 60 mm OD and 40 mm ID with overall length in the range of 1 to 2 m. Because the diameters of candles are usually lower than those of bags, the volume of a filter unit containing a given filtration area is usually lower than for a bag house of the same volumetric throughput. Coupled with the possibility of using higher face velocity, this means that ceramic media present the possibility of greatly reduced unit size. However, because the resistance of the filter medium can be relatively low and the candle diameter is relatively small, the pressure drop of the gas on the "clean side" of the filter can become comparable with the pressure drop through the filter medium itself (Fig. 12). The main contribution to this internal pressure drop arises from the change in gas momentum, but wall friction can also be significant;



Fig. 12 Flow maldistribution in a candle

the effect is that the pressure difference across the candle wall increases towards the open end, causing a corresponding increase in the local face velocity U. During filtration, the increased face velocity towards the open end will, of course, lead to a more rapid deposition in this area and hence to a more uniform distribution of flow<sup>40</sup>. However, even if it occurs only in the initial conditioning stages, a marked flow maldistribution is probably undesirable because it can lead to permanent blinding.

Clift et al<sup>41)</sup> have investigated flow maldistribution both theoretically and experimentally for the case of a cylindrical candle of uniform flow resistance. If the internal pressure drop is relatively small compared with the pressure drop across the wall, the pressure gradient along the candle is approximately proportional to  $U^2$ , whereas the pressure drop across the wall is proportional to U. Hence variations in internal pressure become more significant as the mean face velocity is increased. For short candles and low face velocities, where the internal pressure gradient is negligible, the overall pressure drop is proportional to total gas flow through the candle. However, as the face velocity or candle length is increased, so that the internal pressure gradient becomes more significant, the relationship between flowrate and pressure drop becomes nonlinear. An example of this can be seen in Fig. 13, which shows the expected linear relationship between overall pressure drop and (nominal) face velocity for a short candle, but a markedly nonlinear variation for a long candle.

It is of interest here to consider the effects of increasing temperature and pressure. Increasing temperature increases the gas viscosity and hence the pressure drop across the candle wall, but decreases the gas density and hence reduces the pressure





Fig. 13 Dependence of total candle pressure loss on mean face velocity

(BWF KE85 fibrous ceramic candles)<sup>41)</sup>

- C Experiment
- ---- Theory
- ---- Medium alone L = Candle length

L = Candle length

change along the candle. Thus increasing temperature reduces the problem of flow maldistribution. However, increasing pressure (at constant temperature) increases gas density but has no effect on viscosity; therefore increasing pressure has no effect on the wall pressure drop for a give face velocity but increases the pressure change along the candle. Therefore increasing pressure worsens the problem of maldistribution.

Cheung<sup>15)</sup> and Berbner and Löffler<sup>39)</sup> have investigated the cleaning of ceramic candle filters using reverse pulse, as commonly utilised in practice. Although the only information on cleaning conditions usually given on industrial trials of candle filters is the pulse gas reservoir pressure, this is only tenuously linked to the overpressure inside the candle, which is what determines the cleaning efficiency. On large industrial installations in particular, the pressure loss in pipework may be very significant<sup>42)</sup> and may either prevent effective cleaning or cause gross maldistribution of cleaning gas. It is generally agreed that the overpressure inside the candle depends on the discharge rate of the nozzle (which may be choked), the entrainment of process gas (which depends on the geometry of the nozzle and the candle), and the candle dimensions and permeability (which may vary with time). It will also vary with position inside the candle. In particular, an inappropriate choice of design and operating variables may lead to suction being applied to the region around the candle neck, rather than overpressure, preventing any cleaning from occurring in this region<sup>39)</sup>. Venturis are sometimes used to increase the cleaning effect; Morris et al<sup>43)</sup> discuss the different geometries available for use with fabric filters.

Various methods of candle location and fixing have been used, and candles may be hung vertically from a tube sheet or (in the case of fibrous media) supported horizontally. The latter has some process advantages as the dirty gas can be brought into the filter vessel vertically downwards so that its momentum contributes to settling of the detached cake. Space does not permit further discussion of this rapidly advancing area of development.

#### 7.2 Novel Geometries

Two variations on the "traditional" candle geometry have shown some promise: the Asahi Glass filter<sup>44)</sup>, in which the dusty gas flow passes from the inside out, and the Westinghouse "cross-flow filter"<sup>45)</sup>.

**Fig. 14** shows the Asahi Glass filter concept<sup>44</sup>. The dusty gas enters vertically downwards so that its momentum helps to carry the detached dust down into the hopper. The filter cylinders are cleaned by applying a reverse pulse to the surrounding chamber; thus, the filter medium is in compression during the cleaning pulse, which is claimed to lead to long-term improvement in durability over the conventional candle arrangement. The Asahi Glass filter has been successfully applied in the steel industry in Japan and is now being tested in pressurised fluidised bed combustion and gasification applications.

The Westinghouse "cross-flow filter"<sup>45</sup> (**Fig. 15**) consists of a monolithic block formed with channels through which the dirty gas enters and the clean gas exits. In this form, dust builds up during filtration within the "dirty side" channels. Cleaning is achieved by applying a reverse pulse to the clean side. The cleaning mechanism is likely to be more complex than that given in section 5, because the flow must not only detach the cake but also transport it out of each channel. Cross-flow filters can reduce the total volume necessary to provide a given filtration area, but they are less developed than candles and their durability in service has not, as yet, been sufficiently evaluated in long-term plant trials.

# 8. Simultaneous Removal of Solid and Gaseous Contaminants

The most recent and one of the most exciting





Fig. 14 Asahi Glass filter concept<sup>44)</sup>



developments in hot gas cleaning technology has been the proving of techniques for "dry scrubbing" of acid gases and heavy metals<sup>46,47</sup>. This is done by injecting finely divided reactant or adsorbent solids up-stream of the filter, the solids most commonly employed being calcium carbonate, oxide or hydroxide, to remove SO<sub>X</sub> and HCl, and activated

carbon to remove organic chlorides and heavy metals. In this application, ceramic filters are preferable to fabric filters not only because of their greater temperature range and relative freedom from chemical attack, but also because their lack of flexibility prevents cake cracking, which causes gas by-passing and is thought to be a major source of inefficiency. Dry scrubbing processes are currently attracting considerable research effort and are already being retrofitted to small and medium-sized plants such as incinerators and combustors. Their successful operation depends on the chemical characterisation of the gas-solid system, the hydrodynamic conditions within the dust layer and the mode of operation of the filter.As for any reaction system, the choice of the filter. As for any reaction system, the choice portant parameters.

#### 9. Conclusions

The requirements of the power generation industry and, more recently, the chemical and process industries have led to a rapid development of technologies for gas cleaning at temperatures up to 1000°C, the most promising of these being the rigid ceramic filter. Two distinct types of medium have been developed, granular and ceramic, each with its own advantages. If the operating conditions



are selected appropriately, both will act as surface filters so that the major issue to be addressed is the long-term pressure drop history, which depends on the efficiency of the filter cleaning system. A significant advance in understanding was the recognition that dust cake detachment occurs entirely as a result of the pressure difference imposed across it by the reverse flow of cleaning gas. A full understanding of the detachment of the filter cake from the medium depends on the successful modelling of both the intrinsic adhesion of the dust cake to the filter medium and the way in which the reverse pressure pulse propagates within the filter. Ceramic filters have usually been employed in the form of long cylindrical candles, but the requirement for good flow distribution during both the filtration and the cleaning parts of the operating cycle limits the length-to-diameter ratio which can be employed. Advances continue in the design of candle suspension and fixing systems but in the longer term, non-candle geometries may be adopted more widely. The growth in applications for "dry scrubbing" of gaseous contaminants at high temperatures can be expected to increase interest in the use of ceramic filters still further.

## Nomenclature

dp	: particle diameter (m)
κ <sub>k</sub>	: Kozeny parameter (eq.2) (-)
$k_1$ , $k_2$	: resistances in eq.1 (m <sup>-2</sup> , m <sup>-1</sup> )
k <sub>c</sub> , k <sub>m</sub>	: resistances in eq. 5 & 6 (Pa s m <sup>-1</sup> )
Ρ́	: pressure (Pa)
ΔP	: pressure difference (Pa)
R	: normalised resistance to flow (eq. 3) (m <sup>-1</sup> )
S <sub>0</sub>	: specific surface area (m <sup>-1</sup> )
U	: superficial gas velocity (m s <sup>-1</sup> )
γ	: surface energy (J m <sup>-2</sup> )
3	: void fraction (-)
μ	: gas viscosity (Pa s)
р	: gas density (kg m <sup>-3</sup> )
σ	: stress (Pa)

## Subscripts

с	:	cake
m	:	medium

T : total

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Review

## Discrete particle simulation of gas-solid flows † (From dilute to dense flows)

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## Abstract

Increasing computer power has made discrete particle simulation a practical means for predicting particle motion in industrial processes. Simulation techniques for various particle motions, from dilute to dense phase flows, are explained here. In simulations of this kind, the most important problem is how to model the interactions of particles with walls, with other particles and with the fluid. Calculations based on various models for these interactions are discussed. Particle segregation phenomena, particle mixing in a rotating vessel, dense phase pneumatic conveying, and fluidized bed are shown as examples of simulations which have been made in the author's laboratory.

## 1. Introduction

Since numerical simulation of single phase flows is considered to have attained maturity, attention is being paid to multiphase flows. Fields in which such numerical simulations will play an important role as a prediction method are widespread. For example, flows in manufacturing industries, flows in nature and flows in living bodies are often multiphase. In the simulation of multiphase flows, we must treat both the fluid phase and discrete phase motions. Owing to the great achievements in single phase flows, computation techniques for fluid motion have been established satisfactorily. Now techniques for particle motion are being developed and most techniques can be applied to powder technology.

Multiphase flows are classified into the following four categories; gas-liquid, liquid-solid, gas-solid and gas-liquid-solid. As far as formulation is concerned, the gas-solid flow is among the simplest, because mass transfer and surface phenomena which make the formulation complicated need not usually be taken into account. Simulation of gas-solid flows started from dilute phase flows where particles are dispersed in gas at a low concentration. In the recent several years, the author's research group in Osaka University has been interested in flows with high concentrations. The higher the particle concentration, the stronger the impact of simulation on practical applications. For instance, dense phase flows are closely related to powder technology. Before, it seemed a dream for engineers working in powder technology to design machines based on computer simulation, but the situation is gradually changing. Nowadays computers enable us to deal with the motion of individual particles in dense phase flows where particles are in contact with each other.

#### 2. Eulerian vs. Lagrangian

According to the wellknown classification, numerical methods of multiphase flows are classified as Eulerian or Lagrangian depending on the treatment of the particulate phase. The Eulerian method regards the particulate phase as a continuum. This method is further divided into one-fluid (homogeneous) and two-fluid models. An advantage of the Eulerian method is to apply techniques developed for single phase flows to the particulate phase with fewer modifications. However, it should be noted that a sufficient number of particles must be included uniformly in a control volume for calculation in order to use the Eulerian method. Unfortunately, cases satisfying this condition are limited.

The Lagrangian method computes the motion of individual particles. Its basic ideas and formulations are simple compared with the Eulerian method. However, as the number of particles increases, large memories and long computation time are needed. If the Lagrangian calculation is to be performed rigorously for all the particles in a practical multi-phase

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flow, enormous amount of memory and computation time would be required. This is a substantial disadvantage of the Lagrangian method. Fortunately, progress in computer hardware development is still continuing, which is helpful to the Lagrangian method. Also, our group has made an attempt to apply the DSMC (Direct Simulation Monte Carlo) method, developed in molecular dynamics, to multi-phase flows to avoid the above demerit of the Lagrangian method.

The above classification has been applied to dispersed phase flows in general. The same classification holds true for dense phase flows or granulate flows where the particle concentration is so dense that the particles are in continuous contact with each other. When the Eulerian method is used for such dense phase flows, the most important assumption which has to be made is about the relation between stress and strain of the continuum consisting of particles. Many efforts have been made to obtain this relation, experimentally and theoretically. However, it is not easy to deduce relations for general use.

It has not been long since the Lagrangian method was applied to dense phase flows. Compared with the Eulerian method, the Lagrangian method requires less assumptions and is expected to be a powerful means for predicting phenomena in powder technology.

## 3. Collision

#### 3.1 Irregular bouncing

In dilute phase pneumatic conveying, the gas flow gives momentum and kinetic energy to the particles. That is, particles are accelerated by gas through the drag force. If a particle in a horizontal pipe did not collide with the wall, the particle velocity would be equal to the gas velocity. However the time-averaged particle velocity is always smaller than the gas velocity, because the particles lose momentum due to collisions with the wall. Since the additional pressure drop due to the particles corresponds to the fluid drag which is related to the velocity difference between the fluid and the particles, the energy loss caused by collision must be estimated precisely in the simulation.

Although particle-to-wall collision is an important phenomenon in gas-solid pipe flows, the Eulerian method has disadvantages concerning collision because the effects of collision can not be considered in a direct way. In contrast, the Lagrangian method is suitable for dealing with the collision problem. When the coefficients of restitution and dynamic friction are given as particle physical properties, the collision problem can be solved using the classical dynamics of a rigid body. However, the problem is not as simple as expected. That is, if the simulation were based on the simple assumption that spherical particles collide with a flat plate with a coefficient of restitution smaller than one, particles colliding repeatedly with the wall in a long horizontal pipe would ultimately slide on the wall. To avoid such an unrealistic result, we must take the irregularity of collisions into consideration. If the irregularity is neglected, particles can not be suspended in the gas. Previously, Magnus or shear lift forces and fluid turbulence were often considered as mechanisms suspending particles in a horizontal pipe. It is true that these fluid dynamic forces act on particles and that the effect of these forces are dominant for small particles, but the mechanism suspending large particles in horizontal pipes is the irregular bouncing of the particles against the wall. The irregularity is caused by particle shape deviating from a true sphere and roughness of the wall.

Regarding the irregular bouncing, several models have been proposed so far (Matsumoto et al. 1970a, 1970b, Tsuji et al. 1987, Tsuji et al. 1989, Frank et al. 1991). In general the relation between particle velocities before and after collision are derived using the impulsive equations with the coefficient of restitution and friction coefficient given. We (Tsuji et al., 1991) attributed the irregularity to the non-sphericity of particle shape, and demonstrated a calculation method for three dimensional collision of a nonspherical particle. This method is applicable to particles of arbitrary shape.

We calculated the trajectories of nearly spherical particles in a two-dimensional channel. **Fig. 1** shows the shape of the particle. Calculated results of particle trajectories are shown in **Fig. 2**, where the scale of the longitudinal distance is greatly reduced so that the motion of the particles in the whole channel can be



KONA No.11 (1993)





Fig. 2 Trajectories of a particle in a horizontal channel Particle size = 1.1 mm, Particle density = 1038 kg/m<sup>3</sup> Restitution coefficient e = 0.93, Friction coefficient  $\mu_f$  = 0.28

seen. It was found that even a small deviation from the sphere leads to a considerable irregular bouncing motion.

## 3.2 Inter-particle collision

As the particle concentration becomes higher, interparticle collision occurs more often and the loss of kinetic energy of the particles due to this collision cannot be neglected. Fortunately, as long as the particulate phase is dispersed, it is sufficient to consider only simple collision and not multiple collision. As in the particle-to-wall collision, the impulsive equations are solved to obtain the translation and angular velocities after collision assuming that the coefficients of restitution e and friction  $\mu_f$  are known (Tanaka et al., 1991).

# 4. DSMC (direct simulation monte carlo) method

The trajectories of individual particles are obtained by numerically integrating the equations of particle motion with a time interval  $\Delta t$ . This integration process is straightforward. As described in the above section 3.2, the particle velocities after binary collision are calculated from the values before collision and the physical properties such as the coefficients of restitution and friction. However it is not easy to find pairs of particles colliding with each other when a large number of particles exist in the flow field. If we attempt to find such pairs from the trajectories of individual particles, the computation time would become extremely long as the number of particles increases. The DSMC method, proposed by Bird (1976) to solve the Boltzmann equation of rarefied gas flow has been developed to resolve this difficulty.

In dispersed gas-solid flow involving large particles, the particle inertia forces are dominant, and collisions against a particle or wall are assumed to occur instantaneously. Therefore the motion of the solid phase is similar to that of molecules in rarefied gas except that the kinetic energy of the particle fluctuating motion tends to decay due to the inelastic and frictional characteristics of collision.

The DSMC method has already been applied to calculate particle motion in gas-solid flows by Kitron et al. (1990), Tanaka et al. (1991) and Tanaka et al. (1993). Tanaka et al. (1991) applied the DSMC method to fully developed flows in a vertical pipe and obtained results which agree satisfactorily with whose predicted by the deterministic method (Tanaka & Tsuji, 1991). The outline of the DSMC method is as follows.

- (i) Each simulated particle represents a large number of "physical" particles,
- (ii) The time internal for numerical integration is taken sufficiently small compared with the mean free time of the particles, and thus inter-particle collisions are uncoupled from free particle motion.
- (iii) The flow field is divided into small cells over which change in flow properties is small. Particles are allowed to collide through a Monte Carlo procedure.
- (iv) The calculation of particle motion is carried out by repeating the following procedure:

First, the motions of all simulated particles in the time interval  $\Delta t$  are calculated using the equations of motion without regard for interparticle collisions. If the calculated path of a particle crosses a solid wall, the velocity is replaced with the post-rebound velocity. Secondly, inter-particle collision during the time interval  $\Delta t$  is searched by means of the Monte Carlo procedure. The collision counterpart and geometry of collision are also chosen with the Monte Carlo method. If a particle collides with another particle, the post-collision velocities of the colliding pair are calculated using the impulsive equations as described in Section 3.2. The particle velocities are replaced by the post-collision velocities, but without changing their positions.

Several schemes to find out whether a particle collides with another particle within a time interval have been proposed. We used the modified Nanbu method (Illner and Neunzert, 1987). The probability of inter-particle collision for a particular particle is evaluated from the particle properties included in the cell. The collision probability  $P_i$  of particle i during a time interval  $\Delta t$  is given by,

$$P_{i} = \sum_{j=1}^{N} p_{ij},$$
 (1)

where N is the number of simulated particles in the cell and  $p_{ij}$ , the probability of collision between the particle i and particle j in the cell during the time interval  $\Delta t$ .



In evaluating  $p_{ij}$ , it must be noted that each simulated particle represents many physical particles.  $p_{ij}$  is not a collision probability between a single particle i and a single particle j but that for a physical particle in a field over which physical particles represented by simulated particles i and j are distributed homogeneously. Assuming the particles are spheres having a uniform diameter  $d_s$ ,  $p_{ij}$  is given by,

$$P_{ij} = \frac{n}{N} d_s^2 g_{ij} \Delta t, \qquad (2)$$

Where n is the number density of the real flow at the corresponding position, and  $g_{ij}$  is the magnitude of relative velocity between both particles.

According to the modified Nanbu method, the occurrence of inter-particle collision and the collision counterpart are decided using a random number  $R_{\rm ND}$ obtained from a uniform distribution which ranges from zero to unity. A "candidate" collision counterpart j is selected first using the following equation.

$$\mathbf{k} = [[\mathbf{R}_{\mathrm{ND}} \times \mathbf{N}]] + 1, \tag{3}$$

where  $[[R_{ND} \times N]]$  is defined as the integer part of  $R_{ND} \times N$ . Particle i is then assumed to collide with particle k during the previous time interval if:

$$R_{\rm ND} > \frac{k}{N} - p_{ik}. \tag{4}$$

In this procedure,  $p_{ij}$  for any particle combination in a cell must not exceed 1/N. This condition is satisfied by selecting an appropriate time interval, since  $p_{ij}$  is proportional to  $\Delta t$  as shown in Eq. (2).

If the particle i collides with the particle k, the velocity of particle i (though not that of k) is replaced by the velocity after the collision. The relative

position of the collision is also given using random numbers.

### 5. Contact forces

#### 5.1 Cundall & Strack model

As the particle concentration increases, almost all the particles are in contact with neighboring ones. Since each particle has elasticity, a particle assembly forms a complicated vibration system having multiple degrees of freedom. Moreover the contact points vary with time. The influence of a particle on other particles far from it propagates in a disturbance wave. It is very difficult to consider the interaction between one particle and remote ones. If the time interval in numerical calculation is chosen sufficiently small, it can be assumed that during a single time interval disturbances do not propagate from any particle further than its immediate neighbors. In other words, the instantaneous motion of each particle is determined by the contact forces acting between that particle and particles with which it is in contact. This assumption, proposed by Cundall and Strack (1979), makes it possible to save memory space. Based on this assumption, the motion of each particle in dense phase flows can be obtained by integrating the equations of motion step by step in which the contact forces between a particle and its immediate neighbors are taken into account. However, unlike dispersed phase flows, a method such as DSMC can not be used and trajectory calculation must be performed for all the physical particles.

In this simulation, the contact forces are more important then the inter-particle collision. Cundall and Strack (1979) proposed the model shown in **Fig. 3** to formulate the contact forces between



Fig. 3 Model of contact forces



(10)

two spheres. The model consists of a spring, a dashpot and a slider. The model in **Fig. 3** is similar to the Voigt model known in the field of rheology. The effects of these mechanical elements on particle motion appear through the following parameters;

stiffness	k
damping coefficient	η
friction coefficient	$\mu_{\mathrm{f}}$

When two particles denoted by i and j are in contact, the normal component of the contact force,  $f_{Cnij}$ , acting on the Particle i is given by the sum of the forces due to the spring and the dash-pot;

$$\vec{f}_{Cnij} = (-k_n \delta_{nij} - \eta_n \vec{v}_{rij} \cdot \vec{n}_{ij}) \vec{n}_{ij}$$
(5)

where

- $\delta_{nij}$ : displacement of particle caused by the normal force
- $\vec{v}_{rij}$ : velocity vector of particle i relative to particle j
- n<sub>ij</sub> : unit vector drawn from the center of particle i to that of particle j

The tangential component of the contact force,  $\vec{f}_{Ctij}$ , is given by

$$\vec{f}_{Ctij} = -k_t \vec{\delta}_{tij} - \eta_{tj} \vec{v}_{sij}$$
(6)

where  $k_t$  and  $\vec{\delta}_{tij}$  are, respectively, the stiffness and displacement in the tangential direction. In the above equations, the suffixes n and t represent the components corresponding to the normal and tangential directions, respectively.  $\vec{v}_{sij}$  is the slip velocity of the contact point, which is given by

$$\vec{\mathbf{v}}_{sij} = \vec{\mathbf{v}}_{rij} (\vec{\mathbf{v}}_{rij} \cdot \vec{\mathbf{n}}) \vec{\mathbf{n}} + \mathbf{r}_{s} (\vec{\mathbf{\omega}}_{i} + \vec{\mathbf{\omega}}_{j}) \times \vec{\mathbf{n}}$$
(7)

where  $r_s$  is the radius of the sphere. If the following relation is satisfied

$$|\mathbf{f}_{\mathrm{Ctij}}| > \mu_{\mathrm{f}} | \overrightarrow{\mathbf{f}}_{\mathrm{Cnij}} |, \qquad (8)$$

particle i slides and the tangential force is given by

$$\vec{f}_{Ctij} = -\mu_f | \vec{f}_{Cnij} | \vec{t}_{ij}$$
(9)

instead of Eq. (6). Eq. (9) is the Coulomb-type friction law.  $\overrightarrow{t}_{ij}$  in Eq. (9) is the unit vector defined by

 $\vec{t}_{ii} = \vec{v}_{sii} / |\vec{v}_{sii}|$ 

In general, several particles are in contact with particle i at the same time. Therefore the total force and torque acting on particle i is obtained by taking the sum of the above forces with respect to j.

The same relations as the above equations are

## 5.2 Determination of parameters in Cundall & Strack model

The next step after modeling the contact forces is to determine the values of the stiffness k, damping coefficient  $\eta$  and friction coefficient  $\mu_f$ . Among these parameters, the friction coefficient  $\mu_f$  is measurable and regarded as a parameter given empirically.

Fortunately the stiffness can be calculated using the Hertzian contact theory when the physical properties such as the Young's modulus and Poisson ratio are known. According to the Hertizian contact theory, the relation between the normal force  $P_n$  and displacement  $\delta_n$  is given by

$$\mathbf{P}_{n} = \mathbf{K}_{n} \delta_{n}^{3/2} \tag{11}$$

 $K_n$  is given as a function of the physical properties of two particles. If the two particles have the same properties,  $K_n$  is expressed as

$$K_{n} = \frac{\sqrt{2r_{s}} E_{s}}{3 (1 - \sigma_{s}^{2})}$$
(12)

where r<sub>s</sub> : radius

 $E_s$ : Young's modulus of the particle  $\sigma_s$ : Poisson ratio of the particle

The above equation signifies that the force varies with the 3/2 power of the displacement. Therefore if the above results are applied to the model of the contact forces given in the foregoing section, Eq. (5) can be replaced by

$$\vec{f}_{Cnij} = (-K_n \delta_{nij}^{3/2} - \eta_{nj} \vec{v}_{rij} \cdot \vec{n}_{ij}) \vec{n}_{ij}$$
(13)

As for the relation between the tangential force  $P_t$  and displacement, theories developed by Mindlin (1949) and Mindlin and Deresiewicz (1953) are used (Tsuji et al., 1992).



Regarding the damping coefficient, Cundall and Strack (1979) proposed two expressions, given by the following equations,

$$\eta_{n} = 2\sqrt{m/k}_{n}$$

$$\eta_{n} = 2\sqrt{m/k},$$
(14)

which are derived from the condition of the critical damping of a single degree-of-freedom system consisting of a mass, spring and dash-pot.

We (Tsuji et al., 1992) proposed another method for determining the damping coefficient. In our method, the damping coefficient is related to the coefficient of restitution which is regarded as one of particle's physical properties or can be measured in a simple experiment.

#### 6. Equation of particle motion

Individual particles have two types of motion; translational and rotational motions. The translational motion is caused by the contact force, fluid force and gravitational force. The rotational motion in dispersed phase flows is caused by collision with the wall and particles. The rotational motion in the fluid is affected by viscous dissipation. In dense phase flows where particles are in contact with neighboring ones, the rotational motion is caused by the tangential components of the contact forces.

The equations of translational and rotational motions are

$$\vec{r} = (\vec{f}_{c} + \vec{f}_{D})/m + \vec{g}$$
(15)

$$\vec{\omega} = \vec{T}_{c}/I$$
 (16)

where  $\vec{r}$ : position vector of the particle's gravity center

m : particle mass  

$$\vec{f_c}$$
 : sum of contact forces  
 $\vec{f_p}$  : sum of fluid forces  
 $\vec{g}$  : gravity acceleration vector  
 $\vec{T_c}$  : sum of torque  
I : moment of inertia of the particle  
() : time derivative

The new velocity and position after a time interval  $\Delta t$  are expressed as:

$$\vec{v}_{s} = \vec{v}_{s0} + \vec{r}_{0}\Delta t \qquad (17)$$

$$\vec{r} = \vec{r}_0 + \vec{v}_s \Delta t$$
 (18)

$$\vec{\omega} = \vec{\omega}_0 + \vec{\omega}_0 \Delta t \tag{19}$$

where  $\vec{v}$ : velocity vector suffix 0: previous value suffix s: particle

Regarding the fluid forces, drag, lift (due to rotation and velocity shear) and torque are considered. Various theoretical or empirical formulae are available for such forces acting on particles freely suspended in the fluid. In dense phase flows, the lift and torque due to viscosity can be neglected, and only the drag is taken into account. Such drag can be estimated by considering the pressure gradient caused by the fluid passing through the particle bed, as might be found from established empirical formulae such as the Ergun equation (Ergun, 1952).

#### 7. Equation of fluid motion

It is almost impossible even for modern supercomputers to solve the problem of the instantaneous flow field of small scale between moving particles in multiphase flows. Furthermore, the scale of the phenomena of interest to us is much larger than the size of individual particles. Therefore it is reasonable to perform calculations based on locally averaged quantities according to Anderson and Jackson (1967). As is usual in many numerical calculations of flow fields, the finite difference method can be used to obtain the flow field in the simulation of multiphase flows. Therefore, the flow domain is divided into cells, the size of which is smaller than the macroscopic motion but larger than the particle size. All the quantities such as pressure p and velocity u are averaged in the cell using a weight function. The void fraction & of each cell can be defined by the number of particles existing in the cell.

The equation of continuity is given by

$$\frac{\partial \varepsilon}{\partial t} + \frac{\partial}{\partial x_{i}} (\varepsilon u_{j}) = 0$$
(20)

The equation of fluid motion is

$$\frac{\partial}{\partial \mathbf{x}_{i}} (\varepsilon \mathbf{u}_{i} \mathbf{u}_{j}) = -\frac{\varepsilon}{p} \frac{\partial p}{\partial \mathbf{x}_{i}} + \mathbf{f}_{si}$$
(21)

where p is the fluid density. The last term in Eq. (21) denotes the mutual interaction between particles



and fluid. Eq. (21) signifies that the fluid is assumed to be inviscid. The interaction term depends on the fluid properties, the void fraction and the relative velocity between particles. For details, refer to Tsuji et al., (1993).

## 8. Calculation procedure

As an example of the calculation procedure, flow charts in the simulation of a fluidized bed are given in **Fig. 4**.

## 9. Examples of simulation

## 9.1 Without fluid

Our group in Osaka University has developed computer programs for fluidized beds and pneumatic conveying, in which the fluid forces play important roles. However, simulations neglecting fluid flow also have many applications in powder technology. In fact we have attempted to predict various particulate flows such as particle discharge from hoppers and particle mixing in rotating vessels. In this section, such examples are shown first.

Fig. 5 illustrates the mixing of two types of particles in a rotating square duct. This simulation was made three-dimensionally. From this simulation, the time required for mixing and the optimal rotating speed can be predicated.

**Fig. 6** illustrates a particle flow from a round hopper. Initially, two types of particles are uniformly mixed in the upper hopper. The dark color particles are heavy particles and the light color particles are light ones. As the particles are discharged, particle segregation is observed, that is, the heavy particles tend to occupy the lower and center parts of the lower hopper.

Fig. 7 also illustrates particle flows from round hoppers. The effect of a cone near the gate on the flow pattern can be clearly observed. The case without the cone shows a funnel-type flow pattern while the case with the cone shows a mass flow.

## 9.2 With fluid

**Fig. 8** (Tanaka et al., 1993) illustrates a dispersed gas-solid flow in a vertical channel, where the DSMC method was used. Note that the vertical scale of the channel is compressed in these figures. When the superficial gas velocity is large or the mean solid mass flux is small, the particle concentration has a nearly homogeneous distribution. As the gas velocity decreases and the solid loading increases,



(b) Particle motion



Fig. 4(b) Flow chart

particle clusters in which the solid volume fraction is extremely large are formed near the wall. These particle clusters substantially affect the gas flow. The gas velocity and particle velocity are reduced in particle clusters and in their wakes. The velocities





Fig. 5 Particle mixing in a rotating duct Side length of the dust = 50 mm, Depth of the dust = 25 mm Rotation speed = 120 RPM Properties of large particles: Size = 4 mm, Number = 300, Density = 2700 kg/m<sup>3</sup> Properties of small particles: Size = 2 mm, Number = 200, Density = 2700 kg/m<sup>3</sup>



Fig. 6 Particles discharging from a cylindrical hopper Internal diameter of the hopper = 50 mm Diameter of the hole = 20 mm Properties of heavy particles: Size = 4 mm, Number = 950, Density = 2700 kg/m<sup>3</sup> Properties of light particles: Size = 4 mm, Number = 950, Density = 1000 kg/m<sup>3</sup>

of particles in dense clusters can even become negative, meaning that they drop down along the wall.

Fig. 9 represents a flow pattern obtained in a channel wider than that of Fig. 8, giving rise to clusters forming not only along the walls but also in

the central part of the channel. The close-up of a typical V-shaped cluster formed in the central part of the channel is also shown in **Fig. 10**. The scale of the close-up is not compressed.

Fig. 11 (Tsuji et al., 1992) illustrates a plug flow





Fig. 7 Particles discharging from a cylindrical hopper (Comparison between two cases with and without an inserted cone, Pictures in the large frame show the view in the vertical central plane inside the hopper. Pictures in the small frame show side views.)

Internal diameter of the hopper = 80 mm Diameter of the hole = 40 mm

Properties of particles: Size = 4 mm, Number = 10,000, Density = 3000 kg/m<sup>3</sup>

Fig. 7(a) Before discharge

Fig. 7(b) Without a cone, the flow at the outlet is a funnel-type flow. The cone is effective for producing a mass flow pattern.



Fig. 8 Flow pattern of dispersed gas-solid flow in a vertical channel Channel width W = 0.08 mParticle mass flux Q =  $25 \text{ kg/m}^2\text{s}$ , Restitution coefficient e = 0.94,

Friction coefficient  $\mu_f = 0.28$ 

of cohesionless particles in a horizontal pipe. It can clearly be observed that the plug gives rise to a wave-like motion similar to that of a gas-liquid slug flow. There are stationary particles between the



Fig. 9 Flow pattern of dispersed gas-solid flow in a vertical channel  $(W = 0.30m, Q = 25 \text{ kg/m}^2\text{s}, e = 0.94, u_t = 0.28)$ 

plugs. The plug sweeps up the stationary particles in front and leaves behind a stationary layer. These calculated results agree well with the actual phenomena observed in experiments.





channel. (W = 0.30 m, Q = 25 kg/m<sup>2</sup>s, e = 0.94,  $u_r = 0.28$ )

We have made simulations of fluidized beds having various geometries. Although the simulation is based on simple models, the formation of bubbles and slugs is observed in the same way as in physical experiments. **Fig. 12** represents an example of such simulations. In this case, the particle motion was treated two-dimensionally. The air is issued from three nozzles provided at the bottom.

## 11. Concluding remarks

The author has not reviewed sufficiently the studies made by other researchers in this review. It should be noted that discrete particle simulations without fluids have been made actively in the field of soil and rock mechanics.

It has not been long since discrete particle simulation was applied in powder technology. As computer



Fig. 11 Dense phase pneumatic conveying in a horizontal pipe Pipe internal diameter = 50 mm Superficial air velocity = 2.4 m/s Properties of particles: Size = 10 mm, Number = 1000, Density = 1000 kg/m<sup>3</sup>



Fig. 12 Two-dimensional fluidized bed with three jets. Number of particles = 30,000



power increases, this method will be all the more attractive and useful. As far as particle motion is concerned, we have already succeeded in obtaining qualitatively good correlations. It is expected that from now, research in discrete particle simulation will be developed along the two directions; seeking quantitative correlations or including various influential factors such as effects of humidity, cohesion forces, particle shape and so on. Recently, a commercial software "P-TAK" based on part of our program has been developed for the prediction of particle flows in hoppers and fluidized beds by Yabushita et al., (1993).

## Nomenclature

D	:	pipe diameter
d	:	particle diameter
E	:	Young's modulus
e	:	coefficient of restitution
$\vec{f}_{C}$	:	contact force
$\vec{f}_{D}$	:	fluid drag force
G <sub>s</sub>	:	shear modulus
ġ	:	gravity acceleration vector
Ι	:	moment of inertia of particle
k	:	stiffness
m	:	particle mass
N	:	number of particles
→ n	:	unit vector in the normal direction
Р	:	elastic force
р	:	pressure
Q	:	particle mass flux
Re	:	Reynolds number
r	:	position vector of particle's gravity cent
r <sub>s</sub>	:	particle radius
t	:	time
→ t	:	unit vector in the tangential direction
$\vec{T}_{c}$	:	torque
U	:	bulk gas velocity
u	:	gas velocity
V <sub>s</sub>	:	particle velocity vector
δ	:	displacement
3	:	void fraction (porosity)
η	:	damping coefficient
u <sub>f</sub>	:	friction coefficient
p	:	air density
σ	:	Poisson ratio
$\stackrel{\rightarrow}{\omega}$	:	angular velocity vector of particle
suffix		

center

- normal component : n
- t • tangential component

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## Author's short biography



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Prof. Yutaka Tsuji has been at the Osaka University, Japan since 1970. His major research interest lies in numerical simulation of multiphase flow and optical measurement of fluid-solid two-phase flow. He is the coordinator of the Simulation Committee of the Association of Powder Process Industry & Engineering, Japan.



## Size Enlargement of Pharmaceutical Powders by Wet Agglomeration and Drying Techniques †

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## Abstract

Today, tablets are still the most desired form of dosage due to the convenient administration, the chemical and physical stability of the drug in a solid state, and the high production rate of a tabletting machine based on the compaction of powders or granules. Because direct compression vehicles are still in the minority, pharmaceutical powders have to be processed in order to obtain a tailored particle size distribution exhibiting a good flowability, compressibility, compactibility, wettability, lack of dust, etc. Thus, the size enlargement by wet agglomeration and drying of pharmaceutical powders is an important unit operation in a batch-wise production of granules. For an optimal quality assurance, the starting materials (drug substance, excipients) and the process technologies applied need to be characterized and defined in an appropriate way. Special attention has to be paid to scale-up processes and to monitoring the amount of granulating liquid added to the powder system. Although a batch-wise production is the method of choice from the point of view of a quality assurance department, as a batch can be accepted or rejected, the trend towards lean and just-in-time production focuses the attention on the feasability of continous processes such as a wet agglomeration and drying technique. Besides the subsequent production of tablets, spherical pharmaceutical granules called pellets with a mean particle size in the range of 0.4 mm to 1.4 mm are usually filled into hard gelatine capsules. The controlled production of pellets with an appropriate mean size and narrow size distribution is highly desired. Due to environmental protection and safety, the use of distilled or demineralized water as a granulation liquid for the wet agglomeration process is the first choice. However, the design of innovative novel dosage forms, i.e. the modification of powders, may make the use of an appropriate organic solvent may be a prerequisite. Thus, the production of novel dosage forms, of specially tailored properties of granules, may need a special process technology with a solvent recovery system, i.e. a correlation can be established between novel product properties and the use of novel process technologies, such as the vacuumfluidized bed granulation and drying method.

## 1. Introduction

In the pharmaceutical industry, powders play an important role. In the majority of cases, the raw materials used, i.e. active substances and excipients, are powders. In addition, approx. 80% of the medicinal products sold on the world market are solid dosage forms, i.e. tablets, capsules, drag, etc. Thus the process technologies to modify pharmaceutical powders in order to obtain a final dosage form are of special importance. Due to the high potency of drugs, special attention has to be paid to GMP (good manufacturing practice), to the optimal design of the dosage forms and to a strict quality control. Thus the process technologies concerning size enlargement of powder particles need to fulfill requirements which are specific to the area of pharmaceutics. Total quality control and lean production are important issues. Thus the powders need to be characterized and specified according to specially developed standard operation procedures, unit operations such as the moist agglomeration process have to be validated and should usually be supervised for, e.g. a batch documentation by an intelligent in-process control.

For many reasons, a drug substance cannot be administered in its bulk state. Thus it is important to design a drug delivery system, i.e. dosage form, which is tailored to the properties of the

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drug substance and to the mode of administration. As a consequence, the drug powder has to be modified and processed together with auxiliary substances in order to optimize a number of properties such as, e.g. handling, stability, compactibility, solubility and controlled release of the active substance. The development of a controlled release system showing a well-defined release profile as a function of time and an optimal bioavailability of the drug substance means in many cases a real challenge for the scientists involved. In the case of a controlled release system, a sufficient drug concentration for therapeutic use has to be maintained in the systemic circulation for an extended period of time. Thus the patient may need to administer the dosage form only once a day instead of three times. As a consequence, patient compliance and the therapeutic effect can often be substantially improved.

Another important issue is the safety of a dosage form. Special emphasis has to be given to it in the case of a controlled release dosage form, as a failure - where the total amount of drug is released immediately - may lead to toxic side effects or adverse reactions. This problem can be reduced if instead of a single large, non-disintegrating matrixtype dosage form with a high load of active substance, subunits such as pellets, i.e. small and highly sperical granules with a smooth surface coated with a polymer for the controlled release are used. These pellets may even show a pH-dependent release of the active substance, e.g. an aliquot of the pellets could have an enteric coating, i.e. no drug release at low pH values, e.g. during the residence time in the stomach. Thus a hard gelatine capsule could contain different types of pellets providing a specially tailored drug dissolution in the gastrointestinal tract. Due to the much better distribution of subunits such as pellets or granules within the gastrointestinal tract, the intra-and interindividual variations in the bioavailability of a drug can often be reduced.

Concerning the development of a dosage form, there are numerous technological implications which cannot be treated here in an exhaustive way.

## 2. Characterization of particulate matter

It is much easier to determine the chemical behaviour of particulate matter than to characterize the inherent properties of a powder exhibiting functions such as flowability, compressibility, solubility, inflammability, caking, electrostatic charging, etc. In many cases, these properties cannot be attributed to the powder substance alone, but may be a consequence of a pretreatment, an interaction with moisture content of the surrounding atmosphere, etc. These possible side or main effects have to be kept in mind. In order to complicate the situation even more, properties of the powder can be quantified only with a simultaneous indication of the apparatus and principle used for the measurement of the property in question. Thus the lack of an absolute standard often represents a handicap. Typical examples of such properties are the size distribution (by number, by weight, i.e. sieving), specific surface (BET, Blaine), flowability, etc. Often, the residual moisture content of the powder (adsorbed water, residual content of organic solvent used to crystallize the active substance, etc.) plays an important role.

Recently, [1] Mandelbrot introduced the concept of fractal dimension. This concept is a powerful tool to describe surface characteristics of particles and granules (see Fig. 1a - 1c). Another important concept is the theory of percolation which can be applied in a wide range of research areas [2]. Both concepts are interrelated. Thus different types of particulate aggregation lead to different fractal dimensions of these agglomerates. Actually, both concepts play an important role in the research activities concerning the size enlargement area of pharmaceutical powders. It is important to realize in this respect that a powder mixture behaves differently to a powder consisting of a pure substance. This fact is true with respect to wet and dry agglomeration techniques. In a rough description, a binary powder mixture consisting of different materials (e.g. brittle versus plastic; hydrophilic versus hydrophobic; soluble versus insoluble; pharmacologically active substance versus excipient) compressed to tablets may show important variations in their properties as a function of the mixture ratio, i.e. percolation effects may occur which are comparable to the variation of the electric conductivity in a binary powder system consisting of an electrically conductive material and an insulator. Such effects may become even more pronounced after size enlargement by wet agglomeration and drying techniques with a subsequent production of tablets (see Fig. 2a, **2b** [3]).

## 3. Pocess monitoring in the case of granulation by agitation

Power consumption and/or torque measurements of mixers or rotary granulators as a function of the




Fig. 1a An outline of the surface roughness of a lactose granule [3]. Coastline of a lactose granule with linear fractal dimension  $D = 1.091 \pm 0.007$ .



Fig. 1b Mathematical simulation of coastlines with fractal dimensions D = 1.47, 1.26 and 1.16 [3].



Fig. 1c Scanning electron micrograph of the surface of lactose granules [3].

mass of granulating liquid added per unit time have been used to efficiently control the agglomeration process [4-14]. This type of control facilitates scaleup and scale-down exercises and significantly improves the reproducibility of the desired size distribution of granules and/or pellets. If the amount of granulating liquid cannot be added continuously by a pump but needs to be added at the beginning,



Fig. 2a and 2b The disintegration time as a function of compositions of binary component compacts [3].
a) Potassium chloride/Advicel<sup>R</sup>.

b) Lactose/Starch Rx 1500<sup>R</sup>.

i.e. at t = 0 of the batch production, frequency analysis of power consumption could be the method of choice [10].

Fig. 3 describes a typical power consumption profile. It is important to realize that the mass of granulating liquid has to be metered and added by a pump in a continuous controlled way. Thus a fine tuning of the exact volume of granulating liquid needed is feasible and can be controlled electronically. The amount of granulating liquid to be applied depends on the desired granule size distribution and the intensity of wetting needed, e.g. for a hydrophobic active substance mixed with hydrophilic excipients. etc. It has to be emphasized that the range of mass of granulating liquid which can be added is limited, and corresponds fairly well to the plateau range of the power consumption profile in Fig. 3. Thus it is possible to use the power consumption profile as an analytical tool in the R&D department: if the granulating liquid is not an appropriate one and, e.g. dissolves too much of the solid material, the pattern of the power consumption will deviate considerably from the normal profile described in Fig. 3. It is also





Fig. 3 Typical power consumption profile for the agglomeration of lactose 200 mesh (DMV monohydrate) with 4% (W/W) polyvinyl-pyrrolidone of binder. The solution is added at a constant rate.  $\pi$  Corresponds to the dimensionless amount of granulation liquid added, i.e. to the ratio of interparticulate void space filled up with liquid [12].

possible to detect the formation of, e.g. a hydrate during the granulation process. In such cases, an alternative granulating liquid has to be chosen. **Fig. 4** demonstrates the two possible methods to control the granulation process: the absolute power



Fig. 4 The amount of granulating liquid added is controlled by the power consumption profile, i.e. by the peak detection mode (differentiated signal) or by the level detection mode [6].

consumption level (1) or the first derivative (2) of power consumption level, i.e. the point of steepest ascent can be used to define the end point of the granulation process. The term "end point of the granulation process" was already used before introduction and implementation of the control of granulation processes by power consumption. It is important to realize that the peak detection signal which is measured by power consumption can still be compared to a "land mark" expressing a defined state of cohesivity of the moistened powder bed. Thus the signal is luckily still ahead of the end point and allows subsequent addition of a predetermined, constant amount of granulating liquid. As the relative position of the control signal of the power consumption profile is directly related to the initial particle size distribution of the primary material and to the initial moisture content, smaller variations of these two parameters are automatically compensated. Thus it is possible to obtain a high reproducibility of the granule size distribution. This type of control has been successfully introduced in the production department at Sandoz Ltd., Basel.

A comparison of granule size distributions  $(90\mu m - 710\mu m)$  obtained by manually adding a fixed, and by automatically adding an adjusted, amount of granulating liquid shows a better yield for the automatic mode (91.5% ± 0.4%) than for the manual mode (81.0% ± 2.4%) with a significantly lower standard deviation [14]. It is important to emphasize that the success of this method does not depend on the type of mixer.

# 4. A prototype for a quasi-continuous production of granules

In the food and chemical industry, continuous production lines play an important role, whereas the pharmaceutical industry is mainly based on a batch-type procedure. Concerning the safety of a dosage form and quality assurance, batches are very convenient. Thus a well-defined batch can be accepted or refused by the quality control department. In the case of a continuous process, a batch has to be defined somewhat artificially, i.e. the amount of product, e.g. the amount of granules produced within 6 to 8 hours. On the other hand, continuous processes offer two important advantages: a) there is no difficult scale-up exercise necessary for larger "batches"; and b) it should be possible to realize a 24-hour automatic production line.

In order to combine the advantages of batch-type and continuous production, a prototype for a quasicontinuous production line was developed (see **Fig. 5**). The principle of this quasi-continuous production line is based on semi-continuous production of mini-batches in a specially designed high-shear mixer/granulator which is connected to a continuous multicell-fluidized bed dryer.

In order to study the feasibility of such a quasicontinuous production line, a placebo formulation [4% (W/W) polyvinyl-pyrrolidone (PVP) added as a



binder in a dry state, 10% (W/W) corn starch and 86% (W/W) lactose 200 mesh] was used. The weighing system which is available on the market was not involved in the first experiments. Thus, a predefined amount of powder of the placebo formulation was added to the twin-type mixer and mixed thoroughly. This amount of powder is then granulated by continuously adding granulating liquid up to a fixed amount. This limit is determined by a moisture content signal which is triggered by the power or torque measurement [6]. The moist granules are then discharged through a screen into the first cell of the multicell-fluidized bed dryer unit to disagglomerate imaginative lumps. Due to the twin-type set-up of the high-shear mixers, the first mixer can be fed with a new mini-batch of powder and be thoroughly mixed in a dry state during the time the powder is being agglomerated by granulating liquid in the second mixer/granulator.

Thus the quasi-continuous production of granules can be described as a train of mini-batches passing the compartments of dry mixing, granulation and drying like parcels. The prototype of the multicell dryer consists of five cells which are designed for different air temperatures, i.e. in the first cell the granules are dried at a high temperature, e.g.  $60^{\circ}C$ , and in the last cell, ambient air temperature and humidity can be used to achieve equilibrium conditions.

Due to this principle, a batch defined for quality control purposes consists of a fixed number of n mini-batches. Thus a tight in-process control of the mixing/granulation and drying step provides an excellent "batch" record of the quasi-continuous production of granules, and an excellent opportunity for a continuous validation of the process and the equipment.

### 5. The Controlled Production of Pellets

An alternative to measuring the power consumption consists in measuring the torque of the mixer motor which turns the bottom plate of a rotary granulator [13]. The principle was used in the case of a Glatt fluidized bed rotor granulator (see **Fig. 6**). Due to the differences in the momentum transfer between the bottom plate and the pellets, the torque profile cannot be compared directly to the power consumption profile in a high-speed mixer. However, it was clearly possible to find a relationship between the median pellet size and the torque value obtained when the continuous addition of granulating liquid

#### COMBINED WET GPANULATION AND MULTIPLE CHAMBER DRYING PROCESS



Fig. 5 Flow-chart of a quasi-continous production line for granules



Fig. 6 Glatt Fluidized Bed Rotor Granulator equipped to measure the torque of the bottom plate [13].

was stopped (see **Fig. 7**). With microcrystalline cellulose and demineralized water, a very narrow pellet size distribution was obtained with the following





Median pellet size as a function of the torque measured Fig. 7 after stopping addition of granulating liquid.

yield: between 710µm and 1000µm: 72%; between 710µm and 1400µm: 97%.

It has to be emphasized that these pellets have been produced without adding any seeds. The rationale is the following and follows the same lines as in the case of the controlled production of granules. Due to the possible variations in initial moisture content of the primary material such as microcrystalline cellulose and the variations in moisture content of the inlet air in the rotary-fluidized bed equipment, it is important that the powder material which is used in this process indicates the required amount of granulating liquid needed itself. An alternative way to produce spherical granules is to use a coating procedure to coat seeds (non-pareilles) with active substances and excipients. For this purpose, the same equipment can be used. It is important that the seed particles already have a rather large diameter (e.g.  $-300 - 600 \mu$ m) and a narrow size distribution so that finer particles can be layered on the rolling seed particles.

#### A Novel Fluidized Bed System Operating **6**. **Under Vacuum Conditions**

### Introduction and rationale

This new equipment was designed as a closed-loop system with a solvent recovery facility (see Fig. 8). Thus the advantages of the vacuum drying and of the fluidized-bed process were combined in a unique way. In addition, the superposition of both principles leads to new product properties and consequently to a high potential for innovative and optimized soliddosage forms [15-17, 19].

### The use of vacuum

In the case of organic solvents, vacuum drying is a fast process. It is important that the organic solvents are removed to an acceptable extent as regards the



#### Fig. 8 Vacuum-Fluidized Bed Unit. 3 = solvent recovery system 1 = operating tower

- 2 = closed-loop system
- 4 = chiller unit5 = high-pressure spray system



toxicity of the residual amount.

This process is also advantageous for oxygen and temperature-sensitive materials.

### Explosion hazards

Due to lowering the system pressure to below that of the ignition pressure of organic solvents, the use of an inert gas carrier can generally be avoided. However, it has to be taken into account that the ignition pressure of a hybrid system (organic solvent vapour, residual air, powder) may be different from the minimum ignition pressure of the corresponding binary system air/solvent vapour.

### Use of the fluidization process

A fluidized bed has the advantage of an excellent heat and mass transfer. Geldart [18] classifies different types of powder material as a function of its fluidization ability, e.g. an extremely wet powder which is very cohesive cannot be fluidized. Thus in such a case, pretreatment by vacuum drying the material on the bottom plate of the product chamber would be the method of choice and emphasizes again the combination of the vacuum drying with a fluidized-bed-drying process.

It is important to realize that a fluidized bed can also be established at rather low pressures such as, e.g. 100 mbar, as the gas velocity can be adjusted to maintain a fluidized bed. In the equation which describes the conditions of the fluidized bed, the gas velocity shows a quadratic dependence (see equation 1), whereas the density  $\rho$  decreases linearly with the system pressure p assuming in a first approximation that the ideal gas equation can be applied (see equation 2).

$$\Delta_{\rm p} = \frac{h (1-\epsilon) \, \varrho \mu^2 g c}{d} \tag{1}$$

$$\varrho = \frac{RT}{M} \tag{2}$$

 $\Delta P$  = differential pressure across fluidized bed

- p = system pressure
- $\varrho = gas density$
- R = gas constant
- T = absolute temperature
- M = molecular weight of the gas
- h = height of fluidized bed
- $\epsilon$  = porosity of the fluidized bed
- c = constant
- d = particle diameter
- $\mu$  = gas velocity

### The Vacuum-Fluidized Bed System

The equipment is described in detail in figure 6 and permits operating the fluidized bed in a closed-loop system. The residual air and/or residual vapour of the organic solvent is used at rather high gas velocities to maintain the fluidized bed of powder. The gas is heated by the process gas heater. The pressure difference  $\Delta p$  to maintain the fluidized bed is achieved with the Roots molecular pump. The solvent vapour is partially removed from the closed-loop system by the solvent recovery unit. This unit consists of two condensers and permits recovery rates of 90% to 95% on the low-pressure (vacuum) side, where the recovered solvents show a high purity due to the efficient filter system which prevents particulate contamination. On the high-pressure side, an additional amount of solvent is condensated leading to a total of up to 99% recovery rates. It is obvious that the additional amount of solvent recovered passed through the oil vacuum pump, and is consequently contaminated by traces of oil, etc. If desired, the exhausted air can be additionally filtered by active carbon, i.e. the equipment meets all known requirements concerning optimal environmental protection. Because the closed-loop system normally operates under vacuum, no inert gas carrier is present which has to be cooled down for solvent recovery purposes and recycled, i.e. heated up again to maintain the classical fluidized bed at atmospheric pressure.

Applications of the Vacuum-Fluidized Bed System

# Experiences with drying

In **Figs. 9** and **10**, the decrease in moisture content is plotted as a function of process time. It is evident that an initially high content of moisture is permitted and that fast drying times can be achieved in the case of organic solvents. "Tailing effects" sometimes represent difficulties (see **Fig. 10**), where the final drying time can be shortened by purging the system, usually with an inert gas carrier.

The use of inert gas carriers to purge the system

It is of course possible to use an inert gas carrier, e.g. nitrogen, to purge the system. Thus an additional reduction in the residual content of organic solvent in the final product can be achieved. In special cases, the equipment can also be used as an open-loop system in the final drying stage. As the residual content of organic solvent is already low, the requirements of environmental protection can again be easily







Fig. 9 Drying of an enol ester compound (solvent ethyl acetate) [16].

Fig. 10 Drying of a cephalosporin antibiotic-containing water [16].

met. If desired, an exhaust air-active charcoal filter may be used in addition.

### Granulation

Because no air should be injected into the product chamber, it is evident that a special high-pressure nozzle is needed for the spray solutions (see. Fig. 8). Due to the fact that organic solvents can be used as granulating liquid, a lot of applications in the field of controlled release of active substances and of highly water-sensitive materials become feasible. The following two sections should give a hint concerning the potential for product optimization and for special product properties, which are necessary for product innovation [19, 20].

# Spray Agglomeration; Spray Drying; Product Optimization

Unfortunately, many biologically very active substances show a low water solubility (e.g. <0.01% W/V). Thus the dissolution of the active drug from a solid-dosage form leads to problems, and subsequently in vivo to a poor bioavailability which is unacceptable. In order to improve the dissolution properties of a poorly soluble drug, drug-solid solutions may be prepared, e.g. by spray drying where the drug is embedded into a hydrophilic matrix which can be easily dissolved in water. Polyvinyl-pyrrolidone (PVP) or polyethylene glycol (PEG) is often used as a hydrophilic matrix and acetone as a solvent if the active substance is soluble in acetone. It is evident that such a preparation needs special attention. For this purpose, the vacuum-fluidized bed equipment was used to optimize the product properties and to study the performance of this system used for a spray agglomeration process. Thus an acetone solution containing PVP and the active substance was sprayed on a powder consisting of microcrystalline cellulose, corn starch and polyplasdone XL. For this study, a  $2^4$  factorial design was established. In all cases, the active substance was released in water within 5 minutes. The main results of the  $2^4$  design can be summarized as follows: the mean granule size is increased by a higher system pressure, lower inlet gas temperature, lower spray pressure and higher PVP concentration in the spray solution. Narrow granule size distributions can be achieved with a high system and spray pressure and a low content of PVP in the spray solution. To reduce the residual content of acetone, a low system pressure and a high gas-inlet temperature are advantageous.

Special Properties Related to the Above Vacuum-Fluidized Bed Process

### Granules

It is important to notice that the granules which were obtained showed a high porosity and a high specific surface. Both the narrow and the broad granule size distribution could be used for tabletting without problems [19]. Due to the aspects of the granules it can be concluded that the spray agglomeration process prevailed. However, if the system pressure is lowered to ca. 100 mbar, part of the PVP drug solution is spray-dried leading to typical spherical hollow shells. The samples analysed in an X-ray diffractometer showed that the active substance was present in an amorphous state.

# Tablets

Due to the high porosity of the final tablets, it is not surprising that the active substance was released in water within 5 minutes. The tablets of the sixteen



manufactured granule batches of the corresponding  $2^4$  design were analysed by mercury porosimetry. The mean pore size of the tablets varied between  $1.2\mu$ m and  $2.4\mu$ m, and the specific surface between  $0.97m^2/g$  and  $0.63m^2/g$ . Today, it is possible to describe such a system by the concept of fractal geometry. The fractal dimension of the pore system did not change very much and ranged between 2.82 and 2.86. It is interesting to realise that the fractal dimension of a Menger sponge, i.e. of an idealized three-dimensional network of pores (see Fig. 11), is much lower and equal to 2.72. On the other side, the fractal dimension of an idealized bronchial tree (see Fig. 12) is equal to 2.9.

# Coating in Vacuum-Fluidized Bed System

In order to evaluate the coating performance, metallic magnesium particles (diameter:  $90-140 \ \mu$ m) were used and coated with Eudragit<sup>®</sup> S 100. Eudragit<sup>®</sup> S 100 is a methacrylic acid – methyl methacrylate copolymer (1:2) – and is insoluble in 0.1 n



Fig. 11 Menger sponge (idealized 3-dimensional network of pores) with fractal dimension 2.72 [1].



Fig. 12 Representation of an idealized bronchial tree with a fractal dimension of 2.9 [1].

HCl. Thus this film is used for an enteric coating of granules or tablets. To obtain the spray solution, 3.5% (W/W) Eudragit<sup>®</sup> S 100 was dissolved in an acetone-methanol mixture (12%/88%; W/W) heated up to a temperature of 90°C. At a system pressure of ca. 250 mbar and a gas-inlet temperature of 60°C, the mixture was sprayed from the top onto 9kg magnesium powder at a rate of 80g min<sup>-1</sup>. Thus the thickness of the film on the magnesium particles corresponds to a weight gain of ca. 3% (W/W). As metallic magnesium reacts in 0.1 n HCl extremely fast, i.e. like an explosion of MgCl<sub>2</sub> and H<sub>2</sub>, the amount of H<sub>2</sub> gas was measured. An entericcoating quality of these magnesium particles can be obtained for a film thickness corresponding to a minimum of 4% (W/W) of coating material. The coating of the metallic magnesium powder leads to secondary agglomerates with a mean diameter of ca.  $310\mu m$  exhibiting much better flow properties [17].

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# Hans Leuenberger

Since 1982 Prof. Hans Leuenberger is chairman of the Pharmaceutical Institute of the University of Basel and head of the Department of Pharmaceutical Technology and Biopharmacy. Prof. Leuenberger studied physics at the University of Basel, where he received his diploma in experimental physics in 1967 and his PhD in nuclear physics in 1971. From 1971 till 1982 he worked in the Pharmaceutical R+D labors at Sandoz Ltd., Basel. He served as head of a preformulation lab, research group leader and spent a stage at Sandoz (Spain) Ltd. as head of the Pharma (R+D) Department. With his nomination as an ordinary Professor at the University of Basel, he resigned in 1982 from his position at Sandoz Ltd. Prof. Leuenberger is actually president of the Scientific Council of the Swiss Academy of Engineering Sciences (SATW) and vicepresident of the Academy. He is a fellow of the American Association of Pharmaceutical Scientists (AAPS) and member of the expert group 12 (Pharm. Technology) of the European Pharmacopeia Commission.

Prof. Leuenberger and his coworkers are known for their contributions in the field of powder technology, controlled size enlargement of particles by power consumption measurement, compaction theory, novel process technologies such as vacuum-fluidized bed systems and spray-freeze drying at atmospheric pressure for pharmaceutical proteins, application of percolation theory and fractal geometry for the formulation of controlled release dosage forms as well as resorption models based on cell culture techniques in order to test novel drug delivery systems.



# A Critical Review of Thickener Design Methods †

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### Abstract

In this work we analyze, in the light of their physical foundation, the different methods of thickener design that have been proposed in the literature. We distinguish three types of methods: those based on macroscopic balances, those based on kinematic models and those based on dynamic models. This classification permits the analysis of thickener design procedures with a clear perspective of their applicability and limitations.

# 1. Introduction: Definition, equipments and operation.

Thickening is the process of separating parts of the liquid of a suspension so as to obtain a denser product and a flow of pure liquid. The objective of the process may be focussed on obtaining a thicker pulp or on recovering the liquid of a suspension. In the first case we refer to *thickening* and in the second, we use the term *clarification*.

The mechanism of thickening is sedimentation under the force of gravity. The process is performed industrially in a thickener, a cylindrical vessel where the suspension is allowed to settle. See **Fig 1**. The suspension is fed from the top and center of the tank and two outlets are provided: a cone discharges the thickened pulp at the bottom and center of the thickener and an overflow weir at the top and periphery of the tank eliminates the clear liquid. A raking mechanism, supported by a shaft at the axis of the tank, conveys the settled material to the center discharge cone. Small thickeners may have flat bottoms, but usually their floor is slightly tilted toward the center to aid in the discharge of the product.

According to Coe and Clevenger<sup>1)</sup> four distinct zones can be distinguished in a continuous thickener. At the top, there is a zone of clear liquid labeled zone I. This liquid, that has been separated from the suspension, is recovered at the overflow. When the feed material contains very fine particles, zone I may be turbid unless a chemical reagent is added to flocculate such particles. In this latter case a sharp interface forms at the bottom of zone I, its depth



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† Recieved



depending on the amount of flocculant added. It is precisely by the addition of flocculant that the depth of the clear liquid is controlled in industrial thickeners and, for a safe operation, it is maintained at a minimum of 0.5 to 1.0 m. When zone I is invaded with solid particles we say that the thickener overflows.

Beneath the clear liquid, is zone II, called the hindered settling zone. This zone contains pulp of uniform concentration settling at a constant rate. According to Coe and Clevenger this zone may have a concentration between that of the feed and that of the thickest hindered-settling pulp. Comings et al<sup>2)</sup> observed that the feed is usually diluted on entering the thickener. They reported many experiments which proved that, in a normal operation, the concentration in zone II depends on the solid feed rate rather than on the solid feed concentration. The concentration in zone II is low if the feed rate is low and it increases with the feed rate, reaching a maximum value when the solids settle at the maximum possible rate in this zone. If solids are fed at a rate higher than this maximum, the concentration in zone II will continue being that corresponding to the maximum feed rate and the excess solids will not settle through zone II but will pass to zone I and will be eliminated through the overflow. Comings et al<sup>2</sup> also report that, if the feed concentration exceeds the maximum concentration mentioned for zone II, the concentration in this zone will be that of the feed and the settling capacity of zone II will increase.

Below zone II is a region characterized by a concentration gradient, designated here as zone III, and called the *transition zone* because it makes the transition from a pulp of constant concentration to the sediment underneath. It is not clear whether this zone really exists in all cases. Some research workers (Comings et al<sup>2</sup>), Fitch and Stevenson<sup>3)</sup>, Ecklund and Jernquist<sup>4)</sup>) simply ignore this zone and show a sharp break in concentration between zone II and zone IV.

Finally at the bottom is zone IV, called the *compression zone*, containing a thick pulp or *sediment*. In this region the flocs rest directly one upon another, the ones at the top exerting pressure upon those at lower levels, creating a concentration gradient. Comings et  $al^{2}$  divide zone IV into an *upper compression zone*, with the features discussed above and a *rake-action compression zone*, where the movment of the rake allows further concentration of the pulp resulting in an additional concentration gradient.

The concentration of the discharge is the concentration at the bottom of the compression zone. It depends on the thickness of zone IV because a thicker compression zone implies a greater weight of solids supported by the solid skeleton and therefore a higher bottom concentration. Retention time has also been mentioned by Comings et  $al^{(2)}$  as the cause of differing discharge concentrations for the same thickness of compression zones.

The depth of each zone in a thickener depends on the settling characteristic of the pulp. Coe and Clevenger<sup>1)</sup> defined the *handling capacity* of each zone as the amount of solids that passes down from one zone to the other per unit area and unit time. They reasoned that the settling velocity is a function of the pulp concentration and therefore so is the handling capacity. If no solid passes through the overflow, the same solid flux should pass through all zones in the thickener at steady state, so that those zones with a smaller handling capacity will have a greater depth at the expense of the zones with higher handling capacities.

We say that a thickener overflows if solid particles pass from zone II to zone I. According to Dixon<sup>5)</sup>



Fig. 2 Schematic drawing of an industrial thickener showing the settling zones, according to Coe and Clevenger (1916).



there are three ways in which a thickener can overflow. We have already discussed the first two of these, that is, when the feed contains very fine particles that cannot settle and when the feed rate exceeds the settling capacity of zone II. The third way corresponds to a normal operation of the thickener when the feed rate is higher than the discharge rate. In this case solid particles accumulate in the thickener and are eventually transported to zone I.

When, due to a change in the solid concentration of the feed or when the solid feed rate changes, the discharge concentration diminishes, it is possible to readjust it back to its original value by controlling the discharge volume flow rate. This, in turn, is obtained by manipulating a variable speed pump or, when the discharge is effected by gravity, by varying the outlet aperture of the thickener. The result is that, by slowing down the discharge flow rate, more solids accumulate in the compression zone increasing its depth and therefore producing a more concentrated discharge. The opposite occurs when the discharge rate is increased. These procedures are usually used as thickener control.

As a summary, **Fig. 3** shows the variables that describe the operation and control of a thickener. In this figure c is the depth of the clear water zone (zone I), h is the depth of the hindered settling zone,  $z_c$  is the depth of the compression zone (zone IV),  $q_{f1}$  is the flocculant flowrate, D is the solid mass flowrate in the underflow discharge, F is the solid mass flowrate in the feed,  $F_3$  (x) is the particle size distribution in the feed, Q is the volume flowrate of pulp,  $\phi$  is the volume fraction of solids and F, O and D are the subscripts for feed, overflow and underflow respectively.

2. Macroscopic mass balance in a continuous thickener at steady state: Classical methods of thickener design.



Fig. 3 Variables in a continuous thickener.

#### 2.1 Mishler's method.

The first equation to predict the capacity of a thickener was developed by  $Mishler^{6)}$  in 1912 and corresponds to a simple macroscopic mass balance in the equipment. Consider a thickener working at steady state, as shown in **Fig. 4**. Using the same variables as  $Mishler^{6)}$ , a solid and water mass balance yield:

Solid 
$$F = D$$
 (1)

Water 
$$F \mathfrak{D}_F = D \mathfrak{D}_D + O$$
 (2)

where F and D are the solid mass flowrates in the feed and discharge respectively, O is the water mass flowrate in the overflow and  $\mathfrak{D}_F$  and  $\mathfrak{D}_D$  are the *dilutions* of the feed and discharge. Dilution is a measure of concentration consisting in the ratio of the mass of water to the mass of solid.

The volume flowrate of water at overflow is then:

$$Q_{\rm O} = \frac{F(\mathfrak{D}_{\rm F} - \mathfrak{D}_{\rm D})}{\varrho_{\rm f}}$$
(3)

where  $\varrho_f$  is the water density. According to Mishler<sup>6)</sup> the flowrate of water per unit thickener area  $Q_0/S$ , that is the spatial water velocity in zone I of a continuous thickener, must be equal to the rate of water formed in a batch sedimentation test with the same pulp at the concentration of the feed. Since this rate is equal to the rate of descent of the water-suspension interface in the batch settling test, which we denote by  $|\sigma_I(\mathfrak{D}_F)|$  and is equal to the settling velocity of the solid as we will prove later on, he wrote:

$$|\sigma_{I}(\mathfrak{D}_{F})| = \frac{F(\mathfrak{D}_{F} - \mathfrak{D}_{D})}{\varrho_{f}S}$$
(4)

and the settling area required to treat a feedrate F is then:

$$S = \frac{F(\mathfrak{D}_{F} - \mathfrak{D}_{D})}{\varrho_{f} |\sigma_{I}(\mathfrak{D}_{F})|}$$
(5)



Fig. 4 Macroscopic balance in a continuous thickener according to Mishler<sup>6</sup>.



where S is the thickener area, F is the mass flowrate of solid in the feed,  $\mathfrak{D}_F$  and  $\mathfrak{D}_D$  are the pulp dilutions in the feed and in the discharge respectively and  $|\varrho_I(\mathfrak{D}_F)|$  is the absolute value of the rate of descendent of the water-suspension interface in a batch settling test performed with the suspension at the dilution  $\mathfrak{D}_F$  of the feed.

Mishler used the following units: F in short tons,  $|\sigma_{I}|$  in ft/min and  $|\varrho_{f}|$  in lb/ft<sup>3</sup> and obtained S in ft<sup>2</sup>.

$$S = 0.0222 \frac{F(\mathfrak{D}_{F} - \mathfrak{D}_{D})}{\varrho_{f} |\sigma_{I}(\mathfrak{D}_{F})|} , (ft^{2})$$
(6)

The design method consists in measuring, in the laboratory, the initial settling rate of a suspension with the concentration of the feed to the thickener and applying equation (6) to find the area S of the thickener.

As we have already discussed, the concentration in the zone II of the thickener is not that of the feed and therefore equation (4) is not correct invalidating Mishler's method of thickener design.

### 2.2 Coe and Clevenger's method.

Coe and Clevenger<sup>1)</sup> assumed that a hindered settling zone II will form in a thickener with a dilution  $\mathfrak{D}_k$  having the minimum solid handling capacity. Since the dilution of this zone is not known in advance they proposed to perform a macroscopic balance in the thickener for different dilutions  $\mathfrak{D}_k$  as shown in **Fig. 5**.

The volume flowrate of water eliminated from zone of dilution  $\mathfrak{D}_k$  when the suspension passes from this zone to zone of dilution  $\mathfrak{D}_D$  is:

$$Q_{k} = \frac{F(\mathfrak{D}_{k} - \mathfrak{D}_{D})}{\varrho_{f}}$$
(7)

and the rate of water appearance in batch settling of a suspension of dilution  $\mathfrak{D}_k$  is:

$$Q_k/S = |\sigma_I(\mathfrak{D}_k)| \tag{8}$$

From the above equations, the solid handling capacity F/S of a thickener having a dilution  $\mathfrak{D}_k$  in zone II is:

$$\frac{\mathbf{F}}{\mathbf{S}} = \frac{\boldsymbol{\varrho}_{\mathrm{f}} |\sigma_{\mathrm{I}}(\mathfrak{D}_{\mathrm{k}})|}{\mathbf{F}(\mathfrak{D}_{\mathrm{k}} - \mathfrak{D}_{\mathrm{D}})}$$

and the minimum solid handling capacity, in Coe and Clevengers units (F in lb/h,  $\rho_f$  in lb/ft<sup>3</sup>, S in ft<sup>2</sup> and



Fig. 5 Macroscopic balance in a continuous thickener according to Coe and Clevenger<sup>1)</sup>.

 $|\sigma_{\rm I}|$  in ft/h) results in:

$$\min\left(\frac{\mathbf{F}}{\mathbf{S}}\right) = \min_{\mathbf{D}_{k}} \left\{ 62.35 \frac{|\sigma_{\mathrm{I}}(\mathbf{D}_{k})|}{(\mathbf{D}_{k} - \mathbf{D}_{\mathrm{D}})} \right\}, \text{ (lb/hft^2) (9)}$$

the design method consists in measuring, in the laboratory, the initial settling rate of a suspension at a range of concentrations between that of the feed and that of the maximum hindered settling velocity (critical concentration) applying equations (9) to find the minimum value of the solid handling capacity F/S.

Defining the *basic Unit Area*  $UA_o$  as the reciprocal of the minimum solid handling capacity, we can write, according to Coe and Clevenger:

$$AU_{o} = \max_{\mathfrak{D}_{k}} \left\{ \frac{\mathfrak{D}_{k} - \mathfrak{D}_{D}}{\varrho_{f} |\sigma_{f}(\mathfrak{D}_{k})|} \right\}, \qquad \mathfrak{D}_{c} < \mathfrak{D}_{k} \le \mathfrak{D}_{F} \quad (10)$$

Taggart<sup>7)</sup> and Dalstrohm and Fitch<sup>8)</sup> used the following units:  $\rho_f = 62.4 \text{ lb/ft}^3$  and  $|\sigma_1|$  in ft/h giving AU<sub>o</sub> in ft<sup>2</sup> (short tons/day), then:

$$AU_{o} = \max_{\mathfrak{D}_{k}} \left\{ 1.33 \frac{\mathfrak{D}_{k} - \mathfrak{D}_{D}}{\varrho_{f} |\sigma_{I}(\mathfrak{D}_{k})|} \right\},$$
(ft<sup>2</sup>/short tons/day) (11)

For future reference we will express equation (11) in terms of the solid volume fraction  $\phi$ . Since the dilution is given by:

$$\mathfrak{D} = \frac{\varrho_{\rm f}(1-\phi)}{\varrho_{\rm s}\phi} \tag{12}$$

the unit area becomes:

$$AU_{o} = \max_{\phi_{k}} \left\{ \frac{1}{\varrho_{s} |\sigma_{I}(\phi)|} \left( \frac{1}{\phi_{k}} - \frac{1}{\phi_{D}} \right) \right\}, \quad \phi_{F} \leq \phi_{k} < \phi_{c}$$
(13)



Equation (13), that gives the unit area of a thickener based on laboratory initial settling tests, we call the *Coe and Clevenger's Equation*, and the design method we call the *Coe and Clevenger's Method of Thickener Design*.

If the following units are selected:  $\rho_s$  in g/cm<sup>3</sup>,  $|\sigma_I|$  in cm/s and AU<sub>o</sub> in m<sup>2</sup>/TPD, where TPD = metric tons/24 hours, we have:

$$AU_{o} = \max_{\phi_{k}} \left\{ 1.1574 \times 10^{-3} \quad \frac{1}{\varrho_{s} |\sigma_{I}(\phi_{k})|} \left( \frac{1}{\phi_{k}} - \frac{1}{\phi_{D}} \right) \right\}$$
$$m^{2}/TPD \qquad (14)$$

According to Coe and Clevenger<sup>1)</sup>, when the discharge concentration of a thickener is still in the range of hindered settling, the depth of the tank is of no consequence, except in so far as to permit ample depth of clear liquid to care for fluctuations of the feed. On the other hand, when the consistency of the pulp at the discharge is in the range where it in necessary to expel fluid by compression, sufficient capacity must be given to the tank so that the pulp in compression is retained in the thickener the necessary period of time to reach the required density.

To calculate the height of the compression zone, the time t<sup>\*</sup> to reach the desired discharge concentration  $\phi_D$  is measured in a batch test. The time interval [0,t<sup>\*</sup>] is divided into n smaller intervals  $\Delta t_i =$ [t<sub>i-1</sub>, t<sub>1</sub>] and the height z<sub>i</sub> of each interval is calculated from a volume balance:

$$z_i = \frac{V_i}{S}$$
 ,  $i = 1, ..., n$  (15)

where  $V_i$  is the volume of pulp of an average pulp density  $\overline{\varrho_i}$  and S is the area of the settling column.

The volume  $V_i = \frac{F}{\overline{Q_i}} \Delta t_i$ , where F is the mass flux of pulp. Then:

$$\begin{split} z_{i} &= \frac{F\Delta t_{i}}{\overline{\varrho_{i}}S} \quad , \quad i = 1, \dots, n \\ &= \left(\frac{1}{A.U.}\right) \left(\frac{\Delta t_{i}}{\Delta \varrho \overline{\phi_{i}} + \varrho_{f}}\right) \quad , \qquad i = 1, \dots, n \end{split}$$

and the total sediment depth is:

$$z_{c} = \sum_{i} z_{i} = \left(\frac{1}{A.U.}\right) \sum_{i} \left(\frac{\Delta t_{i}}{\Delta \varrho \overline{\phi}_{i} + \varrho_{f}}\right),$$
  

$$i = 1, \dots, n$$
(16)

where  $\overline{\varrho}_i = \Delta \varrho \overline{\varphi}_i + \varrho_f$  is the average pulp density

and  $\overline{\phi}_i = (\phi_{i-1} + \phi_i)$  the average concentration within the interval i. To this depth  $z_c$ , an extra 0.5 to 1 m must be added to allow for feed space and clear liquid region.

Coe and Clevenger's method of thickener design is correct for obtaining the unit area, but the theory does not establish that this unit area  $AU_0$  is just an asymptotic minimum, as will be shown later. The method, that continues to be most popular in the mining industry, has been successful because a recommendation was made by the authors to use a safety factor "to take into account changes in the character of the pulp and variations in temperature". This safety factor has determined the verification of the method. On the other hand, Coe and Clevenger's method used to obtain the height of the thickener is not correct because it does not take into account the compressibility of the sediment.

# 3. Thickener design methods based on kinematic sedimentation processes.

The establishment of Kynch theory of sedimentation<sup>9)</sup> in 1952 immediately opened a new field of research, the consideration of thickener design from a theoretical point of view and in this way finding a faster and more accurate method of thickener design. Several researchers were involved in this work, leaving their names associated to thickener design procedures. We will restrict our review to some of them, namely W.P. Talmage, B. Fitch, J.H. Wilhelm, Y. Naide, H. Oltmann, N.J. Hasset and N. Yoshioka. In this section we will review the Kynch theory of sedimentation and those design methods based on it.

### 3.1 Kynch theory of batch sedimentation.

Let us consider a mixture of solid particles in a fluid that satisfy the following properties  $^{9,11,12)}$ :

- The solid particles are all small (with respect to the container) and of the same size, shape and density,
- the solid and the fluid components of the mixture are incompressible,
- there is no mass transfer between components,
- the sedimentation velocity at any point in the suspension is only a function of the local particle concentration.

Such a mixture is called an *ideal suspension*<sup>10)</sup> and may be regarded as non-interactive superimposed continuous media consisting of two incompressible



components<sup>11,12</sup>).

The suspension concentration  $\phi$  is in general a function of three space variables and time. In the case of batch settling, a *settling column* is defined as a vessel having a constant cross-sectional area where no wall effect is taken into account<sup>11,12</sup>. The particle concentration is in this case constant at any cross-section of the column and the field variables are functions of only one space variable and time.

The gravity batch sedimentation of an ideal suspension in a settling column is determined by the volume fraction of solids  $\phi(z, t)$  and the velocity of the solid component  $v_s(\phi(z, t))$ . These two field variables constitute a *Kynch sedimentation process* (KSP) if, for all z and t > 0 they obey the following equations in those regions where the variables are continuous<sup>11, 12</sup>:

$$\frac{\partial \phi}{\partial t} + \frac{\partial f_{bk}}{\partial z} = 0 \tag{17}$$

$$\mathbf{f}_{bk} = \mathbf{f}_{bk}(\boldsymbol{\phi}) \tag{18}$$

and at surfaces of discontinuity they satisfy the jump balance, or Rankine-Hugoniot equation, and the Lax entropy condition:

$$\sigma(\phi^+, \phi^-) = \frac{f_{bk}(\phi^+) - f_{bk}(\phi^-)}{\phi^+ - \phi^-}$$
(19)

$$f'_{bk}(\phi^{-}) \ge \sigma(\phi^{+}, \phi^{-}) \ge f'_{bk}(\phi^{+})$$
 (20)

where  $f_{bk}(\phi)$  represents the batch solid flux density function, defined by  $f_{bk} = \phi v_s(\phi)$  and  $\sigma(\phi^+, \phi^-)$  is the speed of propagation of the discontinuity having a concentration  $\phi^+$  at the front and a concentration  $\phi^$ at the rear. Inequality (20) establishes the admissible discontinuities in the suspension. A discontinuity is called a *shock wave* if it strictly satisfies the Lax entropy condition. If one of the equalities is satisfied, the discontinuity is called a *contact discontinuity*.

The kinematic process is completely defined when a constitutive equation is postulated for the batch flux density function  $f_{bk}(\phi)$  and initial conditions are selected for  $\phi$ .

For a vast majority of batch sedimentation experiments the constitutive equation for the flux density function  $f_{bk}(\phi)$  satisfies a function having one inflection point. As an example, consider the case of the suspension described by the flux density function of **Fig. 6a**.

Equation (17) can be written in the form:

$$\frac{\partial \phi}{\partial t} + f'_{bk}(\phi) \frac{\partial \phi}{\partial z} = 0$$
(21)

where  $f'_{bk}(\phi)$  is the first derivative of the solid flux density  $f_{bk}(\phi)$  with respect to the concentration  $\phi$ . Let us assume that the initial concentration  $\phi(z, 0)$  is given by:

$$\phi(z, 0) = \begin{cases} 0, \quad L < z \\ \phi_0, \quad 0 \le z \le L \\ \phi\infty, \quad z < 0 \end{cases}$$
(22)

The solution of the quasilinear hyperbolic equation (21) with initial conditions (22) may be obtained by the method of characteristics, which states that  $\phi$  is constant along characteristic lines of slope dz/dt = f'<sub>bk</sub>( $\phi$ ) in the z-t plane, where the values of dz/dt are the speeds of the waves of constant concentration.

The characteristics starting from the z axis and drawn as parallel lines in **Fig. 6b** have speeds given by:

$$\frac{dz}{dt} = \begin{cases} f'_{bk}(0), & L \le z \\ f'_{bk}(\phi_0), & 0 \le z \le L \\ f'_{bk}(\phi_{\infty}), & z < 0 \end{cases}$$
(23)

These terms can be obtained graphically from **Fig 6a**. The speed of the discontinuity  $\sigma$  (0,  $\phi_0$ ) starting from z = L and t = 0 and separating the liquid from the suspension of initial concentration  $\phi_0$ , is given by:

$$\sigma(0, \phi_0) = \frac{f_{bk}(\phi_0) - f_{bk}(0)}{\phi_0 - 0}$$
$$= \frac{f_{bk}(\phi_0)}{\phi_0} = \sigma_I(\phi_0)$$
(24)

This term may be obtained graphically as the slope of the cord drawn from point (0, 0) to point ( $f_{bk}(\phi_0)$ ,  $\phi_0$ ) in **Fig. 6a**. Another cord can be drawn directly from ( $f_{bk}(\phi_0)$ ,  $\phi_0$ ) to ( $f_{bk}(\phi_0^*)$ ,  $\phi_0^*$ ) obtain the discontinuity  $\sigma(\phi_0, \phi_0^*)$ :

$$\sigma(\phi_0, \phi_0^*) = \frac{f_{bk}(\phi_0) - f_{bk}(\phi_0^*)}{\phi_0 - \phi_0^*}$$
(25)

The intersection of the two discontinuities with the slopes given by equations  $(23_1)$  and  $(23_2)$  defines the point  $(z_1, t_1)$  in the settling plot of **Fig. 6b**.

Extending the characteristics originating from the z axis for 0 < z < L, we can fill the region of the z-t plane separated by the two discontinuities. Ex-



Fig. 6a Solid flux density function with one inflection point.



Fig. 6b Settling plot for the initial conditions of (22).

tending now the characteristics from the z axis for  $z \le 0$  in **Fig. 6b**, we observe that there is a wedge with a vertex at z = 0, t = 0 and sides with slopes  $\sigma(\phi_0, \phi_0^*)$  and  $f'_{bk}(\phi_\infty)$ . We see that the lines with decreasing slopes  $f'_{bk}(\phi)$  for increasing concentrations from  $\phi_0^*$  to  $\phi_\infty$  will fill the wedge in the settling plot. The fan with slope  $f'_{bk}(\phi)$  is called a *rarefaction wave*.

The water suspension interface, that up to the point  $(z_1, t_1)$  has a slope given by equation (24), will now have increasing slopes given by  $\sigma_I$  (0,  $\phi$ ), with concentration  $\phi$  between  $\phi_0^*$  and  $\phi_\infty$ :

$$\sigma(0, \phi) = \frac{f_{bk}(\phi) - f_{bk}(0)}{\phi - 0} = \frac{f_{bk}(\phi)}{\phi}$$
$$\equiv \sigma_{I}(\phi), \phi_{0}^{*} \le \phi \le \phi_{\infty}$$
(26)

The intersection of the discontinuity of slope  $(0, \phi_{\infty})$  with the characteristics of slope  $f'_{bk}(\phi_{\infty})$  defines the critical point  $(z_c, t_c)$ . The slope of the discontinuity starting at  $(z_c, t_c)$  and the separating zones with constant concentrations  $\phi = 0$  and  $\phi = \phi_{\infty}$  is given by:

$$\sigma(\phi_{\infty}, 0) = \frac{f_{bk}(0) - f_{bk}(\phi_{\infty})}{0 - \phi_{\infty}} = 0$$
 (27)

Finally a global mass balance gives  $SL\phi_0 = Sz_{\infty}\phi_{\infty}$ , from which the height of the suspension at the end of the process is calculated:

$$z_{\infty} = L\phi_0/\phi_{\infty} \tag{28}$$

Different possible solutions for Kynch's problem, give different settling plots, and are called *modes* of sedimentation (MS). They are entirely determined by the constitutive equation of the flux-density function and the initial concentration. Flux density functions having one inflection point have three MS and flux-density functions having two inflection points can have a maximum of five MS<sup>12</sup>.

# **3.2** Analysis of the batch sedimentation curve.

Let us consider a batch Kynch Sedimentation Process and draw a sedimentation curve and a characteristic line for the concentration  $\phi_k$ , such as that shown in **Fig.7**. The line Z-T is tangent to the curve at the point  $(z_k, t_k)$ . As we have seen, for all the regions of the settling plot where the variables are continuous it is possible to obtain the settling parameters:  $\phi$ ,  $\sigma_I(\phi)$ ,  $f_{bk}(\phi)$  and  $f'_{bk}(\phi)$  graphically. See **Fig. 5 and 6**.

### Settling Rate.

From the solution of equation (21), already described, we know that the rate of fall of the watersuspension interface  $\sigma_{I}(\phi_{k})$  is given by:

$$\sigma_{I}(\phi_{k}) = \sigma(0, \phi_{k}) = \frac{f_{bk}(\phi_{k})}{\phi_{k}}$$
$$= v_{s}(\phi_{k}) = \frac{dz}{dt}\Big|_{\phi_{k}}$$

therefore,  $\sigma_I(\phi_k)$  is equal to the slope of the settling curve at point  $(z_k,\,t_k)$ 

$$\sigma_{\rm I}(\phi_{\rm k}) = -\frac{Z}{T} \tag{29}$$

### Concentration.

Let  $W_0$  be the total volume of solids present in the settling column per unit cross-sectional area.



Then, the flux of solids crossing the iso-concentration wave  $\phi_k$ , as it travels from z = 0 to  $z = z_k$ , is:

$$W_{0} = \int_{0}^{t_{k}} \phi_{k} \left( -v_{s}(\phi_{k}) + f'_{bk}(\phi_{k}) \right) dt$$
(30)

where  $v_s(\phi_k) = \sigma_I(\phi_k)$  is the settling rate of the suspension of concentration  $\phi_k$ . Since the slope  $f'_{bk}(\phi_k)$  of the characteristic of concentration  $\phi_k$  is constant and the velocity  $v_s(\phi_k)$  is also constant, we can integrate equation (30) directly:

$$W_0 = \phi_k \left( -v_s(\phi_k) + \frac{z_k}{t_k} \right) t_k$$
(31)

From Fig. 7 we can see that:

$$\frac{Z}{T} = \frac{Z - z_k}{t_k}$$
(32)

On the other hand, since at t = 0 the suspension is homogeneous and has a concentration  $\phi_0$ , the volume of solids per unit cross-sectional area present in the column is:

 $\mathbf{W}_0 = \mathbf{L}\boldsymbol{\phi}_0.$ 

Substituting the last two equations into equation (31) yields:

$$\phi_{\mathbf{k}} = \phi_0 \, \frac{\mathbf{L}}{\mathbf{Z}} \tag{33}$$

As a conclusion we can say that, by knowing the settling curve of a batch KSP, for a given suspension having an initial concentration  $\phi_0$  and initial height L, the parameters for any other concentration  $\phi_k$  can



Fig. 7 Analysis of the settling curve.

be obtained graphically from the curve. Summarizing we can write:

$$\phi_{\rm k} = \phi_0 \frac{\rm L}{\rm Z}$$
,  $\sigma_{\rm I}(\phi_{\rm k}) = {\rm v}_{\rm s}(\phi_{\rm k}) = -\frac{\rm Z}{\rm T}$  (34)

$$f_{bk}(\phi_k) = -\phi_0 \frac{L}{T} , f'_{bk}(\phi_k) = \frac{z_k}{t_k}$$
 (35)

# **3.3** Design of continuous thickeners based on the batch Kynch theory.

As we have seen, Coe and Clevenger's method of thickener design uses equation (13) to calculate de basic unit area:

$$AU_0 = \max_{\phi_k} \left\{ \frac{1}{\varrho_s |\sigma_i(\phi_k)|} \left( \frac{1}{\phi_k} - \frac{1}{\phi_D} \right) \right\}$$

where  $\rho_s$  is the density of the solid,  $|\sigma_I(\phi_k)|$  is the initial settling rate of a suspension of concentration  $\phi_k$  and  $\phi_D$  is the discharge concentration.

Coe and Clevenger suggested performing a number of laboratories tests with suspensions of concentrations ranging from that of the feed to that of the critical concentration to find  $|\sigma_I(\phi_k)|$ . If the suspension to be thickened can be considered as an ideal suspension, that is, if  $(\phi_k, f_{bk}(\phi_k))$  constitutes a KSP, one properly selected sedimentation test should give all the information necessary to calculate AU<sub>0</sub>. See equations (34) and (35). To calculate  $\phi_k$  and  $|\sigma_I(\phi_k)|$  a tangent is drawn at any point in the settling curve, and  $\phi_k$  and  $|\sigma_I(\phi_k)|$  are calculated from equations (34a) and (34b).

A completely graphical procedure can be established by realizing that equations (34) and (35) must also hold for  $\phi_D$  (remember that the assumption is that the pulp follows Kynch theory), that is (see **Fig. 8**):



Fig. 8 Thickener design method based on batch Kynch theory.



$$\phi_{\rm D} = \phi_0 \frac{\rm L}{\rm Z_{\rm D}} \tag{36}$$

Substituting equations (34) and (36) into Coe and Clevenger's equation (13) yields:

$$AU_0 = \left\{ \frac{1}{\varrho_s \phi_0 L} \quad \max_{\phi_k} \quad \frac{T(Z - Z_D)}{Z} \right\}$$
(37)

By a properly selected concentration we imply an initial condition for the KSP that would give a continuous settling curve. The best concentration would be that at the inflection point in the flux density function, because it would give a Mode of Sedimentation III (see Concha and Bustos<sup>11)</sup>. Obviously we don't know the concentration at the inflection point and must make a guess. Too low a value for the initial concentration will lead to a Mode of Sedimentation I, with a break from the initial to the final concentration, which would give no possibility of drawing tangents.

# Talmage and Fitch Method.

Talmage and Fitch<sup>15</sup> assumed in 1955 that batch sedimentation of a suspension could be represented by Kynch theory and therefore the settling velocity for a concentration  $\phi_k$  could be expressed, in relation to **Fig. 8**, by:

$$|\sigma_{\rm I}(\phi_{\rm k})| = \frac{Z}{T} = \frac{Z - Z_{\rm D}}{t_{\rm u}}$$
(38)

Substituting this equation into (37) gives:

$$AU_0 = \frac{1}{p_s \phi_0 L} \max(t_u).$$
 (39)

From Fig. 9 we can see that the maximum value of  $t_u$  is obtained when  $t_u$  coincides with  $t_k$ . We will call this time  $t_U$ :

$$AU_0 = \frac{t_U}{\varrho_s \phi_0 L}$$
(40)

Talmage and Fitch method of thickener design may be summarized by the following steps:

- 1. Perform one settling test at an "intermediate" concentration (we have already referred to this concentration as a "properly selected" concentration) and obtain all initial settling velocities  $\sigma_{I}(\phi)$  by drawing tangents to the settling curve, according to Kynch's theory.
- 2. Calculate the height  $Z_D$  using  $Z_D = \phi_0 L/\phi_D$ .
- 3. Draw a horizontal line in the settling plot and

determine the intersection with the settling curve. This point defines the time  $t_U$ .

4. Calculate the Unit area using equation (40).

Since this method has been developed to design industrial thickeners, very often the horizontal line, drawn through the point ( $Z_D$ , 0), does not intersect the settling curve (settling curves of compressible suspensions). In this case, the limiting concentration is the critical concentration and a tangent must be drawn at this point to the settling curve. The intersection of this tangent with the horizontal line defines the time t<sub>U</sub>. See **Fig. 9**.

The main assumption in Talmage and Fitch method is that the suspension follows Kynch theory. As it turns out, and we will prove it later in this paper, this is correct for concentrations under hindered settling conditions. Unfortunately in most cases the settling curves used for calculating a thickener area by Talmage and Fitch method are obtained well beyond the hindered settling region, that is, part of the curve is obtained in the compression region. Obviously that curve is not unique in this case because it depends on the initial height of the suspension.

### Oltmann Design Method.

Since Talmage and Fitch's method usually gives thickener areas larger than those experimentally observed, Fitch and Stevenson<sup>3)</sup> proposed in 1976 the use of an empirical variant of the Talmage and Fitch method, the Oltmann method. Both rely upon identifying the critical compression point. In Oltmann method a straight line is drawn from point (L, 0) to the critical point ( $z_c$ ,  $t_c$ ) extending it beyond this point. The intersection of this line with the horizontal line drawn trough the point ( $Z_D$ , 0) gives the value of  $t_0$ , which replaces  $t_U$  in equation (40). See **Fig. 10**. There is no theoretical justification for this method.



Fig. 9 Talmage and Fitch thickener design method.





Fig. 10 Oltman's method of thickener design.

### 3.4 Kynch theory of continuous sedimentation.

The continuous gravity sedimentation of an ideal suspension in an ideal thickener was studied by Petty<sup>16)</sup> in 1975, by Bustos, Concha and Wendland<sup>17)</sup> in 1989 and by Concha and Bustos<sup>18)</sup> in 1992. It is defined by the volume fraction of solids  $\phi(z, t)$ , the velocity of the solid component  $v_s(\phi(z, t))$  and the velocity of the fluid component  $v_f(\phi(z, t))$ . These three field variables constitute a *Continuous Kynch* sedimentation process (CKSP) if, for all z and t > 0 where the field variables are continuous, they obey the following equations:

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial z} (\phi v_{\rm s}) = 0 \tag{41}$$

$$\frac{\partial}{\partial t} (1-\phi) + \frac{\partial}{\partial z} ((1-\phi)v_f) = 0$$
(42)

Substituting  $f_k = \phi v_s$  in equation (41) and deriving  $f_k$  with respect to  $\phi$ , adding equations (41) and (42) and defining the volume average velocity q by:<sup>17,18</sup>

$$q = \phi v_s + (1 - \phi) v_f,$$
 (43)

we can substitute equations (41) and (42) by:

$$\frac{\partial \phi}{\partial t} + f'_{k}(\phi) \frac{\partial \phi}{\partial z} = 0$$
(44)

$$\frac{\partial q}{\partial z} = 0 \tag{45}$$

At lines of discontinuities in the suspension the field variables satisfy the jump balance, or Rankine-Hugoniot conditions, and the Lax entropy condition:

$$\sigma(\phi^+, \phi^-) = \frac{f_k(\phi^+) - f_k(\phi^-)}{\phi^+ - \phi^-}$$
(46)

$$q(\phi^+) = q(\phi^-) \tag{47}$$

$$f'_{k}(\phi^{-}) \ge \sigma(\phi^{+}, \phi^{-}) \ge f'_{k}(\phi^{+})$$
 (48)

Inequality (48) establishes the admissible discontinuities in the suspension.

The kinematic process is completely defined when a constitutive equation is postulated for the flux density function  $f_k(\phi)$  and initial conditions are selected for  $\phi$ . From equation (43) we can write:

$$q = v_s - (1 - \phi) u$$
 (49)

where  $u = v_s - v_f$  is the solid-fluid relative velocity. Equation (45) shows that the volume average velocity q(t) is independent of z. Then, multiplying the previous equation by  $\phi$ , we can write:

$$f_k(\phi) = q(t)\phi + \phi(1-\phi) u$$
 (50)

The value of q(t) must be defined by boundary conditions. For example, for batch sedimentation, there is no volume flow through the bottom of the settling column so that, for batch sedimentation q(t) = 0. Substituting this value in (50), leads to:

$$f_{bk} = \phi (1 - \phi) u \tag{51}$$

then, the continuous solid flux density function  $f_k(\phi)$  may be written in the form:

$$f_k(\phi(z, t), t) = q(t)\phi + f_{bk}(\phi)$$
 (52)

**Fig. (11)** shows continuous Kynch flux density functions for a suspension characterized by the batch, or *drift flux density function*  $f_{bk}(\phi)$ , and several constant values of the volume average velocity q(t).

## Ideal Continuous Thickener.

The concept of an ideal continuous thickener (Shannon and Tory<sup>10</sup>), Hasset<sup>19</sup>), Bustos, Concha and Wendland<sup>17</sup>), Concha and Bustos<sup>18</sup>) pretends to define the domain of validity of the field equations by idealizing the shape and operation of a real continuous thickener. Only the main attributes of the equipment are retained while the details are ignored.

An *ideal continuous thickener* (ICT) has been defined as a cylindrical vessel with no wall effect, so that the concentration of particles is constant at any cross section. In such a vessel the flow is onedimensional and the field variables are functions of only one space variable and time. The ICT is provided with a feeding, an overflow and a discharge system. See **Fig. 12**.





Fig. 11 Continuous Kynch flux-density functions for several values of the volume average velocity q(t) and a drift flux density with one inflection point.



Fig. 12 Ideal continuous thickener.

The following additional assumptions are made for an ICT:

a) The thickener is fed at z = L through a surface source. If Q<sub>F</sub>(t) is the feed volume flux of the suspension, φ<sub>F</sub>(t) its concentration and S the cross sectional area of the ICT, the solid density at z = L is given by:

$$f_k(\phi(L, t)) = f_F(t) = -\frac{Q_F(t)\phi_F(t)}{S}$$
 (53)

where  $f_F(t)$  is the feed solid flux density. It can be controlled externally by changing  $Q_F(t)$  or  $\phi_F(t)$ .

b) At z = 0 a surface sink discharges the settled suspension at a volume flow rate  $Q_D(t)$  and concentration  $\phi_D(t)$ . Then, the solid flux density and concentration at the discharge are:

$$f_k(\phi(0, t)) = f_D(t) = -\frac{Q_D(t)\phi_D(t)}{S}$$
 (54)

The discharge solid flux density  $f_D(t)$  can be controlled externally by changing  $Q_D(t)$ .

- c) The solid particles are restricted to the settling section (see Fig 12). If the solid particles cross from the feeding level to the clear liquid section we say that the ICT overflows.
- d) The discharge concentration  $\phi_D(t)$  is restricted to values greater than  $\phi(L, t)$ . If  $\phi_D(t) \le \phi(L, t)$ , we say that the ICT *empties*.

Bustos, Concha and Wendland<sup>17)</sup> and Concha and Bustos<sup>18)</sup> studied the transient evolution of the concentration in an ICT when certain initial conditions are established and determined the possible steady states. With the initial conditions consisting of only two constant states  $\phi_{\rm I} = \phi_{\rm L}$  for z > c and  $\phi_{\rm I} = \phi_{\infty}$ for  $z \le c$ , where z = c is an arbitrary height in the thickener, see Fig. 13, they found by the method of characteristics that, depending on the sign of  $f'_k(\phi_{\infty})$  and the value of  $\phi_L$ , three distinct solutions may be obtained for equation (44), which are called Modes of continuous sedimentation (MCS), for flux density functions having one inflection point. The MCS are characterized by the types of settling plots derived from the problem. In all the cases two regions of constant concentrations are established, under the clear liquid-suspension interface, separated by: MCS-I a shock wave; MCS-II a contact discontinuity and MCS-III a rarefaction wave.

Among all the possible solutions, only MCS-II leads to a steady state. If  $\phi_L = \phi_M^{**}$ ,  $\phi_L^* = \phi_M$  a contact discontinuity with a displacement velocity of  $\sigma(\phi_M^{**}, \phi_M) = f'_k(\phi_M) = 0$  is formed from point  $(f_k(\phi_M^{**}), (\phi_M))$  to  $(f_k(\phi_M), \phi_M)$ , so that the concentration changes abruptly from  $\phi_M^{**}$  to  $\phi_M$ , then increases continuously to  $\phi_\infty$  and finally decreases so that the ICT reaches a steady state at  $\phi = \phi_M$ . See **Fig. 14a** and **14b**. The value of  $\phi_L = \phi(L, t)$  can be calculated by solving equation (52) with  $\phi = \phi_I$ :



a) Flux density function with  $f'(\phi_{\infty}) < 0$  and  $\phi_{L} = \phi_{M}^{**}$ 





Fig. 14 Solution for ab MCS-II. b) Settling plot showing that the ICT attains a steady state at  $\phi_D = \phi_M$ 

# Steady State Capacity of an ICT for ideal Suspensions.

The analysis of the continuous Kynch sedimentation process for ideal suspensions having a flux density function with one inflection point shows that the only possible steady state is a CMS-II with a discharge concentration  $\phi_D = \phi_M$  and a conjugate concentration  $\phi_L = \phi_M^*$ . See **Fig. 14**. Since equation (52) must always be satisfied, for the discharge concentration and for its conjugate concentration we must have:

$$f_{\rm F} = q\phi_{\rm M}^{**} + f_{\rm bk}(\phi_{\rm M}^{**}) \tag{56}$$

$$f_{\rm D} = q\phi_{\rm M} + f_{\rm bk}(\phi_{\rm M}) \tag{57}$$

At steady state  $f_F = f_D$ , therefore obtaining q from equation (56) and substituting it into equation (57) yields:

$$f_{F}\left(\frac{1}{\phi_{M}^{**}} - \frac{1}{\phi_{M}}\right) = \frac{f_{bk}(\phi_{M}^{**})}{\phi_{M}^{**}} - \frac{f_{bk}(\phi_{M})}{\phi_{M}}$$

The term  $f_{bk}(\phi)/\phi$  can be defined as the fall of the clear liquid-suspension interface  $\sigma_{I}(\phi)$  in batch settling of a suspension of concentration  $\phi$ . Then, the previous equation may be written in the form:

$$f_{\rm F} = \left(\sigma_{\rm I}(\phi_{\rm M}^{**}) - \sigma_{\rm I}(\phi_{\rm M})\right) \left\{ \frac{1}{\frac{1}{\phi_{\rm M}^{**}} - \frac{1}{\phi_{\rm M}}} \right\}$$
(58)

The capacity of an ICT in terms of mass flow rate per unit area F/S is:  $F/S = -\rho_s f_F$ , then, from equation (58), the steady state capacity of an ICT is given by:

$$F/S = \varrho_{s}(\sigma_{I}(\phi_{M}) - \sigma_{I}(\phi \ M^{*})) \left\{ \frac{1}{\frac{1}{\phi_{M}^{**}} - \frac{1}{\phi_{M}}} \right\}$$
(59)

where  $\phi_{\rm M} = \phi_{\rm D}$ ,  $\phi_{\rm M}^{**} = \phi_{\rm L}$ . The Unit Area is UA<sub>0</sub> = S/F, so that the Unit Area of an ICT for an ideal suspension with a discharge concentration  $\phi_{\rm D} = \phi_{\rm M}$  is:

$$UA_{0} = \frac{1}{p_{s}(\sigma_{I}(\phi_{M}^{**}) - \sigma(\phi_{M}))} \left\{ \frac{1}{\phi_{M}^{**}} - \frac{1}{\phi_{M}} \right\} \quad (60)$$

# Design of continuous thickeners based on the continuous Kynch theory.

We analyze in this section those thickener design methods in which the continuous flux density function has been mentioned explicitly. The researchers involved are N. Yoshioka, N.J. Hasset, J.H. Wilhelm and Y. Naide.

### Yoshioka-Hasset Method.

Yoshioka<sup>20)</sup> developed in 1957 a graphical thickener design method based on the total solid flux density function. From the previous section we know that:

$$f_k(\phi) = q\phi + f_{bk}(\phi)$$

and at steady state  $f_k(\phi) = f_F$ , so that:

$$f_{\rm F} = q\phi + f_{\rm bk}(\phi) \tag{61}$$

Solving equation (61) for  $f_{bk}(\phi)$  with  $q = q_D$ , leads to:

$$f_{bk}(\phi) = f_F - q_D \phi \tag{62}$$

where  $q_D$  is the volume average velocity at the discharge. Equation (62) represents a straight line with  $q_D$  as the slope  $(q_D = -f'_{bk}(\phi_M))$  at  $\phi = \phi_M$ and  $f_F$  as the intercept of the ordinate in a plot of  $f_{bk}(\phi)$  versus  $\phi$ . See **Fig. 15**. Therefore, the intercept of the straight line with the vertical axis in **Fig. 15** gives the continuous flux-density function at steady state. The unit area, of course, is inversely proportional to the feed flux density UA =  $1/(-p_s f_F)$ .

Yoshioka<sup>20)</sup> and Hasset<sup>21)</sup> independently interpreted the result of **Fig. 15** still in another way. If the continuous flux-density function  $f_k(\phi)$  is plotted in-



stead of  $f_{bk}(\phi)$  against  $(\phi)$ , **Fig. 16** is obtained.

Here the solid flux-density at steady state is the horizontal line tangent to the continuous flux density at its maximum with concentration  $\phi_M$ .

Hasset<sup>21)</sup> realized that there was a problem of interpretation in this approach, because **Fig. 16** shows that only two concentrations are possible in the tickener, the limiting concentration  $\phi_M$  and its conjugate concentration  $\phi_M^{**}$  (see our **Fig. 14** and equations (55) and (56)). Hasset says: "Thus, the theory predicted the absence of the feed and discharge concentrations within the thickener, and shows that there must be an *abrupt increase* up to the discharge concentration at the moment of discharge...". It is obvious that this conclusion is absurd, because it would mean that the passage of a suspension through a series of contractions would increase its concentration making the thickener an unnecessary equipment.

The principal objection to these graphical methods of thickener design is that they use the Kynch fluxdensity function for values of concentration that are outside its range of validity. Remember that the Kynch batch flux-density function, is obtained through *initial settling experiments* and, therefore, they are valid up to the critical concentration only. Obviously the definition of flux density is valid beyond this concentration, but in this range it is not a unique function of concentration. We will discuss this fact further in a later section and will give an explanation of Hasset's problems.

### Wilhelm and Naide's Method.

Wilhelm and Naide<sup>22</sup>) also use the continuous flux density function at steady state in the form:

$$\mathbf{f}_{\mathrm{F}} = \mathbf{q}_{\mathrm{D}}\boldsymbol{\phi} + \mathbf{f}_{\mathrm{bk}}(\boldsymbol{\phi}) \tag{63}$$

Since  $f'_F = 0$ , the derivative of this equation at the limiting concentration  $\phi = \phi_M$  yields:

$$q_{\rm D} = -f'_{\rm bk}(\phi)|_{\phi_{\rm M}} \tag{64}$$

They suggest expressing the settling velocity of a suspension of uniform concentration, with the following equation (see **Fig. 17**):

$$v_{s}(\phi)\big|_{\text{batch}} \equiv \sigma_{I}(\phi) = -a\phi^{-b}$$
(65)

where a has the dimensions of  $LT^{-1}$  and b is dimensionless.



Fig. 15 Plot of the batch flux-density function and the Yoshioka construction.



Fig. 16 Plot of the continuous flux-density function and the Yoshioka-Hasset construction.



Fig. 17 Settling velocity versus concentration for coal refuse, according to Wilheim and Naide (1979)<sup>22)</sup>.



Since  $f_{bk}(\phi) = \phi v_s(\phi)|_{batch}$ , we have:

$$f_{bk}(\phi) = -a\phi^{1-b} \tag{66}$$

and

$$q_{\rm D} = a(b-1)\phi_{\rm M}^{-b}$$
 (67)

Substituting equations (64) and (67) into equation (63) yields for the limiting continuous flux-density  $f_F(\phi_M)$ :

$$f_{\rm F}(\phi_{\rm M}) = -ab\phi_{\rm M}^{1-b} \tag{68}$$

On the other hand, since  $f_F = q_D \phi_D$ , substituting into equation (68) yields a relationship between the discharge and the limiting concentration:

$$\phi_{\rm M} = \left(\frac{\rm b-1}{\rm b}\right) \phi_{\rm D} \tag{69}$$

Then, in terms of the discharge concentration, the steady state flux density is given by:

$$f_{\rm F} = -ab \left(\frac{b-1}{b}\right)^{1-b} \phi_{\rm D}^{1-b}$$
 (70)

and the unit area UA =  $1/(-\rho_s f_F)$  is given by:

$$UA = \frac{1}{\rho_{s}ab} \left(\frac{b-1}{b}\right)^{b-1} \phi_{D}^{b-1}$$
(71)

Wilhem and Naide also demonstrated that equation (71) is equivalent to the Talmage and Fitch method of thickener design. To appreciate this, consider equation (40).

$$UA = \frac{t_u}{\rho_s \phi_0 L}$$

From Fig. 9 we see that:

$$\phi_0 L = \phi_D Z_D$$
 and  $t_u = \frac{Z_D}{f'(\phi_k)}$  (72)

Then, substituting into the equation for UA yields:

$$UA = \frac{1}{ab} \left( \frac{b-1}{b} \right)^{b-1} \phi_{D}^{b-1}$$

which is identical to equation (71). Fig. 18 shows a simulation of the thickener capacity in terms of the discharge concentration based on Wilhelm and Naide's data.



**Fig. 18** Prediction of the UA for a continuous thickener treating coal refuse, according to Wilhelm and Naide<sup>22)</sup>.

According to Wilhelm and Naide, when the effect of compressive forces is negligible, for example for thickeners with shallow beds, the method described give unique results, otherwise different results are obtained for each bed height. The recommendation they give in this case, is to carry out batch experiments at similar bed heights as expected in the continuous thickener.

Wilhelm and Naide's method of thickener design may be summarized by the following steps:

- 1. Carry out batch settling experiments with suspensions at initial concentrations between that of the feed and that of the discharge of the thickener to be designed and record the initial settling velocity  $\sigma_{I}(\phi)$ .
- 2. Alternatively, perform one settling test at an intermediate concentration and obtain all initial settling velocities by drawing tangents to the settling curve, according to Kynch's theory.
- 3. Plot log  $(|\sigma_{I}(\phi)|)$  versus log  $(\phi)$ , as in Fig. 17, and approximate the curve with one or more straight lines.
- 4. From each straight line in **Fig. 17** calculate the parameters a and b of equation (65) graphically or by linear regression.
- 5. Using the values of a and b, determined for each section, calculate the unit area using equation (71).
- 6. Plot the curve UA versus discharge concentration  $\phi_{\rm D}$  in a log-log scale as in Fig. 18.

# 4. Thickener design methods based on the dynamic sedimentation process.

The sedimentation of flocculated suspensions, such as those encountered in the Mineral Processing



Industry, cannot be described by Kynch theory because the consolidation of the sediment under its own weight involves forces not taken into account in the kinematic theory.

Careful observations of batch settling of flocculated suspensions show the existence of two zones separated by a discontinuity. The upper zone is in hindered settling and lasts only up to the critical time, while the lower zone is in consolidation from the beginning up to the end of sedimentation.

# 4.1 Batch sedimentation of a compressible suspension.

The simplification of the general sedimentation equations, together with a dimensional analysis (Concha and Bustos<sup>23)</sup>, Concha et al<sup>24)</sup>) leads to the definition of the sedimentation of flocculated suspensions with the following field variables: the solid concentration  $\phi(z, t)$ , the solid flux density function  $f_b(z, t)$  and the excess pore pressure  $p_e(z, t)$ . These three variables must satisfy the following equations in those regions where the variables are continuous:

$$\frac{\partial \phi}{\partial t} + \frac{\partial f_b}{\partial z} = 0 \tag{73}$$

$$f_{b} = f_{bk}(\phi) \left( 1 + \chi(\phi) \frac{\partial \phi}{\partial z} \right)$$
(74)

$$\frac{\partial \varrho_{\rm e}}{\partial z} = -\Delta \varrho_{\rm s} \phi g \left( 1 + \chi(\phi) \frac{\partial \phi}{\partial z} \right)$$
(75)

and at discontinuities they must satisfy the Rankine Hugoniot and the Lax entropy conditions:

$$\sigma = \frac{f_{\rm b}^+ - f_{\rm b}^-}{\phi^+ - \phi^-}$$
(76)

$$f'_{b} \geq \sigma(\phi^{+}, \phi^{-}) \geq f'_{b}$$

$$(77)$$

where  $f_{bk}(\phi)$  is the extended Kynch batch flux density function and  $\kappa(\phi)$  is a measure of the ratio of compressibility of the sediment in relation to the forces available to compress it, in this case, the self weight of the sediment. (The name *extended* comes from the fact that the Kynch function is extended beyond the region where it is valid, that is, beyond the critical concentration  $\phi_{c.}$ ) In terms of the parameter of hindered settling and flow in a porous media  $f_{bk}(\phi)$ is given by:

$$f_{bk}(\phi) = \begin{cases} -\frac{\Delta \varrho \phi^2 (1-\phi) g}{\mu K(\phi)} , \phi < \phi_c \\ -\frac{\Delta \varrho \phi^2 g}{\mu/k(\phi)} , \phi \ge \phi_c \end{cases}$$
(78)

where  $K(\phi)$  is the coefficient of resistance of the suspension in hindered settling,  $k(\phi)$  is the permeability of the sediment, g is the acceleration of gravity and  $\mu$  is the fluid viscosity.

The compressibility of the sediment can be expressed as:

$$\chi(\phi) = \begin{cases}
0 , \text{ for } \phi < \phi_c \\
\frac{\mathrm{d}\sigma_e/\mathrm{d}\phi}{\Delta \varrho \phi g} , \text{ for } \phi \ge \phi_c
\end{cases}$$
(79)

Substituting equation (74) into equation (73) yields:

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial z} \left\{ f_{bk}(\phi) \left( 1 + \chi(\phi) \frac{\partial \phi}{\partial z} \right) \right\} = 0$$
(80)

The initial and boundary conditions for this equation are:

$$\phi(\mathbf{z}, 0) = \phi_0 \tag{81}$$

$$\frac{\partial \phi}{\partial z}\Big|_{z=0} = -\frac{1}{\varkappa(\phi)}\Big|_{z=0}$$
(82)

Equation (82) is obtained by taking  $f_b = 0$  at z = 0 in equation (74).

The position of the clear liquid-suspension interface  $\lambda$  is obtained from the jump balance equations (76):

$$\frac{d\lambda}{dt} = \begin{cases} \sigma_1 = f_{bk}(\phi)/\phi, \ t < t_c \\ \sigma_2 = f_{bk}(\phi_c)/\phi_c, \ t \ge t_c \end{cases}$$
(83)

where  $t_c$  is the time for which the suspension, immediately under the clear liquid-suspension interface reaches the critical concentration  $\phi_c$ .

Since equation (80) is parabolic, no discontinuities exist for regions where the concentration is greater than the critical concentration. In those regions where the concentration is lower than the critical value, equation (80) degenerates into the quasi-linear hyperbolic batch Kynch equation:

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial z} (f_{bk}(\phi)) = 0$$
(84)



This result implies that Kynch's theory is still valid for the sedimentation of flocculated suspensions in the region with concentrations lower than the critical value. This region is said to be in *Kynch regime*. It is bounded by two interfaces, the clear liquid-suspension interface, given by equation (83) and the suspension-sediment interface having a displacement velocity of:

$$\sigma_3 = \frac{f_{bk}(\phi_0^*) - f_b(\phi, \partial \phi/\partial z)|_{\phi_c}}{\phi_0^* - \phi_c}$$
(85)

where  $\phi_0^*$  is the concentration at the point of tangency obtained by drawing a straight line from the point  $(\phi_0, f_{bk}(\phi))$  and tangent to the extended batch flux-density curve. See **Fig. 15**.

Once the concentration distribution  $\phi(z, t)$  is known, the excess pore pressure is calculated using equation (75) with boundary condition  $p_e(\lambda) = 0$ . **Fig. 19** to **21** show the result of batch sedimentation of a flocculated suspension of copper tailings<sup>24)</sup>.

# 4.2 Continuous sedimentation of a compressible suspension in an Ideal Thickener at steady state.

The continuous sedimentation of a flocculated suspension may be defined by the following set of variables<sup>24</sup>: the solid concentration  $\phi(z, t)$ , the solid flux density function  $f(\phi(z, t), t)$ , the volume average velocity q(t) and the excess pore pressure  $p_e(z, t)$ . In those regions where the variables are continuous these variables must satisfy the following equations:

$$\frac{\partial \phi}{\partial t} + \frac{\partial f}{\partial z} = 0 \tag{86}$$

$$\frac{\partial q}{\partial z} = 0 \tag{87}$$

$$f = q\phi + f_{bk}(\phi) \left( 1 + \varkappa(\phi) \frac{\partial \phi}{\partial z} \right)$$
(88)

$$\frac{\partial \mathbf{p}_{e}}{\partial z} = -\Delta \varrho \phi g \left( 1 + \chi(\phi) \frac{\partial \phi}{\partial z} \right)$$
(89)

At discontinuities the field variables satisfy the jump balance and the Lax entropy conditions:

$$\sigma = \frac{\mathbf{f}^+ - \mathbf{f}^-}{\phi^+ - \phi^-} \tag{90}$$

$$f'^{-} \ge \sigma(\phi^{+}, \phi^{-}) \ge f'^{+}$$
 (91)



Fig. 19 Settling plot for a flocculated suspension of copper flotation tailings<sup>24</sup>:



Fig. 20 Concentration profile for the batch settling of the suspension of Figure 19<sup>24)</sup>.



Fig. 21 Excess pore pressure profile for the batch settling of the suspension of Figure 19<sup>24)</sup>.

where f is the continuous flux-density function,  $f' = \partial f/\partial \phi$ , q is the volume average velocity and where all the other variables have the same meaning as previously.

At steady state, equations (86) and (87) become:

$$\frac{\mathrm{df}}{\mathrm{dz}} = 0, \text{ for } 0 \le z \le L, \tag{92}$$

$$\frac{\mathrm{dq}}{\mathrm{dz}} = 0, \text{ for } 0 \le z \le L, \tag{93}$$

with boundary conditions:

$$f(L) = f_p \tag{94}$$

$$\mathbf{q}\left(0\right) = \mathbf{q}_{\mathbf{p}} \tag{95}$$



and where  $f_F = -Q_F \phi_F / S$  and  $q_D = -Q_d / S$ . The solution of equations (92) and (93) give, for any value of z:

$$f(z) = f_F \tag{96}$$

$$q(z) = q_D \tag{97}$$

To obtain the concentration profile in the ICT, substitute the value of f(z) and q(z) from equations (96) and (97) into equation (88) and solve for  $d\phi/dz$ :

$$\frac{\mathrm{d}\phi}{\mathrm{d}z} = -\frac{1}{\varkappa(\phi)} \left\{ 1 - \frac{\mathrm{f}_{\mathrm{F}} - \mathrm{q}_{\mathrm{D}}\phi}{\mathrm{f}_{\mathrm{bk}}(\phi)} \right\}$$
(98)

with boundary condition:

$$\phi(0) = \phi_{\rm D} \tag{99}$$

Since the term  $\varkappa(\phi)$  becomes zero for  $\phi < \phi_c$ , see equation (79), it is necessary to divide the problem into two parts, one for values of z greater than  $z_c$  and one for values smaller than  $z_c$ , where  $z_c$  is the vertical coordinate for  $\phi = \phi_c$ .

Case I:  $z_c < z \leq L$ .

In this region  $\phi < \phi_c$  and equation (98) becomes indeterminate, but from equation (88) we obtain:

$$f_{\rm F} = q_{\rm D}\phi + f_{\rm bk}(\phi), \text{ for } \phi < \phi_{\rm c}$$
(100)

Differentiating with respect to  $\phi$  yields:

$$0 = (q_D + f'_{bk}(\phi)) \frac{d\phi}{dz}, \text{ for } \phi < \phi_c$$

Since the value between the parentheses is not zero, except for special cases,  $d\phi/dz$  must be zero, then:

$$\frac{\mathrm{d}\phi}{\mathrm{d}z} = 0, \text{ for } \phi < \phi_{\mathrm{c}}$$
(101)

The concentration at z = L is  $\phi_L$ , so that the solution of equation (101) is:

$$\phi(z) = \phi_{\rm L}$$
, for  $\phi < \phi_{\rm c}$  (102)

Equation (100) is Kynch flux density function for an ideal suspension. This shows that Kynch theory is valid for the sedimentation of a flocculated suspension

in an ICT at steady state, in those regions where hindered settling exists, that is, where the concentration is lower than the critical concentration. The value of this concentration  $\phi_L$ , known as the *conjugate concentration*, can be determined from the continuous flux density curve, by solving the equation  $f_F = q_D \phi_L + f_{bk}(\phi_L)$  for  $\phi_L$ .

Case II:  $0 < z \leq z_c$ .

The concentration profile in an ICT for values of  $0 < z \le z_c$ , can be obtained by integrating equation (98) numerically with boundary condition (99). For example for the thickening of copper tailings<sup>25)</sup>, the solution of this problem is given in **Fig. 22**.

The hold up of solids in the thickener may be calculated by integrating the concentration profile:

$$W = \int_{0}^{z_c} \rho_s \phi(z) \, Sdz + \rho_s \phi_L Sl \qquad (103)$$

where  $z_c$  is the depth of the sediment layer and *l* is the height of the hindered settling zone.

Once the concentration profile is obtained, the excess pore pressure is obtained by integrating numerically equation (89) with boundary condition  $p_e(L) = 0$ . Then:

$$p_{e} = \begin{cases} \Delta \varrho \phi_{L} g(L - z), \text{ for } z_{c} < z \leq L \\ p_{e}(z_{c}) + \Delta \varrho g \int_{z}^{z_{c}} \phi(\xi) \frac{f_{F} - q_{D} \phi(\xi)}{f_{bk}(\phi(\xi))} d\xi, \text{ for } z \leq z_{c} \end{cases}$$

$$(104)$$

**Fig. 23** shows the excess pore pressure profile in an ICT treating a flocculated suspension<sup>25)</sup>.

### 4.3 Existence of a steady state in an ICT.

For gravity sedimentation to take place, it is necessary that the concentration in a thickener increases downwards or, at least, stays constant. Therefore, a necessary condition for sedimentation is that:

$$\frac{\mathrm{d}\phi}{\mathrm{d}z} \le 0 \tag{105}$$

Since  $\varkappa(\phi) > 0$ ,  $q_D < 0$  and  $f_{bk}(\phi) < 0$ , from equation (98) we see that, for inequality (105) to be always satisfied, the following must be true:





Fig. 22 Concentration profile in an ICT for a flocculated suspension corresponding to conditions shown in Figure  $24^{25)}$ 



Fig. 23 Excess pore pressure profile in an ICT for a flocculated suspension corresponding to conditions shown in Figure 2425).

$$f_p \ge q_D \phi + f_{bk}(\phi)$$
, for all values of  $\phi$  (106)

The right hand side of inequality (106) is the extended continuous Kynch flux density function (for all values of  $\phi$ , including  $\phi > \phi_c$ ) therefore, we can write:

$$f_{f_D} \ge f_k (q_D, \phi)$$
 for all values of  $\phi$  (107)

This result shows that the necessary and sufficient condition for the existence of a steady state in an ICT treating a flocculated suspension, is that, in a flux density plot, the extended continuous Kynch flux density function lies below the line  $f = f_F$ . Fig. 24 shows an extended continuous Kynch flux density function, for a given value of q<sub>D</sub>, together with several lines  $f = f_F$ . All the horizontal lines lying above the curve represent stable steady states<sup>25)</sup>.

# 4.4 Limiting capacity of an ICT treating a flocculated suspension at Steady State.

For every value of  $f_F$ , a different value for the discharge concentration is obtained as the intersection of the corresponding line  $f = f_F$  and the line  $f = q_D$  $\phi$ . Values of f = f<sub>F</sub> that intersect the flux density curve twice do not give valid steady states. The corresponding concentration and excess pore pressure profiles may be seen in Fig. 22 and 23. The concentration profiles for  $f_1$  to  $f_3$  are normal, but that for  $f_4$  is not.

This analysis leads to the conclusion that a limit exists for the capacity of a thickener, which can be obtained by calculating the maximum of the function  $f_k(q_D, \phi)$ . Let us consider a given and constant discharge concentration  $\phi_D$ , then a linear link exists between  $f_F$  and  $q_D$  through  $f_F = q_D \phi_D$ . Inequality (107) can be written in the form:

$$f_{\rm F} \ge \max_{\phi} f_{\rm k} (q_{\rm D}, \phi) \tag{108}$$

where  $f_k(q_D, \phi) = q_D \phi + f_{bk}(\phi)$ . Since  $q_D = f_F / \phi_D$ , we can write:



Fig. 24 Extended continuous Kynch flux density function and several operating lines  $f_1$  to  $f_4$ 



Substituting this equation into inequality (108) and remembering that  $\sigma_{I}(\phi) = f_{bk}(\phi)/\phi$ , yields:

$$f_{\rm F} \geq \max_{\phi} \left\{ (-\sigma_{\rm I}(\phi)) \left\{ \frac{1}{\frac{1}{\phi} - \frac{1}{\phi_{\rm D}}} \right\} \right\}$$
(109)

This inequality expresses the maximum solid flux density that can be fed to an ICT at steady state<sup>25</sup>.

In terms of mass flow rate per unit area,  $F/S = -\rho_s f_F$ , the maximum capacity of the thickener is given by:

$$F/S \ge \max_{\phi} (-\varrho_{s}\sigma_{I}(\phi)) \left\{ \frac{1}{\frac{1}{\phi} - \frac{1}{\phi_{D}}} \right\}$$
(110)

Finally, the Unit Area UA = S/F is given by:

1

$$AU \ge \max_{\phi} \left\{ \frac{1}{-\varrho_{s}\sigma_{I}(\phi)} \left\{ \frac{1}{\phi} - \frac{1}{\phi_{D}} \right\} \right\}$$
(111)

This result indicates that the *minimum unit area* of an ICT, treating a flocculated suspension, depends on the hindered settling velocity  $\sigma_{\rm I}$  of the suspension and not on the compressibility of the sediment. A comparison of this result with Coe and Clevenger equation (13), leads to the conclusion that, the unit area of the thickener should always be greater than the basic unit area  $AU_o$  of Coe and Clevenger equation. Defining the function  $G(\phi, \phi_D)$  by:

$$G(\phi, \phi_{\rm D}) = \left\{ \frac{1}{-\varrho_{\rm s}\sigma_{\rm I}(\phi)} \left( \frac{1}{\phi} - \frac{1}{\phi_{\rm D}} \right) \right\}$$

The basic unit area, given by equation (13) can be written in the form

$$UA_0 = \max_{\phi} G (\phi, \phi_D)$$
(112)

then, we can write<sup>25</sup>:

$$UA \geq UA_0$$

Plotting  $G(\phi, \phi_D)$  the minimum value of the unit area AU can be seen graphically as the maximum value of  $G(\phi, \phi_D)$ . See **Fig 25**.

### 4.5 Adorjan's method of thickener design.

Adorjan<sup>27,28)</sup> was the first researcher to express in a clear and consistent way the sizing of an industrial thickener based on the mass and momentum balance. His results are equivalent to those deduced in the preceeding section, especially equation (111) for the limiting Unit Area and equation (98) with boundary condition (99) for calculating the thickener height.



**Fig. 25** Unit area function  $G(\phi, \phi_D)$  versus  $\phi^{25}$ .



# Thickener Area.

Adorjan argues that a thickener operated under limiting conditions ( $f_F = f_k(q_D, \phi)$ ) requires very considerable pulp depth and therefore it must be operated at only a fraction of the limiting feed rate. This factor he called *loading factor* and defined it by:

$$\lambda = F/F_0 \tag{113}$$

where F is the actual feed rate and  $F_0$  the limiting feed rate. In terms of unit areas:

$$AU = AU_0/\lambda \tag{114}$$

Adorjan related the criteria to select  $\lambda$  to the safety factor in the design, so that a certain deviation from the design capacity would be possible. For example, selecting the arbitrary criteria:

$$\lambda = \frac{0.95}{1 + I_c}$$

where  $I_c$  is the fraction of increase in capacity needed, the area for the thickener is:

$$S = \frac{F}{\lambda} AU_0$$
(115)

where  $AU_0$  is Coe and Clevenger's basic unit area given by equation (13).

### Thickener Height.

The height of the thickener consists of three terms; c is the depth of the clear liquid (zone I),  $\ell$  the depth of the feed and hindered settling zone (zone II and III) and  $z_c$  the thickness of the sediment layer (zone IV).

$$H = c + \ell + z_c \tag{116}$$

Any criteria can be used to size zones I, II and III. For example, let us assume that c = 0.5 m, and  $\ell = 0.5$  m, so that the total height depends only on the depth  $z_c$  of the sediment. This depth is obtained by integrating equation (98) with boundary condition (99):

$$H = c + \ell + \int_{\phi_D}^{\phi_c} \frac{\varkappa(\phi) d(\phi)}{(1 - \lambda)}$$
(117)

where  $\varkappa(\phi)$  is a measure of the compressibility of the suspension, given by equation (79). For example **Fig. 26** gives the result of Adorjan's method for a specific case.

### 5. Parameter estimation.

We have already said that two types of motions can be distinguished in thickening: (1) hindered settling, at the beginning of the batch process or at concentrations lower than the critical value for continuous thickening, is characterized by the absence of cont-



Fig. 26 Adorjan's method of thickener design<sup>27,28)</sup>.



act throughout the solid component. All interaction between the solid particles is produced through the fluid and appears as an interaction force; (2) consolidation, at the final stages of batch sedimentation or at concentrations greater than the critical value in continuous thickening, is characterized by the formation of a network of solid particles, linked by a flocculant, that produces an increase in resistance to compression with concentration. Both stages are separated by the critical concentration. This parameter will be studied in (3).

### (1) Hindered settling.

Hindered settling is characterized by a single parameter, the constitutive equation for the *coefficient* of resistance  $K(\phi)$  of the solid-fluid interaction force m. (m =  $-\mu K(\phi)$  u, where m is the drag force and u the solid-fluid relative velocity). During hindered settling the absence of (or negligible) solid pressure gradient makes the suspension behave ideally, that is, it follows Kynch theory. Therefore, this stage of the process can be used to determine the parameter of hindered settling.

During batch sedimentation of a compressible suspension there is an initial period of time during which the concentration is constant and, therefore, the settling velocity of the suspension is also constant. By carrying out laboratory experiments with the suspension at several initial concentrations lower than the critical concentration, the corresponding hindered settling velocity may be determined by measuring the rate of descent of the water-suspension interface. Once the data has been collected any equation can be fitted to the data. Two types of equations, with two parameters to be determined experimentally, have been succesfully used: (a) Richardson and Zaki equation<sup>14)</sup> and b) Michael and Bolger's equation<sup>26)</sup>.

### a) Richardson and Zaki Equation.

Richardson and Zaki<sup>14)</sup> represent the batch settling velocity of a suspension of particles by the equation:

$$\sigma_{\mathrm{I}}(\phi) = \mathfrak{u}_{\infty} \ (1 - \phi)^{\mathrm{n}} \tag{118}$$

on a log-log plot of  $(-\sigma_{\rm I})$  versus  $(1-\phi)$ ,  $(-u_{\infty})$  corresponds to the intercept of the straight line with the ordinate and n is the slope of the line. For example, for a given copper tailings<sup>24</sup>, the parameters of the Richardson and Zaki equation, as determined from **Fig. 27a** are:  $u_{\infty} = -6.3 \times 10^{-4}$  m/s

and n = 12.6.

Since in batch sedimentation  $\sigma_{\rm I} = (1 - \phi)$  u, from the definition of  $f_{\rm bk}$  in equation (78) and equation (118) we have:

$$K(\phi) = -\frac{\Delta \varrho g}{\mu u_{\infty} (1 - \phi)^{n-1}}$$
(119)

### (b) Michaels and Bolger Equation:

Michaels and Bolgers<sup>26)</sup> applied the Richardson and Zaki equation to a flocculated suspension considering the floc as the fundamental structure rather than the primary particle. They proposed the following equation for the hindered settling of the flocculated suspension when the concentration within the floc is  $\phi_m$ :

$$\sigma_{\rm I}(\phi) = u_{\infty} (1 - \phi/\phi_{\rm m})^{4.65}$$
(120)

where  $u_{\infty}$  is the settling velocity of an individual floc. A plot of  $(-\sigma_{\rm I})^{1/4.65}$  versus  $\phi$  gives a straight line for the hindered settling region. The intercept with the vertical axis gives  $(-u_{\infty})^{1/4.65}$  and the intercept with the horizontal axis is  $\phi_{\rm m}$ . See **Fig. 27b**.

Since in batch sedimentation  $\sigma_{\rm I} = (1 - \phi)u$ , from the definition of  $f_{\rm bk}$  in equation (78) and equation (119) we have:

$$K(\phi) = -\frac{\Delta \varrho g}{\mu u_{\infty} (1 - \phi/\phi_{m})^{5.65}}$$
(121)

### (2) Consolidation.

The consolidation process is characterized by two constitutive properties: a) the compressibility of the sediment and b) the solid-fluid interaction force.

### a) Sediment compressibility.

During the last stage of batch sedimentation the process tends to equilibrium and  $f_{bk}(\phi)$  tends to zero. Then, from equations (74) we can write:

$$\chi(\phi) = -\frac{1}{\partial \phi/\partial z} \Big|_{eq}$$
(122)

and therefore:





Fig. 27a Richardson and Zaki method for hindered settling parameter estimation<sup>14)</sup>.



Fig. 27b Determination of the parameter in the Michaels and Bolger's equation<sup>26)</sup>.

$$\sigma_{\rm e}(\phi) = \Delta \varrho g \int_{z_{\rm c}}^{z} \phi \varkappa(\phi) \, \mathrm{d}\phi \qquad (123)$$

where  $z_c$  is the depth of the sediment.

### a) Sediment permeability.

From equations (74), (75) and (78) we have:

$$\frac{\partial p_e}{\partial z} = \frac{\mu(f - q\phi)}{\phi k(\phi)}$$
(124)

where  $k(\phi)$  is the permeability of the sediment.

When batch sedimentation has reached a near equilibrium, the solid velocity is negligible and  $f\cong 0$ . If then, water is allowed to drip from the bottom of the settling column, the permeability may be obtained by measuring the excess pore pressure  $p_e(z)$  with a manometer, and using the following equation:

$$k(\phi) = -\frac{\mu q}{\partial p_e / \partial z}$$
(125)

where q is the volume average velocity of percolation through the sediment.

### (3) Determination of the critical concentration.

Two methods have been proposed to determine the critical concentration of a flocculated suspension: a) Robert's method and b) Michaels and Bolger's method.

# a) Robert's method.

Robert<sup>29)</sup> considered that hindered settling and consolidation obeyed different mechanisms and therefore it should be possible to distinguish between them by appropriately plotting experimental results of batch sedimentation tests. Robert's method consists of plotting  $\log(z_1 - z_{\infty})$  versus time, where  $z_1$  and  $z_{\infty}$  are the height of the clear liquid suspension interface at any instant and at the end of a batch sedimentation experiment respectively. Usually the results are three straight lines intersecting at two points. The first intersection point corresponds to the time of the jump of concentration from  $\phi_0$  to  $\phi_0^*$  (see section 3.1) and the second intersection to the critical time, that is the time at which the concentration reaches the critical concentration. See **Fig. 28**.

Very often it is difficult to distinguish between these two intersection points and only one can be seen. In those cases it is convenient to use Robert's method for different initial concentrations, and plot the result versus the initial concentration. The critical concentration is that result obtained for an initial concentration tending to zero. See **Fig 29**.





Fig. 28 Critical concentration determined by Robert's method.



Fig. 29 Critical concentrations determined by Robert's method for several initial batch sedimentation tests.

#### b) Michaels and Bolger's method.

A procedure to obtain the critical concentration has been proposed based on the Michaels and Bolger's method to describe hindered settling<sup>26)</sup>. The basis is that Michaels and Bolger's equation is valid during hindered settling and therefore a deviation of the straight line in a plot of  $(-\sigma_I)^{1/4.65}$  versus  $\phi$ would indicate a change in regime from hindered settling to consolidation. The critical concentration would be the concentration at which the deviation occurs. See **Fig. 27**.

Obviously the fitting of all the previous equations may be done by linear or non-linear regression techniques instead of doing it graphically.

### 6. Conclusions.

The review of the principal methods of thickener design available in the literature, have shown that they can be grouped into three categories: those based on a macroscopic balance, those based on a kinematic balance equation and those based on dynamic balance equations. Only the last group provides complete information for design purposes.

The principal method based on a macroscopic mass balance is Coe and Clevenger's method of thickener design. This method leads to the same equation obtained from the more rigorous dynamic balances, but it only gives a lower limit for the unit area, that is, thickeners must have unit areas greater than this basic unit area. The success of this method, which is the most popular in the mining industry, is due to the fact that a safety factor is always used in the design. If this were not the case, problems would be encountered. The justification for this safety factor is not the variability of the material properties or the variation in temperature, as Coe and Clevenger proposed, but rather the fact that the basic unit area is just a limiting value. The final value chosen for the unit area is related to the height of the thickener. Using the basic unit area would lead to an infinite thickener height, which would diminish as the unit area is increased. In conclusion, Coe and Clevenger's method of thickener design is valid for obtaining the limiting value UAo for the unit area. The method proposed by the same authors for estimating the height of the thickener is not correct and is not recommended.

No method based on kinematic balances is recommended. Those methods give no information on the critical concentration and are usually applied to pulps with discharge concentrations well in the consolidation state. The goal of research workers using these methods is to have a simpler and more rapid method to design thickeners. We believe that performing batch settling experiments for several initial concentrations to obtain a reliable flux-density curve is simple and rapid enough not justifying shortcuts, especially when the equipment to be designed is as costly as a thickener.

It is unfortunate that Adorjan's method, the principal exponent of the dynamic methods, is almost unknown to the mining industry and to engineers responsible for the design of thickeners, in spite of the fact that it was published in  $1975^{27}$  and  $1976^{28}$ .

The main problem associated with the dynamic methods is the experimental determination of the



material parameters of the pulps. In the original work, Adorjan proposed the use of a compression cell to determine the compressibility of the sediment. Unfortunately compression cells require much higher pressures than those produced by the self weight of the pulp in thickeners. It is more convenient to measure other variables and calculate the effective solid stress. For example the concentration gradient may be calculated in a batch or continuous test by sampling<sup>30)</sup>, gamma ray absorption<sup>31)</sup>, X-ray absorption<sup>32, 33, 34, 35)</sup>, ultrasonic absorption<sup>36)</sup> and capacitance measurements<sup>37)</sup> and the excess pore pressure gradient is measured with a manometer<sup>38, 39)</sup>. Based on this information the effective solid stress may be calculated using equation (123) and the sediment permeability using equation (125).

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# Nomenclature

а	:	parameter in Wilhelm and Naide equation
b	:	parameter in Wilhelm and Naide equation
с	:	vertical coordinate separating different
-		values of the initial concentration in an
		ideal continuous thickener
fh	:	batch flux-density function
fue	:	extended batch Kynch flux-density function
f	:	continuous flux-density function
f <sub>k</sub>	:	extended continuous flux-density function
f <sup>I</sup> <sub>b</sub>	:	first derivative of f <sub>b</sub> with respect to the
		concentration $\phi$
f′	:	first derivative of f with respect to the
		concentration $\phi$
g	:	gravity acceleration
l	:	height of the hindered settling zone in a
		continuous thickener
q	:	volume average velocity
q <sub>fls</sub>	:	volume flow rate of flocculant
t	:	time
tu	:	parameter defined in Fig. 9
t <sub>U</sub>	:	parameter defined in Fig. 9
u	:	solid fluid relative velocity
u∞	:	settling velocity of a single particle (floc)
		in an unbounded medium
vs	:	solid component velocity
v <sub>f</sub>	:	fluid component velocity

7	· vertical coordinate
2	thickness of the sediment layer for a floc-
z <sub>c</sub>	aulated suspension
_	thiskness of the adiment layer for an
Z∞	: thickness of the sediment layer for an
	ideal suspension at the end of batch seu-
	mentation
F	: solid mass flow rate
$\mathbf{F}_{0}$	: limiting solid mass flow rate
$F_3(\times)$	: particle size distribution in the feed
ICT	: ideal continuous thickener
CKSP	: continuous Kynch sedimentation process
L	: feeding level in an ideal continuous thicke-
	ner
MS	: mode of sedimentation in batch settling
MCS	: mode of continuous sedimentation
0	: mass flow rate of water in the overflow
Q	: volume flow rate
s	: cross sectional area of an ideal continuous
~	thickener
Т	: intercept with the abscissa of the tangent
•	to the settling plot at point $z_{i}$ , $t_{i}$
UΔ	: unit area = $S/F$
	: basic unit area
W	: solid hold up in an ICT
<b>VV</b> <b>V</b>	total volume of solids in the settling colu-
••0	mn per unit area
7	· intercept with the ordinate of the tangent
D	to the settling plot at point $z_{i}$ , $t_{i}$
	· dilution
>	: coordinate of the water-suspension and
Λ	water sediment interface
24	· compressibility of the sediment
К	: compressionity of the sedment
σ	: displacement velocity of a surface of dis-
	continuity
$\sigma_{\mathrm{I}}$	: velocity of fail of the water-suspension
	internace
$\sigma_{\rm e}$	: effective solid stress
٤	. Solid component density
Qf	. Ind component density
Δų 4	· concentration as volume fraction of the
φ	actid component
4	· critical concentration
$\varphi_c$	: critical concentration of a floc
$\varphi_{\rm m}$	· maximum concentration of an ideal auto
$\phi_{\infty}$	ponsion
4	vinitial concentration in continuous test
$\varphi_{\mathrm{I}}$	, mudi concentration difference between the
$\boldsymbol{\varphi}_{\mathbf{k}}$	food and the artical value
	initial componentiation of a batch toot
$\phi_0$	: Initial concentration of a Datch test
$oldsymbol{\phi}_0$	gont to the flux density sums from the
	gent to the nux-density curve nom the



point of coordinates  $\phi_0$  and  $f(\phi_0)$ 

- $\phi_{\infty}^{**}$  : concentration obtained by drawing a tangent to the flux-density curve from the point of coordinates  $\phi_{\infty}$  and  $f(\phi_{\infty})$
- $\phi_L$  : concentration at the coordinate z = L
- $\phi^+$  : solid concentration at the front of a discontinuity
- $\phi^-$  : solid concentration at the rear of a discontinuity
- F : subscript for a property at the feed of the ICT
- D : subscript for a property at the discharge of the ICT
- n : parameter in the Richardson and Zaki equation

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# Review **E-SPART** Analyzer: Its Performance and Applications to **Powder and Particle Technology Processes †**

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### Abstract

The characterization of electrostatic charge and aerodynamic size properties of particles and powders is of critical importance in many electrokinetic processes and research applications. Some of the major particle and powder technology processes that employ electrokinetics of particles are: 1) electrophotography, including laser printing and ink jet printing, 2) powder coating and electrosprays, 3) electrostatic beneficiation of coal and minerals and electrostatic precipitators, and 4) lung deposition of inhaled pharmaceutical aerosols. In these processes, dispersion, transport, and deposition of particles depends significantly upon the electrokinetic behavior of the particles, determined by (1) the aerodynamic diameter - a parameter that includes the particle size, shape, and density, (2) electrostatic charge - both the magnitude and polarity, and (3) fluid flow and electrical fields surrounding the particles.

There are a number of instruments that can be used to characterize the aerodynamic size distribution of particles. Likewise instruments are available to estimate the net average electrostatic charge of particles sampled. However, choice of instruments for real-time simultaneous measurements of aerodynamic diameter and electrostatic charge distributions of particles on a single particle basis is limited. The Electrical Single Particle Aerodynamic Relaxation Time (E-SPART) analyzer can be used for simultaneous characterization of particle size distribution in the range from submicron to 100  $\mu$ m and particle charge distribution in the range from 0 to their saturation charge levels. We present a brief description of the principles of operation of the analyzer, its operational range, its advantages, and limitations. Application of the E-SPART analyzer to some powder technology processes is also briefly discussed, citing current research needs in these processes with examples of experimental investigations. In many of these processes, the E-SPART analyzer can be used to optimize the particle and powder technology processes involving electrokinetic properties of particles.

#### 1. Introduction

Electrokinetic properties of the particles play a significant role in many technology processes<sup>1</sup>). Table 1 shows typical ranges of particle size and electrostatic charge involved in some of these processes. Performance optimization of these processes often require measurement of both particle size and charge simultaneously on a single particle basis. It is also desired that such measurements be made insitu and in real-time. The Electrical Single Particle Aerodynamic Relaxation Time (E-SPART) analyzer<sup>2-4)</sup> meets some of these requirements and has been used for measuring the aerodynamic diameter and electrostatic charge distributions of particles on a single particle

Application

processes involved

Pharmaceutical aerosol	0.2 to 10	0.1-10
Electrophotography		
A) Past	8 - 14	8 - 10
B) Present	6 - 10	15 - 20
C) Future trend	4 - 8	20 - 30
Powder coating	5 - 50	0.1-20
Coal and mineral beneficiation	5 - 1000	0.01 - 10
Electrospray	5-100	0.01 - 10

Table I. Particle size and charge: Typical ranges in

Size  $(d_a \text{ in } \mu m)$ 

Charge-to-mass

ratio (µC/g)

basis in many of these applications. The instrumental method employed in this analyzer is non-invasive, and the measurement of particle size is independent

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of the refractive index and chemical composition of the particle. Since charged particles often deposit on the inner walls of the sampling tube during sampling and measurements because of the space charge and image forces, in-situ characterization is preferred for charged particles. The E-SPART analyzer can be adapted to perform remote measurement of the size and charge on a single particle basis, and to study the particle trajectories as well. Remote, non-invasive, in-situ measurements allow an understanding of the behavior of charged particle clouds where representative sampling is difficult and causes significant perturbations of the process conditions.

### 2. E-Spart analyzer

### 2.1 Principles of operation

The operational principle of this instrument depends upon the phenomenon that when an airborne particle is subjected to an oscillatory external force, such as an acoustic excitation, the resultant oscillatory motion of the particle lags behind the external driving field. This phase lag  $\phi$  relates to the aerodynamic diameter (d<sub>a</sub>) of the particle. To determine this phase lag, the analyzer uses a differential laser Doppler velocimeter (LDV) to measure the motion of individual particles subjected to a combination of an acoustic excitation and a superimposed DC electric field. The DC electric field is used to measure the electrical migration velocity of the charged particles.

The particles are sampled in a laminar flow field through the LDV sensing volume. As each particle passes through the sensing volume, it experiences the acoustic excitation and the superimposed DC electric field in a direction perpendicular to the direction of the laminar air flow sampling the particles. The aerosol is sampled vertically downward whereas the acoustic and electric excitations are applied in a horizontal direction. A typical sampling configuration of the E-SPART analyzer is shown in Fig. 1. An acoustic field induces an oscillatory velocity component of the particle in the horizontal direction. The inertia of each particle causes a phase lag  $\phi$  of the oscillatory motion of the particle with respect to the driving field. Fig. 2 shows two configurations of external field applied in the relaxation cell (Fig. 1) for the measurements of d, and q. The LDV measures the oscillatory velocity component (in the horizontal direction) of the particle and a microphone measures the acoustic field. The phase lag of the particle motion with respect to the driving field is measured by the signal processor and converted to aerodynamic diameter by using a personal computer. The computer stores the aerodynamic size data for the particles sampled and provides the measured size distribution (Fig. 3). In some E-SPART analyzers, no acoustic drive is used; instead an AC electric field drives the charged particles. The process of size measurement is identical to the acoustic system.

The measurement of charge is performed by employing either: 1) a DC electric field superimposed upon the acoustic field, or 2) an AC electric field replacing the acoustic field, as shown in **Fig. 1**. The



Fig. 1 Schematic of the E-SPART relaxation cell. Individual particles are subjected to acoustic and/or electric excitation and the resultant response is measured by LDV to determine d<sub>a</sub> and q.




E-SPART measurements of aerodynamic diameter (d<sub>2</sub>) Fig. 2 and electrostatic charge (q) with (1) acoustic plus DC electric or (2) AC electric excitation of particles.

acoustic field forces the particle in an oscillatory motion and the DC electrical field imparts an electrical migration velocity component (Ve), the magnitude and direction of which will depend upon the polarity and magnitude of the electrical charge q. With acoustic drive, the aerodynamic diameter d<sub>a</sub> can be measured for both electrically charged or uncharged particles by determining the phase lag  $\phi$  (Fig. 2). With an AC electric field as the driving force, the measurement process is applicable only to electrically charged particles. If a particle is charged, it experiences an oscillatory motion due to the applied AC electric field. The aerodynamic diameter d<sub>a</sub> is measured from the phase lag  $\phi$  and the electrostatic charge q is determined from the ratio of the amplitude of particle motion to the amplitude of electric drive. The advantage of AC excitation is the minimization of sampling loss since there is no steady electrical migration velocity. A unidirectional migration velocity caused by the DC electric field may deflect the highly charged particles away from the LDV sensing volume.

#### 2-2. Particle motion in an acoustic field

For a small particle – Reynolds number  $\text{Re}_n < < 1$ , Stokes' law describes the force of resistance for spherical particles moving in a viscous medium:

$$F_{\rm r} = 3\pi\eta d_{\rm p} (v_{\rm p} - u_{\rm q}) / C_{\rm c}, \qquad (1)$$

where

- $F_r$  = force of resistance
- $\eta$  = fluid viscosity
- $d_p$  = particle diameter
- $v_p$  = particle velocity (time dependent)
- $u_g$  = fluid velocity (time dependent)  $C_c$  = Cunningham slip correction fac = Cunningham slip correction factor.

The Cunningham slip correction factor can be computed by using the semi-empirical equation



Fig. 3 Schematic diagram of the E-SPART analyzer.



$$C_{c} = 1 + (2\lambda_{g}/d_{p}) (1.257 + 0.4 \exp(-1.1d_{p}/2\lambda_{g})),$$
(2)

where

 $\lambda_g$  = the mean free path of air molecules (0.065  $\mu$ m).

An equation describing the motion of a particle of .mass  $m_p$  in a sinusoidal acoustic field can be written as

$$m_{\rm p} dv_{\rm p} / dt + 3\pi \eta d_{\rm p} (v_{\rm p} - u_{\rm g}) / C_{\rm c} = F(t),$$
 (3)

where

 $m_p$  = particle mass t = time F(t) = any external force.

In the SPART analyzer, particles are drawn vertically into the sensing volume where they experience a horizontally directed excitation. If an acoustic field is used,

$$u_{\sigma} = U_{\sigma} \sin \omega t,$$
 (4)

and, in the absence of any external field,

$$\mathbf{F}(\mathbf{t}) = \mathbf{0}. \tag{5}$$

If we momentarily neglect some of the correcting terms, the equation of motion of a particle can be written as:

$$\tau_{\rm p}({\rm d}v_{\rm p}/{\rm d}t) + v_{\rm p} = U_{\rm g} \sin\omega t, \qquad (6)$$

where

 $\tau_{\rm p} = m_{\rm p} C_{\rm c} / 3\pi \eta d_{\rm p}, \text{ or,}$ (7)

$$\tau_{\rm p} = m_{\rm p} B \tag{8}$$

where  $\tau_p$  is the relaxation time and is the product of particle mass and its mechanical mobility, B, given by

$$\mathbf{B} = \mathbf{C}_{\rm c} / 3\pi \eta \mathbf{d}_{\rm p} \,. \tag{9}$$

The steady state solution of Equation 6 for t >>  $\tau_{\rm p}$ , is

$$V_{p}(t) = U_{g} \sin(\omega t - \phi) / (1 + \omega^{2} \tau_{p}^{2})^{1/2}, \qquad (10)$$

where the phase lag  $\phi$  of the particle with respect to the acoustic field surrounding the particle is given by

$$\phi = \tan^{-1}\omega\tau_{\rm p}.\tag{10}$$

Equation (11) is an approximation and can be used for  $\phi < 65^{\circ}$ . A more accurate relationship used in the E-SPART measurements is discussed later.

The ratio of the amplitude of particle velocity  $V_p$  and the amplitude of the gas motion due to the acoustic field can be written as

$$V_{\rm p}/U_{\rm g} = 1/(1 + \omega^2 \tau_{\rm p}^{2})^{1/2}. \tag{12}$$

Equations (11) and (12) show that the measurement of either the phase lag of the particle motion relative to the motion of the gas, or the velocity amplitude ratio of the particle in the acoustic field can be used to determine the relaxation time  $\tau_p$  or the aerodynamic diameter of the particle. For a spherical particle of density  $p_p$ , the relaxation time  $\tau_p$  can be written in terms of particle diameter  $d_p$ ,

$$\tau_{\rm p} = p_{\rm p} {\rm d}_{\rm p}^{2} {\rm C}_{\rm c} ({\rm d}_{\rm p}) / 18\eta \,.$$
 (13)

For a particle of any shape,  $\tau_{\rm p}$  can be written as

$$\tau_{\rm p} = p_{\rm o} \mathrm{d}_{\rm a}^{2} \mathrm{C}_{\rm c}(\mathrm{d}_{\rm a}) / 18\eta, \qquad (14)$$

where  $p_o$  represents unit density (1000 Kg/m<sup>3</sup>). The Cunningham slip factor C<sub>c</sub> is represented as a function of d<sub>p</sub> in Equation (12) and as a function of d<sub>a</sub> in Equation (13), respectively.

Fig. 4 shows the relative phase lag with respect to the external drive as a function of the aerodynamic diameter of the particle for several drive frequencies. We have assumed Stokes' law (Equation 3) to be valid in the entire range of phase lag  $\phi$  from 0 to 90 degrees. As phase lag increases, the pressure-force caused by the acoustic compression of the gas increases. The effective mass and the effective mechanical mobility of the particles must be considered, and appropriate correction to the Stokes' equation becomes necessary. Therefore, when an acoustic excitation is used for measuring the aerodynamic diameter  $d_a$  or the relaxation time  $\tau_p$  of a particle, it is necessary to use the correction terms for large values of  $\phi$ . Equation 3 is modified by replacing mass  $m_p$  and the mechanical mobility (B = C<sub>c</sub>/3 $\eta \pi d_p$ ) with the effective mass of the particle  $m_n'$  and the effective mobility (B') of the particle, respectively. The





Fig. 4 Phase lag of the particle motion with respect to the acoustic drive plotted as a function of aerodynamic diameter for different drive frequencies. The phase lag has been calculated from Stokes' law (appropriate corrections to Stokes' law become necessary when  $\phi$  is greater than 74°).

phase lag of the particle  $\phi$  of Equation 11 is replaced by the corrected phase lag ( $\phi - \theta$ ), given by:<sup>5)</sup>

$$(\phi - \theta) = \tan^{-1} \left( \frac{3(\alpha - 1)\zeta(\zeta + 1)}{2(\alpha + \frac{3}{2}\alpha\zeta + \frac{3}{2}\zeta + \frac{9}{2}\zeta^2 + \frac{9}{2}\zeta^3 + \frac{9}{2}\zeta^4)} \right)$$
(15)

where

$$\theta = \tan^{-1} \left( \frac{\frac{2}{3} + \zeta}{\zeta(\zeta + 1)} \right)$$
(16)

$$\alpha = 2p_{\rm p}/p_{\rm g} \tag{17}$$

$$\zeta = \frac{2}{\mathrm{d}p} \sqrt{2\gamma/\omega} \tag{18}$$

where  $p_p$  is the particle density,  $p_g$  is the gas density and  $\gamma$  is the kinematic viscosity  $(\eta/p_g)$ 

**Fig. 5** shows the relative phase lag  $\phi$  (top curve) derived from Equation 11 and  $(\phi - \theta)$  derived from Equation 15 as a function of d<sub>a</sub> for acoustic drive frequency of 100 Hz. The lower curve  $(\phi - \theta)$  shows the influence of the correction term, where maximum phase lag is 74° occurring at 75  $\mu$ m diameter at 100 Hz drive frequency. To operate the analyzer over a wide size range, it is necessary to use more than one frequency of excitation either in tandem inside a single relaxation chamber, or simultaneously in more than one relaxation chamber connected in series. To cover size range from submicron to 70  $\mu$ m in diameter the relaxation cells have been operated at different frequencies, 24 kHz (for 0.3 to 4.0  $\mu$ m) and 1.0 kHz





(for 2.0 to 20.0  $\mu$ m), 444 Hz (5 to 30  $\mu$ m), and 111 Hz (15-70  $\mu$ m). Integration of experimental data arising from the overlapping ranges is accomplished by using test aerosols of known concentration and combining the calibration with an appropriate software package.

**Fig. 6** shows the amplitude ratio  $V_p/U_g$  plotted as a function of  $d_a$  for different drive frequencies. These plots represent Equation 12. The effects of correction terms are negligible on amplitude ratio expression. As noted earlier, measurement of the aerodynamic diameter distributions can be performed either from the phase lag or from the velocity amplitude ratio measurements. It appears that for any given frequency of excitation, the operational range of size measurements can be extended if the measurement of phase lag ( $\phi$ ) is used to determine  $d_a$  at the lower half of the particle size range and amplitude





Fig. 6 Variation of the amplitude ratio  $V_p/U_g$  plotted as a function of the aerodynamic diameter for different acoustic excitation frequencies. The amplitude ratio has been calculated using Stokes' law. There is no significant difference in the relationships calculated with or without correction terms.

ratio  $(V_p/U_g)$  is used to determine  $d_a$  at the larger half of the size range.

#### 2.3 Particle Motion in a DC Electric Field

Along with the acoustic excitation, a DC electric field (E) is also applied in the same direction for measuring electrostatic charge q of the particle. The constant electric field (E) applies an electrostatic force on a charged particle which can be expressed as  $F_e = qE$  where q is the particle charge. A particle of diameter (d<sub>a</sub>) with n elementary charges will move with an electrical migration velocity (V<sub>e</sub>) given by

$$V_e = neEC_c/3\pi\eta d_a, \tag{19}$$

where e is the elementary charge. As shown in Fig. 2, two alternative modes are used for size and charge measurements. If acoustic and DC electric fields are used, the oscillatory acoustic velocity component  $V_{\rm p}\sin(\omega t - \phi)$ , is superimposed on this electrical migration velocity Ve of the particle. For each particle, V<sub>e</sub> is determined to calculate n, the number of elementary charges, after the aerodynamic diameter (d<sub>a</sub>) of the particle is computed from the measured phase lag  $\phi$ . The analyzer also recognizes the direction of V<sub>e</sub> which depends upon the polarity of the charge q of the particle. Thus, from the direction and magnitude of Ve, the polarity and magnitude of particle charge are recorded by the analyzer for each particle whose diameter has been measured. The analyzer also records the number of uncharged particles for each size channel. Currently, E-SPART measurements are made using an acoustic and a DC electric drive;  $d_a$  is determined from  $(\phi - \theta)$  and q from Ve. Alternatively, da can be determined from the measured values of  $V_p/U_g$ , as shown in Fig. 2. Similarly,  $d_a$  and q can be measured by applying an AC electric drive, as described below.

#### 2.4 Motion of a Charged Particle in an AC Electric Field

In this configuration, an AC electric field,  $E_{o}sin\omega t$  is applied (**Fig. 2**) across the two electrodes replacing the acoustic transducers. It is necessary, however, that the particles be electrically charged in order to make size and charge measurements. A charged particle, transiting the LDV sensing volume, will experience an oscillatory electric field,  $E_{o}sin\omega t$ , therefore, an external force,

$$F(t) = qE_{\alpha}Bsin\omega t, \text{ and } u_{\alpha} = 0.$$
(20)

The electrical mobility Z is expressed as

$$Z = qB. \tag{21}$$

The Equation 3 can be written in terms of Z,

$$\tau_{\rm p} dv_{\rm p}/dt + v_{\rm p} = ZE_{\rm o} \sin\omega t, \qquad (22)$$

where  $E_o = V_o/d$ .

The steady state solution for t  $> \tau_n$ ,

$$v_{p}(t) = ZE_{o} \sin(\omega t - \phi)/(1 + \omega^{2}\tau_{p}^{2})^{1/2},$$
 (23)

where  $\phi$  has the same expression as Equation 11 and the amplitude ratio has the similar form of Equation 12.

$$\varphi = \tan^{-1} \omega \tau_{\rm p} \tag{24}$$

$$V_{\rm p}/E_{\rm p} = Z/(1 + \omega^2 \tau_{\rm p}^2)^{1/2}$$
(25)

$$= qC_c/3\pi\eta d_a(1 + \omega^2\tau_p^2)^{1/2}.$$
 (26)

Equations 24 and 25 show that for a charged particle, the aerodynamic diameter  $d_a$  can be determined from the measured value of the phase lag  $\phi$  in a manner similar to the acoustic E-SPART analyzer. The relationships between  $\phi$  and  $d_a$  for different frequencies are shown in **Fig. 4**. The measurement of aerodynamic diameter  $d_a$  is independent of the driving field amplitude  $E_o$  and the magnitude of the particle charge q. Contributions from correction terms are negligible, unlike the case of acoustic drives where the gas is



subjected to compression and rarification. Once d<sub>a</sub> of the particle is determined from  $\phi$ , the analyzer then calculates the electrical mobility Z or the electrostatic charge q of the particle. The polarity of the charge is determined by noting if the overall motion of the charged particle is "in phase" or "180° out of phase" with respect to the electric field.

#### 2.5 Instrument operation

The experimental arrangement of an E-SPART analyzer is shown in Fig. 3. A personal computer is used for operating the E-SPART analyzer with a menu driven program designed to allow the operator to select the various options. Features include sampling time, maximum count per channel, and data storage and retrieval routines. In a typical operational mode, the instrument provides the aerodynamic size distribution of the sampled particles, the electrostatic charge distribution for any of the size channels selected by the operator, and a table showing the particle count versus the magnitude of the electrostatic charge for that given size channel. Table 2 shows a portion of a typical "summary data printout" of an E-SPART analyzer. Particle counts are separated, one for positively charged particles and the other for negatively charged particles. For a given size, the computer calculates the net average electrostatic charge for all the particles counted in that particular size channel and the charge-to-mass ratio for that particular size. The operator can choose any size channel for obtaining the charge distribution for that channel. A summary of data provides the total number of particles counted with the average charge calculated for a given size channel for both positively and negatively charged particles. The software has the capability to provide the following information:

- A. Size distribution
  - 1. Size frequency distribution plot, dN/d log d vs. d<sub>a</sub>.
  - 2. Cumulative numbers distribution, N(d<sub>2</sub>) vs. d<sub>2</sub>.
  - 3. Volume distribution,  $dV/d \log d_a vs. d_a$ .
  - 4. Cumulative volume distribution,  $V(d_a)$  vs.  $d_a$ .
  - 5. Count median aerodynamic diameter (CMAD) in micrometers.
  - 6. Mass median aerodynamic diameter (MMAD) in micrometers.
  - 7. Geometric standard deviation (dimensionless).
- B. Charge distributions
  - 1. Charge distribution for a given size,  $n(d_a)$  vs q(femto Coulomb/particle).

- 2. Table showing charge distribution for a given size.
- 3. Charge-to-mass ratio (q/m) distribution for a given size  $(d_{a})$ .
- 4. 2-D plot showing  $n(d_a)$  and  $q/m vs d_a$ .
- 5. 3-D plot showing  $n(d_a)$  and q/m vs.  $d_a$ .
- 6. Table showing summary of charge distribution for all size channels: channel number, size  $(d_{a})$ , number of particles counted in that size channel with + ve and - ve charge, charge-tomass ratio for positively charged and negatively charged particles, and the net average charge-to-mass ratio for that size channel (see Table 2).

Table	2.	E-SPART	data	on	glass	powder	(2	-	95	μm);
corona charged										

Negative					Positive			
Channel No.	Dia. (µm)	Count	femto-C	μC/g	Count	femot-C	μC/g	Total μC/g
1	2.82	4	-4.76	- 100.90	0	0.00	0.00	- 100.90
2	3.74	9	- 10.17	-41.13	2	5.64	5.64	- 15.02
3	4.47	5	- 7.37	- 31.58	3	5.25	5.25	- 6.48
18	22.13	128	- 1140.11	-1.57	2	18.42	1.62	-1.52
19	24.52	142	- 1255.24	- 1.15	10	89.68	1.16	- 0.99
20	27.11	121	- 1281.03	- 1.01	12	163.15	1.30	- 0.81
29	68.80	42	- 930.96	- 0.13	1	42.73	0.25	-0.12
30	79.76	38	- 1069.22	-0.11	0	0.00	0.00	-0.11
31	91.79	22	- 834.55	~ 0.09	0	0.00	0.00	- 0.09
	N	Negative			Positive		Total	
Count		1500.00			95.00		1595.00	
Mass (nan	)	59886.91			920.21			

(Only a few selected channels are shown here as examples)

	Negative	Positive	Total
Count	1500.00	95.00	1595.00
Mass (nano-gram)	59886.91	920.21	1595.00
Charge (femto-C)	-17472.83	793.40	- 60807.12
Charge/Mass ( $\mu$ C/g)	-0.29	0.86	-0.27

Max particle charge (neg) = -75.05 femto-C

Max particle charge (pos) = 42.73 femto-C

Count median diameter = 24.278 micrometers Mass median diameter = 65.588 micrometers

#### 2.6 Range of operation

A. Size Measurements: The prototype E-SPART analyzer was operated in a range 0.3 to 70  $\mu$ m in aerodynamic diameter. Fig. 7 shows the cumulative number distributions of aerosol containing fairly monodisperse polystyrene latex spheres (PLS) of 0.8  $\mu$ m diameters as measured by the E-SPART analyzer operating at 25KHz. Fig. 8 shows the cumulative volume distributions of aerosol containing bis-ethyl hexyl sebacate (BES) droplets of uniform size with diameters 3.0, 10.0, 20.0 and 30.0 µm in diameter as measured by an E-SPART analyzer operating at 444 Hz and 111 Hz, respectively. Also shown in Fig. 8 is a cumulative volume distribution of a dry powder containing polystyrene particles of average





Aerodynamic diameter (micrometers)

Fig. 7 Size frequency distribution dN/dlogd\_ for polystyrene latex sphere (PLS) containing 0.8 µm diameter particles measured with an acoustic E-SPART.



Fig. 8 Aerodynamic size distributions of calibration particles measured by prototype advanced E-SPART analyzer operating at two acoustic frequencies 111 Hz and 444 Hz A. 3 µm, B. 10 µm, C. 20 µm, D. 20 µm, E. 30 µm, F. 44  $\mu$ m particles. A, B, and C were measured at 444 Hz, and D, E, and F were at 111 Hz.



Fig. 9 Particle size distribution of toner as measured by a Coulter Multisizer and an E-SPART analyzer.

diameter 44  $\mu$ m. Fig. 9 shows the size distribution of toner particles measured by an E-SPART analyzer.

The number distribution is compared with the number distribution measured by a Coulter counter. Fig. 10 shows cumulative number distributions of two monodisperse test aerosols containing BES droplets of 19.0 and 29.0  $\mu$ m diameters and a polydisperse dry powder paint of average particle diameter 52  $\mu$ m. The measurements were taken by using an AC drive. The BES droplets were generated by using a Vibrating Orifice Aerosol Generator which produces charged droplets. Fig. 10 shows that measurements of size distribution can be performed with an AC drive replacing the acoustic drive.

B. Mass Measurements: For each particle, the aerodynamic diameter (d<sub>a</sub>) and the charge (q) are determined in the E-SPART analyzer and the average value of charge-to-mass ratio is computed. For a spherical particle of diameter d<sub>p</sub> and specific gravity  $p_n$ , we can write an approximate relationship:

$$d_{p}^{2}p_{p} = d_{a}^{2}p_{o}.$$
(27)

The mass  $m_p$  of the particle can be computed from the measured value of  $d_a$ , if  $p_p$  is known.

Thus,

$$m_{p}(d_{a}) = (1/6)\pi d_{a}^{3}(p_{p})^{-1/2}.$$
 (28)

C. Charge Measurements: The desired range of measurement of electrostatic charge on each particle is from zero charge to its saturation value with positive or negative polarity. The saturation charge-tomass ratio for tribocharged, dielectric solid particles varies inversely with particle diameter (Equations 29, 30). Fig. 11 shows the variation of the chargeto-mass ratio of a toner sample measured as a function of aerodynamic diameter. The data show that the analyzer can measure particle charge up to their saturation limits.

D. Count Rate: The E-SPART analyzer can be used to measure aerodynamic size and electrostatic charge distribution of particles in real time and on a single particle basis. The measurement of size and charge (magnitude and polarity) is simultaneous and noninvasive. The method permits continuous sampling or in-situ measurements. The maximum particle count rate depends upon the frequency of operation -- from 10 particles/s to 2,000 particles/s depending on the size range of operation, from 70 µm down to  $0.3 \ \mu m$  in aerodynamic diameter. Further extensions





Aerodynamic diameter (micrometers)

Fig. 10 Cumulative number distribution of BES droplet aerosols for two different sizes: 19  $\mu$ m-dia and 29  $\mu$ m-dia, and a powder paint with 52.0  $\mu$ m MMAD measured by an E-SPART analyzer using AC electric drive.



Fig. 11 The charge distribution of a tribocharged and corona charged toner sample as measured by an E-SPART analyzer. The solid line shows the saturation charge calculated from the Gaussian and Pauthenier limits, respectively. The experimental data show the E-SPART can measure particle charge to its saturation limit. Particles smaller than 7  $\mu$ m dia acquired higher charge than the values predicted by the Pauthenier equation, whereas larger particles acquired charge-to-mass ratio less than the predicted values.

of this range and count rates are possible, but require critical control of the sampling process and instrument operation.

#### 3. Applications

**Fig. 12** shows some of the particle technology applications where particle size and charge measurements play important roles in process characterization and control. The following is a brief description of E-SPART analyzer applications.



Fig. 12 Different industrial applications of the E-SPART analyzer.

#### 3.1 Electrophotography

Electrophotographic processes as applied to copiers and laser printers, employ electrostatically charged toners as the imaging material. For example, in a copying machine, a photoconducting surface is charged by using a corona charger to record a latent image of the original document and the charged toner particles are used to develop the image on the surface of a paper or a film. The charge properties of toners are determined by the size and shape, composition, and concentration of toners in the developer. Although the physics of the charging process are not completely understood, empirical approaches based partly on theory and partly on trial and error have been successful in optimizing the process variables to meet the increasing demand of image quality, color balance, cost, and size reduction of the copying and printing devices. Experimental approaches require both basic and applied research supported by accurate quantitative measurements.5-7)

Perhaps the two most critical parameters of toners are their size and charge distributions. For example, higher resolution can be obtained when toner size is decreased. Early copying machines used toner 8-14 $\mu$ m in diameter (see **Table 1**); currently, the majority of office copiers use toners in the 6-10  $\mu$ m range, however, for higher resolution use of toner 4-6  $\mu$ m in diameter (microtoners) has been suggested. The use of microtoners may have some problems: 1) toner q/m values increase (q/m is proportional to 1/d), which adversely affect toner mass transfer to the latent image development since the mass of toner



deposited per unit area is proportional to 1/(q/m); 2) dust problems caused by uncharged fine particles; 3) cleaning residual toners from the photoconductor may become very difficult; and 4) the presence of "wrong-sign" toner could contribute more to background development compared to using large-size toner.

In electrophotographic processes, toners are charged by triboelectrification. The size and charge distributions of a positive toner sample measured by the E-SPART analyzer are shown in **Figs.13 and 14**. The net charge q on a particle increases as the particle diameter  $d_a$  increases  $(q \alpha d_a^2)$ , however, the charge-to-mass ratio decreases with increasing diameter since m is proportional to  $d_a^3$ . **Fig. 15** shows charge distributions for three particle sizes for a negative toner sample. The maximum surface charge density is limited by the electric field which produces ionization of the gas surrounding the particles. This charging limit, called Gaussian limit<sup>1)</sup>, can be approximated for air, as

$$Q_s = 2.64 \times 10^{-5} \text{C/m}^2 \tag{29}$$

$$q_{max} = \pi d^2 Q_s$$
;  $(q/m)_{max} = 6 Q_s/d_p$  (30)

Equation (30) shows that (q/m) is inversely proportional to  $d_p$ . This relationship is an approximate one, since the ionizing field not only depends on the surface charge density, but also on the curvature of the surfaces or the particle diameter. Fig. 11 shows the variation of (q/m) of a tribocharged black toner sample as a function of d as measured by an E-SPART analyzer.

#### 3.2 Powder coating

In this process, a dry powder is fluidized, electrostatically charged, and then sprayed over the workpiece for uniform coating1). Next, the workpiece, coated with powder, is heated and the powder melts and adheres to the surface. The advantage of electrostatic powder coating is that the coating process quickly produces a chemically resistant, durable painted surface. The paint thickness can be easily varied, and since no solvent is used the process eliminates the environmental pollution caused by the emission of volatile organic compounds (VOC) used in solventbased painting processes. Due to the elimination of VOC, the process is now widely used in the US, Europe, and Japan for coating metal and plastic surfaces for products ranging from appliances to automobiles. Powder coating in the automotive industry is limited mostly to painting of internal surfaces and













to external clear coats. Most of the external surface coating is still performed by solvent-based painting. To date, the surface finish achieved by solvent-based coating is more glossy and better weather resistant; however, with research and advancements in powder coating, it is conceivable that the solvent-based





Fig. 16 Aerodynamic diameter and electrostatic charge-to-mass ratio distributions plotted for a powder paint after tribocharging. The charge distributions show bipolar charging of the particles.

process will eventually be replaced by the dry electrostatic process. The quality of powder coating is being improved to eliminate the so-called "orange peel" effects from the painted surface so that auto industries can use this process. The demand for powder coating is rising, primarily because of its environmental safety, operational efficiency, labor cost reduction, and the high quality durable painting it produces.

Adjustments for achieving high quality powder coating involve 1) the production of powders in the desired particle size range, 2) fluidization of powders, 3) pneumatic conveying of powders to the charger, 4) electrostatic charging and spraying of the powder, 5) coating of the powder on the work surface, and 6) heat treatment and bonding of the paints to the work surface.

In-situ measurements of particle size, charge, and particle trajectories around the work surface are of importance in powder coating research. The particles are charged either by corona charging or by tribocharging. Both methods have certain advantages and disadvantages in producing the desired chargeto-mass ratio distribution of the particles. For example, in a corona charger, the charging process is inefficient but predictable and controllable and produces a charge distribution of particles which is primarily unipolar. In contrast, the tribocharging process is efficient but unpredictable, and it produces a bipolar charge distribution of powders. In both cases, there is a complex interaction of the fluid flow field with the local electric field during the deposition process. Corona charging is more widely used in powder coating than tribocharging. In corona charging, the limiting value of the surface charge, known as the Pauthenier limit, can be expressed as:

$$Q_{\text{max}} = \pi \varepsilon_0 \left[1 + 2\left(\frac{\varepsilon r - 1}{\varepsilon r + 1}\right)\right] d^2 E$$
(31)

where  $\mathcal{E}_{o}$  is the permittivity of the free space,  $\mathcal{E}_{r}$  is the relative permittivity of the powder, d is the particle diameter, and E is the electric field. The maximum charge on a particle is limited by the field strength E but its maximum value is still limited by the ionization of the medium, expressed as the Gaussian limit.

Fig. 10 shows a size distribution of a powder paint taken by an E-SPART analyzer. Fig. 16 shows electrostatic charge distribution of a powder paint after tribocharging. The particles, when tribocharged, acquired a bipolar charge distribution, as shown in Fig. 16. The upper half of the plot shows (1) chargeto-mass (q/m) ratio (broken line) and particle counts plotted as a function of  $d_a$  for positively charged particles. The lower half of the plot represents negatively charged particles.

#### 3.3 Coal beneficiation

In the electrostatic beneficiation  $process^{8,9}$ , the coal is first pulverized into a fine powder -- in the size range  $5-1000 \ \mu m$  in diameter. The powder is then electrostatically charged by contact and triboelectrification. Once these coal particles come in contact with such metals as copper, the organic coal particles become positively charged and the pyrites and inorganic mineral particles become negatively charged. When charged particles pass through an electrostatic separator consisting of two parallel plates across which a high voltage is applied, the powdered material separates on the basis of particle charge and its polarity. The organic coal particles are attracted toward the negative plate, whereas the pyrites and mineral fines are attracted toward the positive plate.

Size reduction is very critical because particles must be small enough for selective liberation of pyrites and minerals from coal yet large enough for minimizing the energy needed for grinding the particles into fine powders. Electrostatic beneficiation provides a method of dry coal cleaning, avoiding potential stream pollution that occurs in wet cleaning



process. One crucial aspect of dry beneficiation is the understanding of the electrophysical properties of powdered coal needed to enhance bipolar charging of coal and mineral particles for efficient separation. In this application, the measurement and control of electrostatic charge and particle size distributions are important for optimization. **Fig. 17** shows the charge distributions of pulverized coal and mineral particles. The particles are bipolarly charged, and once these particles are separated, the major mass fraction of the positively charged particles should contain coal and the negative particles should contain minerals.

#### 3.4 Electrostatic spray deposition of pesticides

Pesticides and herbicides are sprayed on plants and vegetation. Electrostatic spray has been successfully used for achieving a better coating of spray on the leaf surface and minimization of soil and water contamination.<sup>10,11)</sup> It has been found that electrostatic spraying improves the deposition efficiency and reduces loss and thereby minimizes the amount of material needed to coat the surface. Further, the coating can penetrate dense plant foliage canopies and form an even distribution of small droplets on top of the foliar surface as well as leaf undersides within the lower portion of the canopy. As in powder coating applications, the particle size and particle charge both play a very significant role in electrostatic spray process in agriculture. In-situ measurement and control techniques are needed for efficient foliar surface coating and minimization of any soil, and groundwater contamination.

In spraying liquid herbicides or pesticides, generally air-atomizing nozzles are used, aided by electrostatic induction charging. Induction charging has the advantage that the voltage requirement for charging is generally low, typically below 1,000 volts DC with current requirement less than 100  $\mu$ A. The droplet size for optimum coating is kept below 100  $\mu$ m in diameter and preferably above 30  $\mu$ m in diameter to minimize complete drying and causing air pollution. In induction charging, the droplets can acquire high electrostatic charge with a charge-to-mass ratio close to the charge saturation limit.

#### 3.5 Lung Deposition of Pharmaceutical Particles

Deposition of inhaled pharmaceutical particles in the human respiratory tract depends primarily upon: 1) the aerodynamic size distribution of particles, 2) the breathing pattern, and 3) the airway geometry. It has also been found that many physical properties



Fig. 17 Aerodynamic size and electrostatic charge distributions of tribocharged pulverized Illinois #6 coal powder measured by an E-SPART.

of the particles, such as shape, hygroscopicity, and electrostatic charge, have significant influence on particle deposition within the human lung.<sup>12-14</sup>)

For the appropriate therapeutic effect, it is necessary that the pharmaceutical aerosols (particle size, ranging from submicrons to  $10 \ \mu m$ ) deposit accurately in the targeted sites of the lung and in acceptable quantities. Since direct measurements of the deposition pattern of the inhaled pharmaceutical aerosols inside a human lung is not possible with currently available instrumentation, both physical and mathematical models are extensively used to study the lung deposition pattern. Such models are used to improve targeted deposition of the inhaled aerosol by adjusting the particle size distribution and the breathing pattern. The possibility of increasing the total deposition and shifting of the deposition to a particular portion of the respiratory tract by controlling the electrostatic charge or by manipulating hygroscopic growth of the particles has been suggested by many investigators. In-situ measurement of particle size and electrostatic charge distributions in real-time within a physical lung model provides a means to make observations of the particle deposition pattern in a simulated flow field environment. Fig. 18 shows the change in the fractional deposition efficiency of the particles in a lung model as a function of electrostatic charge. The experimental data shows that by increasing electrostatic charge it is possible to target particles in the smaller airways of the lung when particle size and the breathing patterns are both controlled.





Fig. 18 Calculated values of lung deposition fraction of inhaled particles as a function of aerodynamic diameter plotted for different magnitude of electrostatic charge. The computation was based on a physical lung model.

#### 4. Summary

The above examples of powder and particle technology processes show that characterization of electrokinetic behavior of particles often requires simultaneous measurements of their size and electrostatic charge on a single particle basis. Such characterization also requires appropriate sampling or in-situ measurements to minimize sampling losses. The E-SPART analyzer can be conveniently used in a number of such applications.

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#### Nomenclature

C <sub>c</sub>	= Cunningham Correction factor, dimen-
d.	= aerodynamic diameter of particles, m
d	= particle diameter (geometric) m
-р Е	= electric field. $Vm^{-1}$
e	= electronic charge. C
F.	= force of resistance. N
F(t)	= external force. N
m_	= particle mass. Kg
n	= number of elementary charge
Ν	= number of particles
q	= electrostatic charge, Coulomb
R <sub>en</sub>	= particle Reynolds number, dimensionless
t	= time, s
ug	= gas velocity, ms <sup>-1</sup>
V	= volume, m <sup>3</sup>
V <sub>p</sub>	= particle velocity, ms <sup>-1</sup>
Z	= electrical mobility, $m^2 s^{-1} v^{-1}$
η	= viscosity of the medium, Kg $m^{-1}s^{-1}$
pg	= gas density Kg m <sup>-3</sup>
p <sub>o</sub>	= unit density
p <sub>p</sub>	= particle density Kg m <sup>-3</sup>
$ au_{\rm p}$	= relaxation time, s
λ <sub>g</sub>	= mean free path of gas, m
ω	= frequency in radians/s
arphi	= phase lag, radians
$\theta$	= correction term to phase lag $\phi$ , radians
v	= kinematic gas density $(\eta/p_g)$
<sup>0</sup> 3	= permittivity of free space, $\overline{F}$ m <sup>-1</sup>
8 <sub>r</sub>	= relative permittivity, dimensionless

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## Experimental Study of Horizontal Plug Flow of Cohesionless Bulk Solids

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#### Abstract

Plug flow of polyethylene pellets was studied in a 50 mm i.d horizontal pipe. The evolution of plug length and velocity along the pipe was deduced from relationships based on mass balances at the front and back of the plug.

The average pressure profile along the pipe was analysed with the help of the Ergun equation which governs interstitial gas flow in the plugs. In the case of low pressure gradients, it was demonstrated that the ratio of the plug length over void length,  $\frac{L_b}{L_V}$ , is constant along the pipe. How this ratio is correlated with gas flowrate was established through solids hold-up measurements.

#### 1. Introduction

The transport of granular materials in dense-phase regime at low particle velocity (plug flow) is often suitable when solids breakage and pipe attrition are to be minimised. The plug flow, as a dense regime, is also of particularly low specific energy consumption, and great solids flowrates can be easily achieved. That is why the conveying of plugs of cohesionless solids is generally used for the transport of agricultural products.

In spite of these interesting characteristics, only a few papers handle the plug flow regime, and its theoretical analysis remains crucially missing. Some papers that address the issue are Tomita [1], Tsuji [2], Konrad [3], Legel [4].

Plug flow is a nonstationnary flow regime. Plugs, periodically generated at the inlet, increase in length along the pipe. Consequently, most of the flow parameters vary along the pipe and it is necessary to use time and length averaged parameters for characterisation. One might wonder whether a maximum plug length will be attained.

In this paper we will present two aspects of the plug flow regime:

- The first one concerns the flow structure characterisation. The different velocities related to the plug flow regime (plug front, plug back and particle velocities) are defined, measured and a relationship between them is developed. In this part, the particle velocity will be considered as a reference to which the plug front or back velocities will be compared.

- The second part concerns the hydrodynamic flow characterisation. The time average pressure profile will be compared to the average pressure profile in the pipe calculated with the Ergun equation. This investigation will lead to solids hold-up analysis in the pipe and gas expansion effect on the flow characteristics along the pipe. In the case of a linear pressure profile, the ratio  $\frac{L_b}{L_v}$  is shown to be constant along the pipe.

#### 2. Experimental apparatus and procedure

Fig. 1 give a schematic view of the experimental set up. The conveying line is 25 to 70 m long and has a 50 mm i.d.. It is made of stainless steel, except for the first 10 m which are made of Plexiglas in order to allow visual observations. This Plexiglas portion can be easily removed and placed in another portion of the line. The solids feeding system consists of three superimposed hoppers. The lower one at the line entrance is monitored to feed the transport line continuously at a controlled solids flowrate. The intermediate one is either fed by the solids coming from the upper storage hopper or emptied by discharging into the feeding hopper. The upper hopper receives the returned solids and is used for storage. It is weighed continuously (load cells) so as to give the circulating solids flowrate.

This loop configuration allows continuous operation. The carrying gas is air. It is mainly introduced

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Fig. 1 Schematic view of the experimental set-up 1-feeding hopper 3-pneumatic valves 5-storage hopper 7-intermediate hopper

2-experimental tube 4-pressure taps 6-load cells 8-air injection line

through an injector located in the feeding hopper 1, but also comes from aeration points located at different places in the 3-hopper feeding system in order to balance pressure and allow solids flow to the line.

The compressed air flowrate is measured with a rotameter. The solids used are polyethylene pellets of 3.09 mm mean diameter and having a 920 kg/m<sup>3</sup> density. Black particles of about the same dimension and density were used as tracers. The pressure profile in the experimental section of the pipe is measured with a pressure transducer (0-3.5 bar).

During each run, the data from the load cells and pressure transducers were sampled at 50 Hz by a data acquisition system. A high shutter speed video camera was used to observe the solids flow pattern. This camera has a speed of 25 frames per second. If the maximum particle velocity at the wall is 2 m/s, then the distance covered by a particle between two frames (40 ms) will be equal to 8 cm.

In addition, solids and plug velocities were determined using a fibre optic probe technique (Fig. 2).



Set-up for velocity measurements with fibre optic probe Fig. 2 technique

It consists of two sets of emitting and receiving fibres located at a given distance to each other (0.2 m). The signals that they send to the photo detectors have a characteristic time delay (Fig. 3). Frequency and recording time are adjusted depending on plug length, so that the two signals appear on a single screen.

On the two channels, a beginning and termination time for a plug is obtained (time  $t_1$ ,  $t_3$  and  $t_2$ ,  $t_4$ ). Knowledge of the distance separating the two probes allows determination of front and back plug velocities.



velocity

distance between the two probes

$$V_a = \frac{\text{distance between the two probes}}{t - t}$$

#### Experimental results and discussion 3.

The plugs behave like small horizontal moving beds with a uniform solid velocity profile, Daoud [5]. They move along the pipe, sweeping up a stationary layer of particles in front of the plug and releasing a stationary solid layer behind it. Under such conditions, the velocity of the solids in the front  $V_{f}$  (or the back, Va) part of the plug is the sum of the solids velocity measured in the plug Vp and the velocity due to the particles swept up at the front (or deposited at the back) of the plug (Fig. 4). We can write:



Fig. 4 Definition of front (back) plug velocity as the sum of the solids velocity in the plug Vp and the velocity due to the particles being swept up at the front (or deposited at the back) of the plug



$$V_{f} = \frac{1}{S} \quad \frac{d\nu_{1}}{dt} + \frac{1}{S} \quad \frac{d\nu_{3}}{dt}$$
(1)

with: 
$$\frac{1}{S} \quad \frac{d\nu_1}{dt} = V_p$$
 (2)

Where:

 $\nu_1$  represents the volume occupied by the particles in the plug (velocity  $V_p)$  during the time dt.

 $\nu_3$  represents the volume of swept-up particles during the time dt.

$$d\nu_3 = S(h) dx$$
(3)

S(h) represents the cross-section of the stationary solids layer which is deposited at the bottom of the pipe. Its height is considered as a single function of gas flowrate, Tsuji [2].

Assuming the upper surface of the stationary layer is horizontal, S(h) can be calculated according to the following equation:

$$S(h) = 0.5R^2 (\varphi - \sin \varphi)$$
<sup>(4)</sup>

$$\varphi = \arccos \frac{R-h}{R}$$
(5)

With  $\varphi$  as defined in (**Fig. 5**).



Fig. 5 Cross-section of the stationary layer in the pipe

Substituting Eq. (2) and (3) in Eq. (1), the particle front and back velocities are:

$$V_{f} = \frac{S(h)}{S} V_{f} + V_{p}$$
(6)

$$V_a = -\frac{S(h)}{S} V_a + V_p$$
(7)

The particle velocity within the plug is obtained from the video camera by counting the number of frames required for a particular marked black particle to move over a 3 or 4 cm distance. The average value of  $V_p$  obtained by film recording when compared to the mean particle velocity predicted

by Eq. (6) and (7) agrees well, (Fig. 6).

This result was confirmed by comparing the measured plug length along the pipe with the one deduced from the calculated back and front velocities (Eq. (6) and (7)). The difference in velocity between the front and the back of the plug along the tube makes the plug length increase (**Fig. 7**).







Fig. 7 Comparison of front and back plug velocities along the pipe. Wg = 0.0040 kg/s

Thus, the time duration necessary for the front of the plug to move over a given distance x is expressed by the relationship:

$$\Delta t = \int_{0}^{X} \frac{1}{V_{f}} dx \qquad (8)$$

During that time, the back of the plug covers the same distance minus the plug length:

$$\Delta t = \int_{0}^{x-L_{b}} \frac{1}{V_{a}} dx \qquad (9)$$

Integrating Eq. (8) and (9) gives the  $L_b$  value which can be compared with the experimental one, (**Fig. 8**).

If the plug can be considered as a moving packed bed, the pressure drop due to interstitial gas flow





Comparison between experimental plug length measured Fig. 8 at several positions from the inlet with calculated value from Eq. (8) and (9).

can be calculated by using the modified Ergun equation as was confirmed by Konrad [6] and Tomita [1]. Then:

$$\frac{\Delta P}{L_b} = K_1 (V_g - V_p) + K_2 (V_g - V_p)^2$$
(10)

where:

 $V_g$  represents the interstitial air velocity:  $V_g = \frac{Q_b}{A\epsilon_b}$  $V_p$  is the particle velocity within the plug;  $L_{\rm b}$  is the plug length.

Assuming that the pressure drop through the  $L_v$ pipe portion separating two plugs is negligible compared to the one through the plug itself, pressure drop per unit length along the line can be written as:

$$\frac{\Delta P}{L_{T}} = \frac{\Delta P}{L_{b}} \frac{L_{b}}{L_{b} + L_{v}}$$
(11)

In a previous publication, Daoud [7] showed that the gas-particle slip velocity within a plug remained constant if the average pressure profile was linear along the pipe at a given gas flowrate. Therealong the pipe at a given gas howrate. There-fore  $\frac{\Delta P}{L_b}$  and  $\frac{\Delta P}{L_T}$  are constant. From Eq. (11), we can deduce that  $\frac{L_b}{L_V}$  remains constant along the pipe, and this has been confirmed experimentally. The variation of  $\frac{L_b}{L_V}$  with gas flowrate was difficult to come by from local measurements with the video camera. An indirect method was used. It was based on solids hold up measurements over a ten metre test zone (see Fig. 1). For a given gas flowrate, two pneumatic sliding valves were closed simultaneously and the solids hold-up weighed.

Since we have a series of plugs and slugs, the total mass of solids collected in such experiments are:

$$M_{s} = L_{b}Sp_{s} (1 - \varepsilon_{b}) + L_{v}S(h) p_{s} (1 - \varepsilon_{1})$$
(12)

where  $\epsilon_{\rm h}$  and  $\epsilon_{\rm l}$  are respectively the plug and the stationary layer porosities, both considered to be equal to  $\epsilon$  the bulk porosity.

The section of the stationary layer S(h) is deduced from Eq. (4) and (5) as a function of the gas flowrates (Fig. 9) by measuring the height of the solid layer for several gas flowrates at different points along the line. h was found to be constant along the line for a given gas flowrate. This was previously observed by Tsuji [2]. h (or S(h)) decreases with increasing Wg.



Fig. 9 Variation of the section of the stationary layer with line gas flowrate

In order to check the influence of the feed conditions on the flow behaviour along the line, the solids hold up measurements were performed using 3 different orifice plates located between the feeding hopper and the conveying pipe. The results presented in Fig. 10 show that the solids hold-up depends



Fig. 10 Variation of solids hold up between the two pneumatic valves 10 m apart with inlet gas flowrate for several orifice plate diameters

only on the volumetric gas flowrate at the entrance of the pipe, no matter what the orifice plate diameter is at the entrance of the pipe. On the other hand, the solids flowrate is strongly dependent on the orifice plate diameter as presented in Fig. 11. Solids





Fig. 11 Variation of solids flowrate with inlet gas flowrate for several plate diameters

flowrate is strongly dependant on the whole setup, whereas solids hold-up is specific to the horizontal plug flow regime. From visual observation, no difference appears when a diaphragm is introduced.

On the left side of figure 10, when Qt < 0,003 m<sup>3</sup>/s, the concentration  $\alpha$  defined by:

$$\alpha = \frac{M_s}{p_s (1-\varepsilon) S L_T}$$
(13)

is constant. In other words, the decrease of S(h) is compensated by the increase of the ratio  $\frac{L_b}{L_V}$  as shown in **Fig. 12**. The relationship between  $\frac{L_b}{L_V}$  and S(h) is obtained by substituting  $\alpha$  as defined in Eq. (13) into Eq. (12).



Fig. 12 Variation of  $L_b/L_v$  with inlet gas flowrate for several orifice plate diameters

On the right side of figure 10, the solids hold-up decreases linearly with the gas flowrate, and consequently the  $\frac{L_b}{L_V}$  value decreases as can be seen in **Fig. 12**.

We have shown in another work devoted to local plug length along a pipe that at any location, the plug length decreases with the gas flowrate (**Fig. 13**) and that for a given gas flowrate, the plug length



Fig. 13 Variation of plug length with gas flowrate. Measurements at location A (Fig. 1) 4 m after the elbow

increases along the pipe.

#### 4. Conclusion

In this work we examined the pneumatic transport of noncohesive granular solids in a horizontal pipe. From a previous article [7], the pressure drop through the plug is found to be well estimated by the modified Ergun equation. With this basic equation, we deduced - in the case of linear pressure profile – that the ratio  $\frac{L_b}{L_v}$  remains constant along the pipe for a given gas flowrate. We have also shown in this paper that when the solids hold-up is independent of the gas flowrate, this ratio increases with gas flowrate and decreases when the solids hold-up decreases with increase in gas flowrate. In the first part of this paper, we showed that the front (or back) velocity of the plug is the sum of two terms: the particle velocity within the plug and a velocity due to the sweep up (deposition) of particles at the front (or at the back) of the plug.

#### Nomenclature

А	: cross-section of the pipe
D	: pipe diameter
$D_0$	: orifice plate diameter
h	: height of the layer
$K_1$ and $K_2$	: constants of the Ergun equation
L <sub>b</sub>	: plug length
L <sub>v</sub>	: slug length
L <sub>T</sub>	: length of the horizontal pipe
Ms	: solid mass collected between the two
	pneumatic valves
Qt	: volumetric air flowrate introduced into
	the pipe
R	: pipe radius
S	: pipe cross-section
S(h)	: cross-section of the stationary layer
t	: time



V <sub>f</sub>	: velocity at the front of the plug
Va	: velocity at the back of the plug
Vp	: particle velocity within the plug
Vg	: interstitial air velocity
$\nu_1$	: volume occupied by the particles in the
	plug during the time dt.
$\nu_3$	: volume of swept-up particles during the
	time dt.
Ws	: solids flowrate
Wg	: gas flowrate
x	: axial abscise
$\frac{\Delta P}{I}$	: total pressure gradient
$\Delta \mathbf{P}^{\mathrm{T}}$	, programs anotiont in a plug
L <sub>b</sub>	: pressure gradient in a plug
α	: average superficial concentration
ε <sub>b</sub> , ε <sub>1</sub>	: porosity within the plug and in the stationary
	layer, respectively
3	: bulk porosity
$\varphi$	: angle defined on figure 5
p <sub>s</sub>	: solid density

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## Author's short biography



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Jean-François Large is born 1942. He graduated from the University of Nancy (Ecole Nationale Supérieure des Industries Chimiques), MSc (1965), PhD (1970). From 1973, he is Professor of Chemical Engineering at the Technical University of Compiègne and his research activity is mostly oriented to fluidization and particle technology. He is also scientific director for the engineering division of Rhône-Poulenc.



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## Rheological Investigation of Suspensions and Ceramic Pastes: Characterization of Extrusion Properties †

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#### Abstract

A large number of complicated catalyst geometries are produced by extrusion of plastic ceramic materials. The demands for high precision in the forming process and adequate formability of the materials are extremely stringent. As a first approximation, plastic ceramic materials can be treated as ordinary concentrated suspensions. Rheometric methods, in particular capillary rheometry, are especially suitable for testing of these materials. However, the flow processes occurring during extrusion are very complex, with many special effects such as wall slip, shear-thinning, shear hardening and high entrance pressure loss. As a result, apparent viscosity functions are not material functions. In spite of these difficulties, capillary rheometry, when critically applied, is an advantageous tool in the development of easily extrudable ceramic materials. The correlation of rheometrical test results with the extrusion process during production of honeycomb geometries is presented using aluminium oxide ceramics as an example.

#### 1. Introduction

A large number of products based on ceramic materials are shaped by extrusion. This is normally a continuous manufacturing process with its related technical and economic advantages. Traditional building trade products such as bricks and pipes are formed by extrusion of ceramic pastes.

The precision demands on these products are not very high, ranging up to tenths of a centimeter. Because ceramic pastes possessing natural formability have been handled for thousands of years, such low-precision requirements are easy to achieve. In recent years, ceramics have become important high-tech-materials in mechanical, electrical and chemical engineering as well as in the field of medicine. The precision demanded for such products is the same as that demanded for parts made from metals, i.e. in the range of microns. Many such products are formed by extrusion.

The typical objects made in enormous numbers by continuous extrusion include honeycomb-formed ceramic catalyst carriers for automobiles. An example of such a catalyst which has a cell wall thickness of less than two hundred microns is illustrated in **Fig. 1**. One can imagine that the development of the extrusion technology specially for the production of this highly complex item was extremely expensive and time consuming, even if the extruded material possessed a natural formability.

All clays based on flat, disc-like mineral particles possess good formability, even when tempered with pure water. These are materials with "natural formability". Other ceramic materials such as metal oxides possess no natural formability. The attempt to extrude catalysts from these materials may result in defective parts, such as shown in **Fig. 2**. Extrudable pastes require plasticizers as flow additives such as, for example, high-molecular-weight polymers.

At first glance, extrusion appears to be an ordinary flow process. Thus it seems reasonable to use rheometric methods for the straightforward development of the formability behaviour of pastes which do not possess natural formability.

Typical instruments for the investigation of the flow properties of pure and complex fluids such as particleliquid systems are shown in **Fig. 3**. Because of its correspondence to extrusion machines, the capillary rheometer seems to be the preferable instrument to characterize the formability of ceramic pastes. The velocity distribution within the measuring capillary is thought to be similar to the schematic in **Fig. 4** which corresponds to adhesion of the fluid to the capillary wall (v(R) = 0). It is important to note that all rheological quantities calculated from capillary

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Fig. 1 View of the cross-section of a ceramic catalyst for automobiles with a total diameter of 110 mm



Fig. 2 Catalyst carriers with typical extrusion defects



Fig. 3 Fundamental rheometric instruments





Fig. 4 Velocity distribution v(r) in a capillary for non-Newtonian fluids with wall adhesion

experiments, such as the shear stress  $\tau$  and the shear rate  $\dot{\gamma}$ , are related to the capillary wall.

From a rheological point of view, ceramic pastes are particle-fluid suspensions, with a flow behaviour which depends on the viscosity function of the liquid itself, the solid-liquid ratio (volume fraction of the solid), the particle size, or particle size distribution and the particle shape. It is generally well-known that the viscosity of a suspension increases with increasing solids content. Recent investigations show that at high shear stresses (or shear rates) the shear stress function of suspensions is primarily determined by the shear stress function of the suspending liquid (for both Newtonian and non-Newtonian liquids) [1]. This means that the flow behaviour of the suspension is controlled by the hydrodynamic forces within the pure liquid (i.e. between the particles).

At low shear rates, low shear stresses are generated within the suspension. In this case the relatively weak particle-particle interaction forces, which are generally independent of the relative velocity between the single particles, begin to dominate the total stress state. Therefore, in the case of low shear stresses, particle properties such as size, shape and surface activity determine the flow behaviour. The flow behaviour of suspensions is quite different from that of the pure liquid. Suspension behaviour is often significantly non-Newtonian, (especially at high solids concentrations) and a yield stress approaching  $\tau_o$  may exist. At stresses lower than  $\tau_o$  the fluid is not deformable.

As shown in **Fig. 5**, one generally finds that particle size affects the flow behaviour of concentrated suspensions in a manner comparable to solids concentration [2, 3].

From the shear stress function  $\tau(\dot{\gamma})$  of the pure silicone oil, one observes a slight deviation from Newtonian behaviour (pseudoplasticity) at high shear rates. At high shear rates, the shear stress functions of the suspensions filled with limestone par-



Fig. 5 Shear stress functions of a pure slightly non-Newtonian silicon oil and several limestone suspensions of different average particle size x. All suspensions have a solid volume fraction  $c_v$  of 30 %

ticles of various size form a unique curve. In the direction of the shear rate axis, a constant distance exists between this curve and the shear stress function of the suspending fluid despite an increase in the average particle size in the different suspensions from  $\times = 1.7$ to  $\times = 20.5 \ \mu m$ . The volume fraction solids is held constant at  $c_v = 0.30$ . This means that the flow behaviour is dominated by the shear stress function of the suspending fluid and remains independent of particle size, which is a surprising result. At low shear rates (and therefore low shear stresses), a significant influence of particle size on the shear stress function of the suspensions becomes apparent. With decreasing particle size, the shear stress measured at the same shear rate increases. This increase correlates with the increase in the number of single particles with decreasing particle size at a constant solids volume fraction.

- The influence of the particle collective (i.e. degree of polydispersity) on the flow behaviour of suspensions is (relatively) stronger at low than at high shear stresses.
- The shape of the particles, however, exerts a significant influence on the flow behaviour in both the high, as well as the low, shear rate region.

When investigating the formability of ceramic pastes by rheometric methods, different "shear stress functions" are usually measured when using different types of rheometers, as shown in **Fig. 6**. The "shear stress functions"  $\tau(\dot{\gamma}^*)$  of the same kaoline paste calculated from measurements with cone and plate-, couette and capillary-rheometers differ, in some instances, by a factor of ten. Even when  $\tau(\gamma^*)$  is determined using a single capillary rheometer with different capillaries, one obtains functions which differ significantly. A prediction of the flow behaviour in





Fig. 6 "Shear stress functions" of a china clay determined with different types of rheometers

a real process is therefore not possible. These "shear stress functions" are called apparent and are not real material functions. This uncertainty is a general problem in the rheology of highly filled suspensions which is often not taken into consideration in published measurements.

One reason for this uncertainty is that a velocity profile v(r), as demonstrated in **Fig. 4**, only exists in the case of fluid adhesion to the wall. If the paste slips at the wall of the shear gap, a complex velocity distribution emerges and the shear rate  $\dot{\gamma}^*$ calculated without considering slip is not the true wall shear rate. The quantity  $\dot{\gamma}^*$  is normally termed the apparent shear rate. The velocity distribution across the capillary when considering slip and internal deformation is shown in **Fig. 7**.



Fig. 7 Complete velocity distribution v(r) in a circular capillary for a fluid with wall slip effects.  $v_{\rm G}$  is the slip velocity and  $v^*(r)$  the velocity as a function of r due to the internal deformation of the fluid alone (the fluid has no yield stress)

The velocity distribution is a superposition of the velocity profile  $v^*(r)$  due to the internal deformation

of the fluid and a constant velocity  $v_{\rm G}$  which represents the slip velocity of the fluid in the proximity of the wall. The slip velocity  $v_{\rm G}$  has no influence on the internal deformation. The total volumetric flow rate  $\dot{V}$  is composed of two parts:

a cylindrical contribution  $\dot{V}_G$  from  $v_G$  and a parabolic contribution  $\dot{V}_S$  from  $v^*(r)$ . The real internal shear rate  $\gamma$  must be calculated from  $v^*(r)$  alone. For the calculation of the total volumetric flow rate  $\dot{V}$ , at least two separate material functions should be known: the slip velocity as a function of the shear stress  $v_G(\tau)$ , in order to calculate  $\dot{V}_G$ ; and the well known shear stress function  $\tau(\dot{\gamma})$ , which describes the internal deformation for the calculation of  $v^*(r)$  or  $\dot{V}_S$ . Experimental methods have been developed to separate  $v_G$  from  $v^*(r)$  [4 - 6].

#### 3. Typical flow properties of ceramic pastes

Ceramic pastes are, in principle, suspensions of very small particles dispersed at a high concentration in a liquid which may even be pure water. All of the previously discussed problems concerning high concentrations, influence of particle size and wallslip effects must be considered if the real flow functions of such materials are to be determined for the calculation of flow through complicated dies. This was not possible until now.

Bearing in mind the complicating effects which influence results obtained when testing concentrated suspensions, rheometric measurements with capillary rheometers were conducted to optimize the formability of ceramic pastes. An example test procedure is outlined in **Fig. 8** [7, 8].

The piston of a capillary rheometer can be moved at different constant speeds vst. This movement produces constant volumetric flow rates V<sub>i</sub> of paste through the capillary which are recorded with time t. The volumetric flow rate  $V_i$  generates a pressure drop  $p_i$ , measured simultaneously to  $V_i$  and also recorded with time. From V<sub>i</sub> and p<sub>i</sub>, the apparent shear stress function  $\tau(\dot{\gamma}^*)$  is calculated normally without considering the non-Newtonian flow profile and slip effects. For ideal ceramic pastes, a unique shear stress function is expected when using a single capillary. In the case of bad formability, the real rheometric measurements for ceramic pastes appear quite different, and no well-defined shear stress functions can be recorded. Typical shear stress functions of real pastes are presented in Fig. 9.





Fig. 8 Schematic of a capillary rheometer with typical diagrams  $\dot{V}(t)$ , p(t) and  $\tau(\dot{\gamma})$  as can be used for testing ceramic pastes

I:

If the ceramic paste is inadequately prepared and the suspension thus possesses an inhomogeneous water-solid distribution, no strict correlation will be obtainable between the pressure and the volumetric flow rate. The pressure oscillates with varying solid concentration and the shear stress function degenerates into a shear stress spectrum.

#### II:

The consistency of the paste can be influenced by the extrusion procedure itself. Because of the pressure drop, a disproportionately high volume flow rate of water through the capillary is possible (dewatering) and the solids concentration in the remaining paste is elevated. A steady increase of the pressure will be recorded even at constant volume flow rates. The shear stress function is only the lower boundary of an infinite shear stress range of infinite height.

#### III:

A pressure trend similar to that which results from dewatering can also be caused by micropore effects.

Because of the elevated pressure, a certain amount of the suspending liquid can be pressed into micropores. As the free water content is reduced, the paste becomes stiffer, and a pressure increase is recorded. Contrary to the dewatering process, a steady-state pressure is reached and the suitable shear stress function occupies a range between lower and upper limits (which depend on the duration of the experiment).

#### IV:

A very disadvantageous flow behaviour which causes severe damage to the extrudate is indicated in the pressure plot of example IV. At elevated volumetric flow rates, extremely high pressure values can be measured and consequently, the shear stress function becomes very steep at high shear rates, with a broad range of scattering. This effect is caused by a layer of hardened dry material which forms at high flow rates and high extrusion pressures along the capillary wall.

#### V:

A pressure plot which indicates excellent extrusion





Fig. 9 Characteristic pressure-time plots p(t) of real ceramic pastes with the suitable apparent shear stress functions  $\tau(\gamma^*)$ 

properties is demonstrated in example V. The steadystate pressure is nearly independent of the volumetric flow rate, whereby maximal and minimal values of the pressure only exist at the transition point to a higher or lower flow rate. This is the behaviour of a nearly ideal plastic material such as ceramic pastes with natural formability, e.g. china clays. The shear stress function has a plateau range in which the shear stress is essentially independent of the shear rate.

# 4. Experimental results from exemplary ceramic pastes

In order to correlate rheometric measurements with the real extrusion behaviour, the same material has to be tested in a complex forming tool. In **Fig. 10**, a tool for the extrusion of honeycombshaped catalyst carriers is shown [8]. The alternately



Fig. 10 Alternately coloured layers of ceramic pastes for the detection of flow patterns in the honeycomb extrusion

coloured ceramic paste in the cylinder can be pressed through the tool by the movement of the piston in the upper right of the picture. The differently coloured paste discs allow the flow patterns to become visible.



The volumetric flow rate functions and the pressure-time plots of two different ceramic materials are presented in detail in **Fig. 11**. The flow rate



Fig. 11 Volumetric flow rate-time and pressure-time plots of a plasticized technical catalyst carrier material, Pural SB (1) and a natural clay (2)

history (lower diagram) was the same for both materials. The clay with an almost pure plasticity (2) has a natural formability. The steady-state pressure values are nearly independent of the three different volumetric flow rates. Pressure peaks were only registered at the points when the volumetric flow rate was increased. After a short time, the pressure returns to a steady-state value. The decreasing transient pressure is caused by thixotropy of the material due to the structural arrangement of the flat clay particles along the capillary wall. The reduction of the volumetric flow rate in the last test range induces a pressure minimum followed by attainment of the original steady-state pressure.

The shear stress function  $\tau(\dot{\gamma})$  of the clay in **Fig. 12** has a plateau range which extends over nearly two decades of the shear rate. This is the typical trend of a shear stress function for a material possessing good formability. This material exhibits



Fig. 12 Shear stress functions of two different ceramic pastes

virtually no shear deformation in a capillary flow and the shape of the coloured discs remains undeformed as they pass through the cylinder of the test extruder [7, 8] (left-hand illustration of **Fig. 13**). The honeycomb catalyst carriers which were extruded from this material are exactly formed and possess a good surface quality (right-hand picture in **Fig. 13**).

This material shows a nearly pure slip behaviour without any internal deformation when pressed through a capillary. A true shear rate cannot be calculated for such ceramic pastes.

An apparent shear stress function with a steep increase of  $\tau$  at high shear rates was found in rheometric measurements of a paste based on a solid material called Pural SB (catalyst carrier material) with Luviskol as plasticizer in the liquid phase, **Fig. 14**. The pressure plot at high volumetric flow rates reveals very high maximas and extremely scattered values, as displayed in example IV of **Fig. 9**. The extrudate which emerges from the rheometer capillary is irregularly shaped and has a smaller diameter than the capillary itself (see inset diagram in **Fig. 14**).

A cross-section of the coloured paste sample reveals very irregular deformations, as seen in **Fig. 15**. The flow patterns reveal three distinctly separate regions: 1) a narrow range near the wall without



Fig. 13 Left: Cross-section through an alternately coloured natural clay sample which has passed through a cylindrical tube





Fig. 14 Shear strees function of a ceramic paste with poor extrusion formability



yields "negative" slip velocities as predicted by Schlegel and Weller [8]. The extrusion of a regularlyshaped honeycomb catalyst is not possible as the photo on the right-hand side of **Fig. 15** demonstrates. This Christmas-tree shaped body was intended to become a honeycomb catalyst carrier.

The same ceramic material Pural SB can be the basis of a paste with good extrusion properties provided that suitable plasticizers are used. The advantageous flow properties are evident from the shear stress functions shown in **Fig. 16** which are flat in comparison with the one shown in **Fig. 14** for the same basic ceramic material. Flat shear stress functions, with a smoothly increasing shear



Fig. 15 Flow patterns of a ceramic paste possessing unfavourable extrusion properties [7, 8]

axial deformation; 2) a rather small range with extended axial deformation where shear flow occurred; and 3) a broad core region with only small deformations. The undeformed paste near the wall (where the highest shear stress exists) indicates a shearhardened material layer. Most of the flow deformation occurs in a rather thin region whereas the core remains as undeformed as the narrow wall region. The attempt to separate the shear and slip flows



Fig. 16 Shear stress function of a ceramic paste based on Pural-SB with advantageous extrusion properties attained by the addition of suitable plasticizers

stress for an increasing shear rate, are similar to shear rate functions of natural clay, and generally indicate suitable extrusion properties. The reason for these good flow properties is that such materials form a plug-like velocity profile in a tube, with most of the deformation occurring in a thin flow layer near the wall, so that the main volume of the "flowing" material remains almost undeformed. This can be seen in the flow patterns on the left-hand picture of **Fig. 17**.

Contrary to the flow of a pure fluid, most of the paste transport occurs by slip effects in an extremly thin film at the wall. Only slight deformations can be identified across the bulk of the sample. The catalyst carrier depicted in the right-hand illustration demonstrates the formability of this paste.

Rheometric measurements on ceramic pastes with good natural or artificial formabilities lead to rather flat shear stress functions which sometimes include a plastic plateau range. In a capillary flow, only small internal deformations occur within the bulk of sample resulting in "plug flow" (like a rigid rod) through the capillary.

Part of the total pressure drop occurs immediately at the capillary inlet to shape the slim rod for the capillary. The degree of this inlet pressure loss can





Fig. 17 Left: Flow patterns of a ceramic based on plasticized Pural SB paste with rather good extrusion properties Right: Honeycomb catalyst carrier extruded from this material

be quantified by a method developed by Bagley [9] for the investigation of the true shear stress functions of polymer melts, as shown in **Fig. 18**.



Fig. 18 Bagley plot for the determination of entrance pressure losses  $% \left( {{{\mathbf{F}}_{{\mathbf{F}}}} \right)$ 

The total pressure loss of a fluid flowing at a constant volume rate must be measured with capillaries of different length. If the flow is isothermal and the viscosity independent of the hydrostatic pressure, then the total pressure loss itself increases linearly with the capillary length. The extrapolation of this straight line to zero capillary lengths yields the entrance pressure loss (as demonstrated in **Fig. 18**). This entrance pressure loss is sometimes predominant in the capillary flow of pastes. The true shear stress within the capillary can only be determined from the pressure gradient within the capillary and is equal to the slope of the straight lines in **Fig. 18**. If the shear stress from capillary experiments is calculated from the total pressure loss disregarding the entrance pressure loss, then an "apparent" shear stress is obtained, resulting in a separate shear stress function for each capillary length (even for a constant capillary diameter), as shown in **Fig. 19**.



Fig. 19 Apparent shear stress functions for the ceramic paste "A" measured by use of capillaries of different lengths

Since the entry pressure loss is a relatively high share of the total pressure drop (as can be seen in Fig. 19 for the example of the ceramic paste "A"), higher apparent shear stresses will be calculated from the total pressure drop when measured with a short capillary. In order to derive the real "viscous" pressure loss over the capillary, the entrance pressure must be subtracted from the total pressure. This procedure is known as the Bagley correction, and leads to "true" shear stresses. The true shear stress (lowest shear stress function in Fig. 19) of the ceramic paste "A" is independent of the shear rate or volumetric flow rate. Thus, the ceramic paste "A" (Pural SB with hydroxyethylcellulose as plasticizer) is a material with a good formability. The increase of the apparent shear stress with increasing extrudate velocity is only caused by the increase of the entrance pressure loss (Bagley pressure).

If the Bagley pressure measured for material "A" is plotted as a function of the total extrusion pressure p, one obtains a straight line with a 45 degree slope



as can be seen in **Fig. 20**. The increase of the extrusion pressure is equal to the increase in the Bagley pressure. For this ceramic paste, the internal capillary pressure loss is constant, and is independent of the total extrusion pressure.



Fig. 20 Relation between the extrusion pressure and the Bagley pressure

The flow patterns of the ceramic paste are shown in **Fig. 21**. They exhibit nearly ideal plastic behaviour similar to that obtained with natural clay, shown in **Fig. 13**. This flow behaviour is caused by a special type of plasticizer.



Fig. 21 Flow patterns for ceramic paste A

The ceramic paste "B" is also based on Pural SB but with NAL (ammonium alginate) as the plasticizer. The apparent shear stress function measured with two capillaries of different length also yields higher apparent shear stresses for the shorter capillary. The increase of  $\tau$  (Fig. 22) is stronger with increasing extrudate velocity in comparison with ceramic paste "A".

The essential difference in the results for paste "B" compared with paste "A" is that not only the apparent shear stress, but also the true shear stress increases significantly with extrusion velocity or shear rate. **Fig. 20** shows that the Bagley pressure increases nearly proportionally to the total extrusion pressure. At all extrusion velocities, the total pressure drop consists of proportional contributions from



Fig. 22 Apparent shear stress functions for ceramic paste "B" measured with capillaries of different length

the deformation processes at the capillary inlet (entrance pressure losses) and from losses within the capillary.

The flow patterns in Fig. 23 indicate that within the capillary, the ceramic paste is subjected to weak shear deformations different from those exhibited by ceramic paste "A", which passes through the capillary in a rod-like shape. Good honeycomb catalysts may be extruded from both materials.



Fig. 23 Flow profiles for the ceramic paste "B"

The flow behaviour of the ceramic pastes "A" and "B", which are based on the same solid material, was altered by changing the type of liquid phase. Separation of the entrance pressure losses from the "flow" pressure drop within the capillary can help in distinguishing the internal deformation behaviour of "externally" similar materials.

#### 5. NMR-Imaging of ceramic pastes

Good knowledge of the flow patterns is extremely helpful in understanding and predicting the extrusion properties of pastes. In order to visualize the defor-



mation process, the paste can be marked by alternately coloured layers. This technique has been used successfully in Figs. 10, 15, 17, 21 and 23. A new and very promising alternative method of visualizing paste flow patterns is the NMR-Imaging technique. This has been employed in |10| to investigate the extrusion behaviour in a ram extruder. Results using limestone pastes with water contents between 23% and 29% and oxide ceramic pastes (Pural) with water contents of 23% to 76% have shown that NMR-imaging is a non-invasive technique which allows successive exposures to be taken of a single sample during an experiment, thus providing an animation of the flow process in the interior of the specimen.

**Fig. 24** shows a schematic of the ram extruder used. The paste is prepared by marking individual layers with a contrast medium (Magnevist). In addition, 2 mm glass spheres are imbedded, providing information concerning the axial and radial displacement of the paste.



Fig. 24 Schematic of the ram extruder

Fig. 25 shows a sequence of 8 successive NMRimages of a limestone paste with 25% water during extrusion. Fig. 26 presents particle trajectories constructed from the displacement of the glass spheres.

**Fig. 27** shows a series of subsequent images (from left to right) of Pural paste, with hydroxyethylcellulose as an additive, in the immediate vicinity of the right wall. Obviously a thin wall shear layer exists, in which the paste is subjected to extremely large shear deformations.

#### 6. Final remarks

Ceramic pastes are, in principle, suspensions possessing extremely high solid concentrations. Their flow behaviour at low deformation rates is dominated by particle-particle interactions and is therefore



Fig. 25 Limestone with 25% moisture content at six successive instants



Fig. 26 Particle trajectories of the 2 mm glass spheres in a 76% moisture content Pural paste with a cellulose additive (1% of the fluid mass)



Fig. 27 Series of a Pural paste with hydroxyethylcellulose near the wall

totally different from that of the suspending liquid. The flow laws derived for moderately concentrated suspensions cannot be applied, since they only quantify flow behaviour changes as a function of solid content and/or particle characteristics.

Investigations of the extrusion properties of ceramic pastes by rheometric methods must be conducted with care because the paste transport through a capillary is not simply an ordinary flow process. The transport is a mixture of different phenomena such as wall slip, internal shear deformations, shear hardening near the wall, and extraordinarily high



capillary entry pressure losses. The combination of these phenomena defines the formability of ceramic pastes. Flow functions calculated from capillary measurements without considering these different effects are not real material functions, and therefore cannot form the basis for quantitative predictions of extrusion processes.

All these phenomena can be separated by applying rheometric methods and may also be separately influenced by the addition of specific plasticizers. Because the basic solids of ceramic material are normally invariant, the formability of such pastes can only be optimized by changing the properties of the suspending fluid (which also changes the particle-particle interactions). The influence of specific particle properties can only now be directly quantified for high solid contents.

Optimization of the extrusion properties of ceramic catalysts will be a future research programme once the fundamental problems have been solved. The formability of ceramic pastes can only be optimized in a reasonable manner by rheometric measurements.

Materials with good extrudability can be identified by their specific apparent shear stress function. Capillary rheometry, when critically applied, is therefore an advantageous tool in the development of easily extrudable ceramic pastes.

#### Nomenclature

c <sub>v</sub>	: solid volume fraction in a suspens	sion
D	: capillary diameter	[m]
Dĸ	: diameter of the barrel	[m]
F	: cross-sectional area of the barrel	[m <sup>2</sup> ]
FA	: axial force	[N]
Ĥ	: cylinder height	[m]
L	: capillary length	[m]
M <sub>d</sub>	: torque	[Nm]
N <sub>1</sub>	: first normal stress difference	[Nm <sup>-2</sup> ]
p	: pressure difference	[Nm <sup>-2</sup> ]
p <sub>B</sub>	: Bagley pressure correction	[Nm <sup>-2</sup> ]
r	: radius	[m]
R	: maximal radius	[m]
R <sub>a</sub>	: outer shear gap radius	[m]
R	: inner shear gap radius	[m]
R	: mean value of gap radius	[m]
s	: width of shear gap	[m]
t	: time	[s]
v	: piston speed	[m s <sup>-1</sup> ]
v <sub>D</sub>	: extrudate velocity	[m s <sup>-1</sup> ]
v <sub>G</sub>	: slip velocity	[m s <sup>-1</sup> ]
v*(r)	: radial velocity distribution	[m s <sup>-1</sup> ]

V	: volume rate	[m <sup>3</sup> s <sup>-1</sup> ]
V <sub>G</sub>	: slip volume rate	[m <sup>3</sup> s <sup>-1</sup> ]
	: shear volume rate	[m <sup>3</sup> s <sup>-1</sup> ]
x	: mean value of particle size	[m]
α	: shear gap angle	[radian]
$\dot{\gamma}$	: shear rate	[s <sup>-1</sup> ]
$\dot{\gamma}^*$	: apparent shear rate	[s <sup>-1</sup> ]
$\dot{\gamma}_{ m ap}$	: apparent shear rate	[s <sup>-1</sup> ]
$\dot{\gamma}_{i}^{-r}$	: shear rate at the inner radius	[s <sup>-1</sup> ]
η	: viscosity	[Nm <sup>-2</sup> s]
ω	: angular velocity [ra	dian s <sup>-1</sup> ]
τ	: shear stress	[Nm <sup>-2</sup> ]
$ au_{ m B}$	: shear stress (Bagley corrected)	) [Nm <sup>-2</sup> ]
$ au_{:}$	: shear stress at the inner radius	s [s <sup>-1</sup> ]

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## The Use of Standpipes for Increasing Limiting Gravitational Flowrate from Mass Flow Bins †

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#### Abstract

This paper provides an experimental and theoretical examination of the use of standpipes to increase the limiting flowrate by gravity from mass flow bins. The results indicate that the effect of a standpipe attached under the hopper outlet is greater as the particle size becomes smaller and the length of the standpipe becomes longer, provided the standpipe remains full of solids.

#### 1. Introduction

It is recognized that the flowrate of fine powder from mass flow bins can be orders of magnitude less that the flowrate obtainable for coarse powders<sup>1)</sup>. It is clear that the limiting flowrate of fine material mainly is caused by the self-generated negative air pressure gradient at the outlet of a bin. Therefore, one of the most important strategies for increasing the limiting flowrate is to reduce the interstitial pressure gradient, especially that at the outlet. There are various possibilities to achieve this improvement in flowrate, such as reducing the surcharge level, air permeation techniques, and the use of a standpipe. Of these possibilities, the use of a standpipe, which can assist in increasing the flowrate of fine powders without reducing the storage capacity in the bin (as in reducing the surcharge level) or requiring a low pressure supply of high quality air (as in air permeation), is a practical technique applying to industrial problems. The simple addition of a vertical non-converging pipe to the bottom of an existing mass-flow hopper produces a pressure gradient in the standpipe and creates a vacuum at the hopper outlet. This suction effect substantially increases the flowrate of bulk solids from the hopper, as found in many research studies<sup>1-9)</sup>. The effect of the standpipe increases as the particle size becomes smaller and the length of the standpipe becomes longer.

However, most researchers such as Yuasa et al.<sup>3)</sup>,

Ginestra et al.<sup>6)</sup> and Chen et al.<sup>7)</sup> studied a very long standpipe with the ratio between standpipe length and diameter being more than 100. This kind of long standpipe is not applicable in industry for the purpose of increasing the flowrate of bulk solids from bins, due to headroom restrictions. Hence, some work needs to be done to study the extent to which the flowrate is increased by a standpipe with a limited length. In this paper some experimental observations and a pilot theoretical investigation on the flow of bulk solid from a mass flow bin and standpipe configuration are reported.

#### 2. Experiments and observations on standpipes

#### 2.1 Test Apparatus

The experiments were carried out on a modified double-bin apparatus; a standpipe was installed at the outlet of the test bin of the double-bin apparatus, as shown in **Fig. 1**. The standpipes used in the experiments had length-to-diameter ratios  $(L/D_0)$  of 1, 2, 3, 4, 5 and 10 ( $D_0 = 0.0445$  m). The joint between the standpipe and the outlet of the hopper was sealed to avoid air leakage. A belt feeder was only used for the longer test standpipes ( $L/D_0 = 5$ , 10) to obtain a steady flowrate. A chart recorder was used to record the mass variation in the bin-standpipe configuration versus discharge time. The flowrate was calculated by differentiating the mass curve with respect to time.

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<sup>&</sup>lt;sup>†</sup> This paper is based on a paper presented at the 4th Int Conf an Bulk Materials Storage Handling and Transportation and 7th Int Symp on Freight Pipelines, sponsored by the Institution of Engineers Australia and held at Wollongong, Australia on 6-8 July 1992.





Fig. 1 Standpipe installed at the outlet of the test bin.

#### 2.2 Experimental Observations

i) Attainable Flowrate by Using the Standpipe

Observations were made on the flowrate improvement attainable using alumina as the bulk solid. Fig. 2 summarizes the results. Generally, the flowrate increased with the length of the standpipe. Specifically, as the standpipe length increased the flowrate increased slowly at first then at a faster rate. For instance, a short standpipe ( $L/D_0 = 1$  and 2) increased the flowrate by less than 20% while the standpipe with  $L/D_0 = 5$  provided an increase in flowrate of 200% for the alumina. However, as the standpipe became longer, the flowrate did not continue to increase at this rate. Actually, the rate of the increase in flowrate reduced, e.g., the flowrate increased by 300% for the standpipe with  $L/D_0 = 10$ .



Fig. 2 Flowrate vs.  $L/D_0$  ratio of standpipe for alumina (Surcharge level H = 0.31 m)

#### ii) Problems When Using a Standpipe

As the higher flowrates were approached with the long standpipe, fluctuations in the flowrate were observed. These fluctuations are explainable by two typical discharge modes observed for material flowing through the standpipe: in one mode the standpipe was partially filled with the bulk solids, while in the other mode the standpipe was filled fully with the solids. The higher flowrate occurred only as long as the standpipe was full of material; in this situation the bulk solid discharging from the standpipe effectively entrains the air in the voids between particles inducing an efficient suction on the particle flow from the hopper. For a partially filled standpipe this suction is not generated as effectively resulting in a lower flowrate. The transition state between these two flow modes resulted in flow instability. Matsen<sup>10)</sup> suggested that this instability is caused by a bubble held stationary in the standpipe. Instability of the flow is a common phenomenon when using a standpipe. The same problems have been also reported by Johanson<sup>9)</sup> and Leung et al.<sup>11,12)</sup>. In addition a jump phenomenon has been reported by Chen et al.<sup>7)</sup> between the upper and the lower bound flowrate in some situations, with the actual bounds differing by an order of magnitude.

To reduce the extent of these fluctuations and to ensure that the standpipe remained full at all times a belt feeder was installed under the standpipe. With the belt feeder installed, the maximum steady flowrate attained, using the standpipe of  $L/D_0 = 5$ , was 0.728 kg/sec (**Fig. 3**), which represents 97.4% of the maximum attainable flowrate for discharge from this test bin. As Johanson<sup>9)</sup> pointed out, it is essential that the feeder controls the flow slightly below the limiting rate as the higher flowrate occurs only as long as the standpipe remains full of solids.



Fig. 3 Flowrate vs. feeder belt velocity for different clearances between feeder and standpipe  $(L/D_0 = 5)$ 



For a short standpipe, e.g.,  $L/D_0 = 1$ , a significant increase in flowrate cannot be obtained. This is due to the low suction effect generated or even, in most cases, an ineffective suction due to the boundary effect (the outlet of the standpipe is close to the hopper outlet).

# 3. Modelling the flowrate of bulk solids from a bin-standpipe configuration

A theoretical model, based on the model developed by Gu et al.<sup>13,14)</sup> for predicting the pressure gradients and the flowrate of bulk solids, has been established to explain the experimental observations for the standpipe.

In this model the geometry of the mass flow bin with a standpipe installed is divided into four regions, as shown in **Fig. 4**.



Fig. 4 Four regions for bin-standpipe configuration

The assumptions used are as follows:

- i. The bulk solid and interstitial air flows are continuous so that the model presented can be based on continuum mechanics theory. The flowrates of particles and air at any cross-section in a mass flow bin are constant.
- ii. The dynamic deaeration at the top surface of bulk material is proportional to the flowrate of particles.
- iii. The principal stresses are assumed to be vertical in region I, radial in region III while the region II is regarded as a transitional region. The standpipe remains dull of bulk solid with the stress distribution in region IV being linear with respect to height.
- iv. The walls of the hopper and the standpipe are smooth so that the effect of wall friction can be disregarded.

v. The location of the minimum interstitial air pressure for the bin-standpipe configuration  $(h_{mp})_{sp}$  is in the hopper section between  $h_{mp}$  and  $h_0$  for a standpipe with a limited length. The effective suction induced by the standpipe is assumed to be dependent on the length of the standpipe.

$$(\eta_{\rm mp})_{\rm sp} = \eta_0 \ 1 + \frac{\eta_{\rm max} - \eta_0}{1 + \eta_0} \ e^{-\frac{\lambda L}{D_0}}$$
 (1)

where

- $\lambda$  = standpipe effect coefficient; (0 <  $\lambda$  < 1).
- $\eta = \frac{h}{h_1}$  for all the relevant subscripts depicted in Fig. 4.

The assumption v. does not allow the minimum interstitial air pressure to be located in the standpipe section and, consequently, to induce a flowrate greater than that possible without any negative air pressure effect. It is believed that this assumption is reasonable for standpipes with limited length, however, the location of the minimum interstitial air pressure in the standpipe section is possible with longer standpipes.

Considering the above assumptions, the air pressure gradient at the hopper outlet for the bin-standpipe configuration will be evaluated in a similar way to that in Gu et al.<sup>13)</sup> while the flowrate of bulk solid will be predicted by the flowrate model in Gu et al.<sup>14)</sup>. By adopting these models the following quadratic equation, for predicting the flowrate of bulk solid from the bin-standpipe configuration, is obtained:

$$q_1 Q_p^2 + q_2 Q_p - g = 0$$
 (2)

where the first term represents the inertial force of flowing bulk solid; the second term evaluates the resistance to flow caused by the interstitial air pressure gradient and the third term evaluates the effect of the body force due to gravity. The coefficients  $q_1$ and  $q_2$  are determined by the flow properties of the bulk solid (bulk density constants  $-p_0$ ,  $b_1$ ,  $b_2^{-15}$ ), permeability constants  $-C_0$ ,  $a^{-15}$ , internal friction angle of the bulk solid  $\delta$ ), the geometry of the binstandpipe configuration (the hopper half angle  $\alpha$ , the diameter of outlet  $D_0$ , the diameter of the vertical bin section D, and the length of the standpipe L) and the extent of material storage in the bin (material surcharge level H).



#### Theoretical predictions and discussion 4.

To verify this theoretical model, the flowrates of alumina flowing from the test bin with a 0.0445 m outlet have been predicted and compared with the observed flowrates. A comparison of the theoretical results with the experimental results, for a sequence of fixed values of the coefficient  $\lambda$ , is depicted in Fig. 5. The value of  $\lambda = 0$  implies no effect of the standpipe on the minimum pressure position.

The comparison indicates that the predicted flowrate increases with increase in standpipe length, although for the standpipe with a lower L/D<sub>0</sub> ratio the theoretical results are over-predicted. The overprediction of the flowrate at lower  $L/D_0$  ratio may be caused by a different flow mode in the standpipe. In particular the theoretical results are based on the assumption of the standpipe being completely filled with solids. As the belt feeder was only used in the experiments with the long standpipe  $(L/D_0 = 5)$ , it may be possible that the "standpipe-full" condition for the lower L/D<sub>0</sub> ratio standpipes did not match the assumption. Hence a lower suction effect may have occurred in the experimental standpipe mentioned in Section 2.2.

The predicted and measured flowrates depicted in Fig. 5 lie between the flowrate bounds calculated assuming maximum negative air pressure gradient at the hopper outlet (lower bound) and no air pressure gradient at the hopper outlet (upper bound). This confirms that the location of the minimum interstitial air pressure is in the hopper section for a standpipe with a limited length and it is affected by the length of the standpipe. For the results obtained in Fig. 5, it seems that  $\lambda = 0 \sim 0.05$  as  $L/D_0 \le 4$  and  $\lambda = 0.75$ as  $L/D_0 \ge 5$ , although further systematic work is required before reaching a general conclusion. For the moment, the further discussion is based on the results



Fig. 5 Predictions of flowrate vs. L/D<sub>0</sub> ratio

for the case of  $\lambda = 0.75$ .

The theoretical model can be used to predict the effect of material permeability on the flowrate from a bin standpipe configuration. In particular this effect can be quantified by defining an enhancement factor  $F_{sp}$  as the ratio of the flowrate with a standpipe to that without a standpipe. Fig. 6 shows the calculated variations of enhancement factor  $F_{sp}$  with  $L/D_0$  ratio for alumina, Sand MD2 and Sand M1, which have the permeability constants 398, 1054 and 6518\*10-9  $(M^4N^{-1}Sec^{-1})$  respectively. The variations depicted in Fig. 6 clearly indicate that a standpipe can create a higher flowrate enhancement for finer bulk solids than for coarse materials. Specifically, the flowrate enhancement factors produced by a standpipe with  $L/D_0 = 7$  are 4, 2 and 1.06 for alumina, Sand MD2 and Sand M1 respectively. These results coincide with other researchers' results, as illustrated in Table 1, indicating that the use of a standpipe increases the flowrate more effectively for fine material than for coarse material.



Fig. 6 Enhancement factor for different materials

The increase in flowrate using the standpipe is caused by the vacuum suction at the hopper outlet and a reduction of the negative air pressure gradient. This is evident from Fig. 7 and Fig. 8 which show the variations of predicted air pressure and air pressure gradients at the hopper outlet for the fine



Fig. 7 Predicted air pressure at the hopper outlet


Researcher	Material used (Particle size or permeability constant)	Diameter of standpipe D <sub>0</sub> (m)	Dimensionless length of standpipe L/D <sub>0</sub>	Enhancement factor F <sub>sp</sub>
Chen et al. in 1984 <sup>7)</sup> (Experimental	Fine sand $d_{50} = 154 \mu m$ Coarse sand	0.0254	130	8
results)	$d_{50} = 556 \mu m$			2.5
Ginestra et al. in 1980 <sup>6)</sup> (Predicted results)	Unnamed material $\delta = 30^{\circ}$ $V_t = 0.1$ m/sec.	0.030	100	7 ~ 8
Knowlton et al.	Sand 53 - 177μm			6.4/5.6
in 1986 <sup>8)</sup> (Measured/	Sand 177 – 420µm	0.038	185	4.6/5.3
predicted)	Sand 420 – 840μm			3.3/3.6
	Glass beads $d_{50} = 127 \mu m$			5.9
Yuasa et al. in 1972 <sup>3)</sup>	Glass beads d <sub>50</sub> = 254µm	0 0091	165	3.25
(Measured results)	Glass beads $d_{50} = 505\mu m$	0.0001	100	2.11
	Glass beads $d_{50} = 1015\mu m$			1.5
Current experimental results	Alumina $d_{50} = 100 \mu m$ $(C_0 = 398.38)^*$	0.0445	5	3.14
Predicted	Alumina $d_{50} = 100\mu m$ $(C_0 = 398.38)^*$			4
results by current model	Sand MD2 $d_{50} = 200\mu m$ $(C_0 = 1054.4)^*$	0.0445	7	2
	Sand M1 $d_{50} = 310\mu m$ $(C_0 = 6517.5)^*$			1.06

Table	1	A	summary	of	the	results	in	using	standpi	nes
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\* permeability constant  $C_0$  (\*10<sup>-9</sup> m<sup>4</sup> N<sup>-1</sup> s<sup>-1</sup>)

material alumina and coarse material Sand M1, respectively. Corresponding to these results, **Figs. 9** and **10** show the air pressure distributions in the bin and standpipe generated by alumina and Sand M1 respectively.

From Fig. 9 and Fig. 10 it can be seen that the predicted air pressure distribution in the standpipe is a linear function of the depth for short standpipes, while it is a nonlinear variation for long standpipes.

In contrast, Yuasa et al.<sup>3)</sup>, Chen et al.<sup>7)</sup> and Knowlton et al.<sup>8)</sup> observed an almost linear relationship between negative air pressure and the depth in the standpipe in most of their experiments. The nonlinear relation produced by the current model may be caused by the constraint of the minimum air pressure position within the hopper section. Indeed, for a very long standpipe, the experimental results obtained by Yuasa et al., Chen et al. and Knowlton et al. (for standpipes





Fig. 8 Predicted air pressure gradient at hopper outlet



Predicted air pressure distributions in the bin and the Fig. 9 standpipe for alumina.



Fig. 10 Predicted air pressure distributions in the bin and the standpipe for sand M1.

of  $L/D_0 \ge 100$ ) show the occurrence of the minimum air pressure below the hopper outlet. In this case, a higher flowrate can, theoretically, be produced by the standpipe since the positive air pressure gradient developed at the hopper outlet accelerates the particle flow.

#### 5. **Concluding remarks**

The use of standpipes to increase the limiting flowrate by gravity was examined both theoretically and experimentally. The results indicate that

• the use of standpipes can increase the flowrate

significantly for fine particles (lower permeability materials) and insignificantly for coarse particles (higher permeability materials);

- The longer the standpipe, the more significant the suction effect induced by the standpipe and the higher the flowrate that can be obtained. However, the rate of increase in flowrate due to the suction effect is not proportional to the length of standpipe with three different periods being apparent, as the length of standpipe increases. This suggests that
- a standpipe with a length limited by practical i) constraints, can be efficiently used for increasing the flowrate;
- ii) the flowrate enhancement to be gained by using standpipes with very large L/D<sub>0</sub> ratios may not warrant the extra headroom required.

A standpipe is only efficient when it is kept full of bulk solid. This suggests that some precaution needs being taken to ensure that the standpipe remains full, for instance, by using a feeder under the standpipe outlet to control the flowrate. There seems to be an optimal standpipe L/D<sub>0</sub> value to achieve beneficial flowrate enhancement and the prediction of this optimal value needs further investigation.

#### Nomenclature

а	: exponent used to relate permeability to
	consolidation stress
b <sub>1</sub> , b <sub>2</sub>	: constants in consolidation-related bulk
	ensity equation models
C <sub>0</sub>	: bulk solid permeability at lowest com-
Ŭ	paction, *10 <sup>-9</sup> (m <sup>4</sup> N <sup>-1</sup> s <sup>-1</sup> )
d <sub>50</sub>	: median particle size (µm)
D	: diameter of vertical section of the bin (m)
D <sub>0</sub>	: outlet diameter of the hopper, diameter of
Ū	the standpipe (m)
F <sub>sp</sub>	: flowrate enhancement factor due to the
σp	use of standpipe (-)
g	: gravitational acceleration (m/s <sup>2</sup> )
h	: vertical distance measured from vertex
	of hopper (m)
h <sub>o</sub>	: vertical distance from vertex of hopper
0	to outlet hopper (m)
h,	: vertical distance from vertex of hopper to
1	transition of a hopper (m)
	** · · ·

- $h_{0sp}$ : vertical distance from vertex of hopper to outlet of standpipe (m)
- : vertical distance from vertex of hopper to h <sub>mp</sub> minimum pressure position - no standpipe case (m)



- $(h_{mp})_{sp}$  : vertical distance from vertex of hopper to minimum pressure position with standpipe (m)
- H : material surcharge level, defined as the height of bulk solids in vertical section of the bin (m)
- L : length of the standpipe (m)
- $\mathbf{q}_1,\,\mathbf{q}_2$  : coefficients for flowrate model, eqn (2)
- $Q_p$  : flowrate of a bulk solid (kg/sec)
- $V_t^{F}$  : terminal velocity of a bulk solid (m/sec)
- $\alpha$  : hopper half angle (degree)
- δ : bulk solid effective angle of internal friction (degree)
- $\eta$  : dimensionless vertical distance from the vertex of hopper,  $\eta = \frac{h}{h_1}$
- $\lambda$  : standpipe effect coefficient
- $p_0$  : bulk solid density at lowest compaction  $(kg/m^3)$

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## Interparticle Friction in Granular Ceramic Materials †

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#### Abstract

The frictional behaviour of dry ceramic materials in the form of spherical beads, sand and spray dried powders has been studied. Measurements were made using standardized flow time, shear cell methods and die pressing. Flow time was found to provide a poor measure of internal friction for coarse material. Internal friction increased with decreasing particle size and deviations from sphericity. Powders with high specific surface area had low apparent and tap density and flowed poorly if at all under gravity loading conditions. However, shear cell and die press experiments showed the coefficient of internal friction measured at load was not sensitive to this parameter. The coefficient of internal friction calculated from shear cell measurements in which the maximum stress was 0.4 MPa was in good agreement with that deduced from die stresses during die pressing to 300 MPa, even when particle fracture occurred at the higher pressures, provided the morphology did not change appreciably.

#### 1. Introduction

The flow characteristics of granular materials depend to a great extent on friction between adjacent particles. This mechanism is of great importance in many problems involving the flow of granular or powdered materials in bulk materials handling and the powder metallurgy and ceramic fabrication industries.

Of engineering interest is the flow behaviour over a wide range of loading conditions ranging from neargravity loading in hoppers and die filling operations, to high pressure loading of the kind used in crushing or compaction operations. This flow behaviour affects, amongst other things, loads on containment surfaces and uniformity of bulk density.

Interparticle friction is known to depend on particle morphology and size distribution. It is commonly characterised in terms of the average bulk behaviour of representative samples of the granular material. A number of measures are in widespread usage. Some apply to flow and packing under gravity load conditions. Examples include flow-time tests for a known mass, apparent and tap density, and derived quantities such as the Hausner ratio 1). Other measures are based on the response of the granular material to applied load using for example shear cells of the kind developed to study the failure characteristics of soils and similar granular materials 2, 3). The shear cell measurements provide the coefficient of internal friction in the granular body up to applied normal stresses of about 2 MPa. The nature of this internal friction depends on the nature of the load applied to the granular material. At low loads it may be due to just interparticle friction processes as relative movement occurs between adjacent particles. At higher loads after particle interlocking occurs, it may be some complex combination of this and the yield or fracture properties of the particle material. Measurements of axial and radial stresses in rigid die pressing during either quasi-static 4, 5, 6) or dynamic 7) compaction, or triaxial cell stress measurements 8) can also provide measures of internal friction at applied loads at least 2 orders of magnitude higher than those available in shear cells.

Considerable progress has been made in characterising the flow behaviour of specific granular materials 9, 10) but the linkage between micromechanical features and macroscopic measures of internal friction is not well understood.

This paper describes a study of the frictional characteristics of several dry ceramic granular materials including course beads, sand and spray dried powders, in which the influence of particle morphology, size and size distribution on internal friction was considered. The internal friction was characterised using a number of methods valid individually over

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a range of applied stresses. Thus, the generality of the measures of internal friction, and their relation to morphology and size characteristics could be determined.

#### 2. Experiment and analysis

#### 2.1 Granular materials

Particle size, shape factor and specific surface area were chosen to characterise the granular material studied. Many descriptors are used to characterise morphology. Those adopted in this study were chosen as representative of those in widespread use. Shape factor provides a simple measure of geometry effects at the particulate level, whereas specific surface area is related, at least in part, to particle surface texture.

In all, 15 different samples of granular material were used in the study. These are shown together with important particle parameters in **Table 1**. The diameter and shape factor were calculated from two dimensional images generated on a Quantimet 570 Image Analyser. The mean diameter shown is the spherical equivalent given by  $(4A/\pi)^{0.5}$  whereas the shape factor is  $P^2/(4\pi A)$  in which P is the perimeter and A the projected area. So defined, the shape factor for a sphere is 1. For materials 13, 14 and 15, the specific surface area was measured using the

BET method. For the coarser powders for which a figure is shown it was estimated for comparative purposes assuming a closely spherical shape. As such it is a lower limit only approached by material with near unity shape factor and no surface roughness or porosity.

Materials 1, 2 and 3 were solid beads made from yttria stabilized tetragonal zirconia polycrystal (Y-TZP) supplied by ICI Advanced Ceramics, Melbourne. These were chosen for their near spherical geometry and smooth surface as shown in **Fig. 1** for material 3, that of nominal diameter 0.1 mm. The surface details shown were typical of that observed for all the bead material (1, 2 and 3). Materials 4, 5 and 6 were precisely measured blends of the bead material, blend 6 corresponding to the maximum packing density possible from spheres of these sizes 11). These spherical particle systems were included in the study to unambiguously decouple size and shape effects on frictional behaviour.

Commercially available sands from two local sources were also studied. One, sand (a), was from Stradbroke Island. A micrograph of this material is shown in **Fig. 2**. This in its "as supplied" form was material 7 in the study. The sieve analysis for this sand was done according to BS 410-1986 and the results are shown in **Fig. 3**. Two of the sieve fractions of this

	TABLE 1 – MATERIAL TESTED									
No.	Material	Mean Dia. (µm)	Mean Shape Factor	Specific Surface Area (m <sup>2</sup> /g)	Apparent Density (kg/m <sup>3</sup> )	Tap Density (kg/m <sup>3</sup> )				
1	Y-TZP monosized beads	946	1.05	0.0010	3655	3656				
2	Y-TZP monosized beads	294	1.06	0.0034	3581	3608				
3	Y-TZP monosized beads	94	1.04	0.0106	3272	3752				
4	60/40 wt% of 2/3	103	1.0	0.0096	3789	4128				
5	70/30 wt% of 2/3	108	1.0	0.0092	3848	4096				
6	66.4/24.5/9.1 wt% of 1/2/3	116	1.0	0.0085	4044	4136				
7	SiO <sub>2</sub> sand (a) (as supplied)	290	1.48	0.0038	1412	1550				
8	212-300 µm fraction of 7	250	1.19	0.0045	1432	1552				
9	150-212 $\mu$ m fraction of 7	190	1.16	0.0051	1382	1531				
10	SiO <sub>2</sub> sand (b) (as supplied)	310	1.28	0.0036	1486	1613				
11	212-300 µm fraction of 10	220	1.22	0.0051	1537	1651				
12	150-212 μm fraction of 10	180	1.52	0.0063	1416	1568				
13	Y-TZP (SY-ULTRA)	0.92	1.17	15.4	1132	1294				
14	Y-TZP (SYP-ULTRA)	31.34	1.14	7.1	995	1137				
15	Y-TZP (TIOXIDE)	28.38	1.09	19.9	885	1043				



material were chosen as materials 8 and 9 for the study of particle size effects. It can be seen from **Table 1** that these sub-samples were made up of particles of nearly spherical shape.



Fig. 1 SEM of Y-TZP Beads of Nominal Diameter 0.1 mm. The other bead materials had very similar morphology.



Fig. 2 SEM of Material 7 - Stradbroke Island Sand (As received).



Fig. 3 Sieve Analysis of Material 7 - both in the "as received" state and after pressing to 300 MPa.

The other sand (b) was from Moreton Bay which in its "as supplied" state is shown in **Fig. 4**. This was also subjected to a sieve analysis and the results are shown in **Fig. 5**. In its "as supplied" state and in sieved sub-samples, it formed materials 10, 11 and 12 in the study.

Commercial spray dried zirconia powders were also studied (materials 13, 14 and 15). These were all of yttria stabilized tetragonal zirconia polycrystal (Y-TZP). Like the bead material described above, they were also supplied by ICI Advanced Ceramics, Melbourne. Two of these (13 and 15) were without binders. The third (14) was manufactured with a proprietary inbuilt binder system. Optically, all had similar morphology consisting of agglomerates made up of sub-micron fundamental particles (**Figs. 6a** and **b**). However, agglomerate size and size distribution varied significantly between the spray dried powder samples, as shown by the size distributions given in **Figs. 7a**, **7b** and **7c**.



Fig. 4 SEM of Material 10 - Moreton Island Sand (As received).



Fig. 5 Sieve Analysis of Material 10 - both in the "as received" state and after pressing to 300 MPa.

#### 2.2 Flow behaviour

The flow behaviour of the materials were experimentally measured for three different conditions.

- (1) Free flow
- (2) Shear under limited stress (interparticle friction)
- (3) Die compaction (internal friction)





Fig. 6a SEM of Material 14 (Spray dried SYP-Ultra). The other spray dried powders had similar morphology (Light bar = 100 micron)



Fig. 6b Higher Magnification SEM of Material 14 showing agglomerate structure (Light bar = 1 micron)

#### 2.2.1 Free flow

Free flow behaviour and apparent density were measured using the Hall flowmeter according to standards ASTM B212 and B213. Tap density was found by repeated tapping of a known sample in a measuring cylinder. Prior to these tests, powders were oven dried and cooled in a desiccator. The tests were then conducted at prevailing atmospheric conditions within 15 minutes removal of the granular material from the desiccator. In **Table 2** the Hausner ratio is tap/apparent density and the apparent and tap densities are shown in the form of relative densities. These were calculated using solid phase densities of 6046, 2682, and 2671 kg m<sup>-3</sup> for the Y-TZP, sand (a) and sand (b) respectively.

#### 2.2.2 Shear measurement

An annular shear cell was used to measure the flowability characteristics (angle of interparticle friction) of the bead and sand materials (materials 1-12 in **Table 1**). The annular cell could not be used with the finer spray dried powders because these



Fig. 7c Size distribution of spray dried Y-TZP powder (TIOXIDE)

materials worked their way up the clearance in between the annular ring and its housing leading to errors in the friction measurement. Instead, a direct (Jenike) cell was used with these powders.

The angle of internal friction was calculated using the Mohr-Coulomb yield criterion which can be written 12),

$$\tau = \sigma \tan \theta + c \tag{1}$$

	TABLE 2	2 – FRICTION	AL CHARA	CTERISTI	cs		
		Flow	μ	μ	Hausner	Relative D	ensity (%)
No.	Material	(sec)	Shear Cell	Die Press	ratio	App't	Тар
1	Y-TZP monosized beads	30.2	0.24	0.47	1.00	60.5	60.5
2	Y-TZP monosized beads	18.9	0.31	0.58	1.01	59.2	59.7
3	Y-TZP monosized beads	16.4	0.65	0.70	1.15	54.1	62.1
4	60/40 wt% of 2/3	14.7	0.40	0.55	1.09	62.7	68.3
5	70/30 wt% of 2/3	15.3	0.30	0.64	1.06	63.6	67.7
6	66.4/24.5/9.1 wt% of 1/2/3	21.9	0.29	0.47	1.02	66.9	68.4
7	SiO <sub>2</sub> sand (a) (as rec'd)	59.6	0.58	0.60	1.10	52.6	57.8
8	212-300 µm fraction of 7	60.0	0.58	0.55	1.08	53.4	57.9
9	150-212 μm fraction of 7	57.1	0.58	0.60	1.11	51.5	57.1
10	SiO <sub>2</sub> sand (b) (as supplied)	58.5	0.58	0.63	1.09	55.6	60.4
11	212-300 µm fraction of 10	57.7	0.55	0.56	1.07	57.5	61.8
12	150-212 μm fraction of 10	56.7	0.58	0.55	1.11	53.0	58.7
13	Y-TZP (SY-ULTRA)		0.54	0.67	1.14	18.7	21.4
14	Y-TZP (SYP-ULTRA)		0.72	0.66	1.14	16.5	18.8

0.41

where  $\tau$  is the shear stress,  $\sigma$ , the normal stress,  $\theta$ , the angle of interparticle friction and c, the cohesion. The coefficient of internal friction is given by  $\tan \theta =$  $\mu$ . The granular materials considered in this work were cohesionless, and so the value of c was therefore zero.

Y-TZP (TIOXIDE)

The standard annular cell (Wykeham Furrance Engineering Ltd, type WF -25850) used for the bead and sand measurements has a normal stress capacity of 1.4 MPa. To accommodate testing to higher normal stresses, the load capacity of the cell was increased to 4.7 MPa by reducing the width of annular crosssection, from 15 to 5 mm. This modification also gave the added advantage that smaller samples were needed for a test. It did however lead to an increase in the ratio of wall to powder body shear forces, but for the materials tested, the grain-wall friction was small and, with the exception of the largest beads, the particle sizes were small compared to the annular width. It has been shown 6) that negligible error was introduced by this modification of the annular shear cell.

In the interest of repeatability, it was important to standardize initial density of the test specimens charged in the cell. With like materials, this was achieved in practice with a charging accuracy of 3%. During experiments, all the specimens were subjected to a constant strain rate of 5 mm per minute. For each material, the limiting shear stresses at progressively higher applied normal stresses were plotted in the form of Mohr's stress diagrams. The coefficient of internal friction  $(\mu)$  and cohesion (c) were obtained from equation 1 applied to the line drawn tangential to the series of Mohr's stress diagrams.

14.6

17.3

1.18

#### 2.2.3 Die compaction

0.64

The quasi-static compaction experiments were done in the 25 mm diameter instrumented punch and cup die arrangement shown schematically in Fig. 8.



Fig. 8 Instrumented Die for Pressing Measurements

15

Following Kuhn 13), the die ring was designed to remain elastic for radial stresses up to 300 MPa. It was made from EN 26 steel hardened to 62  $R_c$  and ground in the longitudinal direction in order to minimise die-wall friction. A strain gauge was mounted circumferencially on the die-ring at an appropriate location to measure strain during die calibration and granular material testing. Further details are given in 14).

Two sets of punches were used, one for calibration and the other for powder compaction experiments. For given depths of material fill in the die, the output from the strain – gauge attached to the die ring was calibrated using oil in the die loaded to known pressures by means of the top punch. Die wall friction was minimized in the loading experiments with granular materials by only using depths of loaded material smaller than that necessary to produce measurable die wall friction. Loading of the top punch was affected using an 'Instron' hydraulic testing machine. The accuracy of Instron was 0.2% of full range, corresponding to a die pressure of 1000 MPa.

For testing, a 20 g sample of the granular material was charged in the die and the fill height measured. It was then compacted with a punch displacement rate of 50 mm per minute on an Instron testing machine. The experimental measurements were recorded on a x-y recorder, in the form of a load-strain plot that were subsequently converted to axial-radial stress plots using the die ring strain-gauge calibrations.

The relationship between axial and radial stresses developed during the compaction of granular materials (powders) has been studied by a number of researchers 14). Pederson 5) developed an analytical expression for the stress field during compaction which, for the case of negligible die wall friction and interparticle cohesion, can be written,

$$\sigma_{\rm r} = \frac{(1+\mu^2)^{0.5} - \mu}{(1+\mu^2)^{0.5} + \mu} \sigma_{\rm a}$$
(2)

where  $\sigma_r$ ,  $\sigma_a$  are the radial and axial stresses and  $\mu$  is the coefficient of internal friction. Equation 2 was



used to interpret the slope of the axial-radial stress plots in terms of coefficient of internal friction.

#### 3. Results

The frictional characteristics of all materials studied are summarized in **Table 2**. The major consolidation stress for the shear cell experiments quoted was 0.4 MPa and for the die press experiments, 300 MPa. Flow time measurements were not possible with the spray dried powders. Even after careful drying, these powders were so highly frictional under gravity loading conditions that they would not flow reliably through the standard funnel used for this test.

#### 3.1 Particle size effects

The results for the monosized beads provided frictional data in which only particle size was the variable. Comparing the frictional characteristics of the monosized beads (Table 3), two important observations can be made -a) there is in fact a negative correlation between flow time and shear cell measures of internal friction and b) there is a marked increase in internal friction with decreasing particle size. The first observation is important - flow time is commonly used in powder metallurgy and other industries to measures frictional behaviour. With the relatively coarse bead particles used in this part of the study, this measure clearly leads to serious errors in the quantification of internal friction. The second observation, although not new, quantifies the effect very clearly for materials where the only difference between them is particle size-material and geometry are exactly the same. The higher friction with smaller particle size was manifested by higher coefficients of internal friction as measured in both the shear cell and die press (equation 2) experiments, although the absolute values obtained from the die press experiments were higher. Higher friction was also indicated by lower apparent density. For these materials, the tap density changed little with particle size, but because of the lower values for apparent density for the more frictional small

	TABLE 3 – SIZE EFFECTS - MONOSIZED SPHERES									
		Mean Flow $\mu$ $\mu$ Dia Time Shear Die			$\begin{array}{c ccc} Mean & Flow & \mu & \mu \\ Dia & Time & Shear & Dia \\ \end{array}$	$\begin{array}{c cccc} Mean & Flow & \mu & \mu \\ Dia & Time & Shear & Die \\ \end{array}$	μ Die	Hausner	Relative D	ensity (%)
No.	Material	(μm)	(sec)	Cell	Press	ratio	App't	Tap		
1	Y-TZP monosized beads	946	30.2	0.24	0.47	1.00	60.5	60.5		
2	Y-TZP monosized beads	294	18.9	0.31	0.58	1.01	59.2	59.7		
3	Y-TZP monosized beads	94	16.4	0.65	0.70	1.15	54.1	62.1		



sizes, the Hausner ratio was higher for these materials too.

The blends of the monosized beads (**Table 4**) had friction coefficients somewhere between the extremes associated with the monosized components. Of particular note is the result for material 6, the blend of these 3 component sizes producing the highest possible bulk density. The friction coefficient for this material is only marginally higher than that for material 1, the largest sized component which also had the lowest friction coefficient. This suggests that in appropriately blended size ranges, the frictional behaviour is dominated by the largest particle size present.

#### 3.2 Particle geometry effects

The sand based materials (7-12 in **Tables 1** and **2**) were more irregular in shape than the beads as can be seen from **Fig. 1**, **2** and **4**. As naturally occurring materials they also comprised a blend of sizes. The shape factors listed in **Table 1** and the size distributions shown in **Fig. 3** and **5** quantify these effects.

The friction coefficients determined in the shear cell for this range of materials are, with one exception, all higher than the monosized or blended beads. Since the size range is similar with the beads, and since there was little difference between any of the sieved sub-samples (materials 8, 9, 11 and 12) and as received materials (7 and 10), it would be reasonable to conclude that the higher friction observed in the sand based materials was largely a consequence of their more irregular shape. Comparing materials 2, 8 and 11 (**Table 5**), they are all of similar size, but of different shape factor. Flow time, shear cell internal friction and Hausner ratio all indicate higher friction in the more irregularly shaped material.

Specific surface area (ssa) is a mass-based measure. However, the difference in density between the materials studied only varied by a factor of about 2. Even allowing for this density difference, the specific surface area of the spray dried powders (materials 13, 14 and 15) was orders of magnitude higher than that for any other material tested. The friction results for the spray dried powders are compared with other typical values in **Table 6**. Material 9 was chosen as a comparison material on the basis that its shape factor was similar (**Table 1**). Unfortunately, it was a coarser powder than the spray dried materials. Nevertheless, allowing for the larger size and the different density material, the coefficients of internal

TABLE 4 - SIZE EFFECTS - BLENDS OF MATERIALS 1, 2, 3								
		Mean Flow		μ	μ	Hausner	Relative Density (%)	
NO.	Material	$(\mu m)$	(sec)	Cell	Die Press	ratio	App't	Tap
4	60/40 wt% of 2/3	103	14.7	0.40	0.55	1.09	62.7	68.3
5	70/30 wt% of 2/3	108	15.3	0.30	0.64	1.06	63.6	67.7
6	66.4/24.5/9.1 wt % of 1/2/3	116	21.9	0.29	0.47	1.02	66.9	68.4

	TABLE 5 – SHAPE FACTOR EFFECTS : 212-300µm PARTICLES							
N-	Mataria 1	Mean	Flow	μ	μ	Hausner	Relative D	ensity (%)
INO.	матепал	Snape Fator	(sec)	Cell	Die Press	ratio	App't	Tap
2	Y-TZP monosized beads	1.06	18.9	0.31	0.58	1.01	59.2	59.7
8	212-300µm fraction of 7	1.19	60.0	0.58	0.55	1.08	53.4	57.9
11	212-300 $\mu$ m fraction of 10	1.22	57.7	0.55	0.56	1.07	57.5	61.8

TABLE 6       –       SPECIFIC SURFACE AREA (SSA) EFFECTS								
		Mean	SSA $\mu$		μ Dio	Hausner	Relative Density (%)	
No.	Material	μm)	(m <sup>2</sup> /g)	Cell	Press	ratio	App't	Тар
9	150-212μm fraction of 7	190	0.0051	0.58	0.60	1.11	51.5	57.1
14	Y-TZP (SYP-ULTRA)	31.3	7.1	0.72	0.66	1.14	16.5	18.8
15	Y-TZP (TIOXIDE)	28.3	19.9	0.41	0.64	1.18	14.6	17.3



friction were comparable for the materials shown. On the basis of both size and higher ssa, materials 14 and 15 would have been expected to have higher internal friction, but this was not so. The Hausner ratio figures also do not discriminate between these materials. However, the raw figures for both apparent and tap density are much lower for the spray dried material. This suggests that these measures are poor indicators of the frictional behaviour of these materials when under higher than gravity loads.

#### 3.3 Loading effects

The results for the coefficient of internal friction for selected samples are shown in Table 7 at two values of the major consolidation stress. The first (395 kPa) was achieved in the shear cell experiments whereas the second (300 MPa) was achieved in the die pressing experiments. The results for the monosized beads showed effects that were typical of the range of materials tested. A significant fraction of the large beads (material 1) fractured at the higher load. This meant that there was partial loss of the spherical shape throughout the powder body which lead to a significantly higher friction coefficient at the higher loads. In contrast, the small beads (material 3) were stronger and did not fracture at applied pressures up to 300 MPa. It can be seen that the friction coefficient did not change much between the two load conditions.

With the sand materials, in most cases there was a slight increase in friction with increasing load, but the striking feature is that there is really very little change. The results for material 7 shown in **Table 6** were typical of this type of material. This result was obtained despite measurable particle fracture in the diepressing experiments, as can be seen from the "before and after" sieve analyses shown in **figures 3** and **5**. However for this class of material, the fracture

TABLE 7 - LOAD EFFECT ON INTERNAL FRICTION						
	Major consolidation stress	395 kPa	300 MPa			
No.	Material	μ Shear Cell	μ Die Press			
1	Y-TZP monosized beads	0.24	0.47			
3	Y-TZP monosized beads	0.65	0.70			
7	SiO <sub>2</sub> sand (a) (as rec'd)	0.58	0.60			
13	Y-TZP (SY-ULTRA)	0.54	0.67			
14	Y-TZP (SYP-ULTRA)	0.72	0.66			
15	Y-TZP (TIOXIDE)	0.41	0.64			

debris was similar in shape to the original material.

In contrast, there was much greater fracture in the spray dried powders at the high loads experienced in the die pressing experiments. The results for these materials (13, 14 and 15) in Table 7 show a marked change in the friction between the shear cell and die pressing experiments. There was significantly different friction between the powder samples in the shear cell results, but very little in die pressing results. Bearing in mind the large difference in major consolidation stresses between these measurement techniques, this difference in frictional behaviour is consistent with substantial particle fracture. The large agglomerates would have dominated frictional behaviour at the lower stresses present in the shear cell, in contrast to the die experiments at high loads where the frictional behaviour would have been dominated by the debris from the broken agglomerates. This debris would be typified by the basic crystallite size (~  $0.6\mu$ m), virtually the same for all of 13, 14 and 15 materials. This mechanism is supported by the constancy of friction coefficient across all spray dried materials, despite the large difference in this property between these materials at the lower testing load.

#### 4. Conclusions

At least for coarse granular materials, flow time measures of frictional characteristics give a poor indication of the coefficient of internal friction.

In mono-sized granular material, the internal friction increases with decreasing particle size. In granular materials blended with respect to component particle sizes, the internal friction lies within the range set by the lowest and highest for the component sizes used. With appropriate size blending, a high bulk density can be achieved with little increase in the internal friction over that due to the size component with the lowest friction used. Since in the present work these were the largest particles, the results suggest that, in such blends, the frictional behaviour is controlled by the largest particles present.

Other things being comparable, granular bodies with particles having higher shape factors also have higher internal friction. Powders with high specific surface area were found to have low apparent and tap densities, but more direct measures of frictional behaviour indicated that the specific surface area had negligible effect on the coefficient of internal friction.



At least for hard ceramic granular materials, measurements of internal friction in a shear cell at consolidation stresses of 0.4 MPa give a good indication internal friction during rigid die pressing to consolidation stresses at least up to 300 MPa. This is so even when particle fracture occurs during pressing, provided particle morphology does not change significantly as a result of the fracture.

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## Solution Approaches to the Dynamic, Population † Balance Modeling of Grinding with Transport

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#### Abstract

The solution of the dynamic population balance model (PBM) with transport is problematic. The fact that the dynamic PBM model equation solution to the Inverse Problem for grinding systems is degenerate or underspecified is demonstrated. Two numerical solution approaches to the Inverse Problem are used. These are: 1) providing additional constraints on breakage selection functions or 2) performing the Arbiter-Bhrany (or other) normalization of the selection functions. Actual experimental anthracite batch grinding data is used to demonstrate the nonunique functionality of the batch dynamic mill selection and breakage functions for a real physical system. The Levenberg-Marquardt algorithm for systems of constrained non-linear equations is used to solve the batch dynamic PBM grinding equations to obtain the grinding selection and breakage rate functions. Different solutions to the same PBM transport equations are provided. The mill was modeled as a CSTR operating at various retention times. Batch dynamic PBM data was used to provide the mill kinetic and breakage selection function data. Two different solutions were obtained depending on the numerical solution approach. The severity of the non-uniqueness problem for dynamic grinding is demonstrated. Each solution approach to a dynamic PBM with transport, while giving the same prediction for a single batch grinding time, gives different solutions or predictions for mill composition for other grinding times. This fact makes dynamic nodal analysis and control problematic. The fact that the constraint solution approach gives a solution may suggest that normalization is not necessary.

#### 1. Introduction

The PBM for simulating comminution in grinding mills has been solved assuming linearity using matrix methods (Broadbent and Calcott 1960, Meloy and Gaudin 1962, Agar and Charles 1962, Meloy and Bergstrom 1964, Reid 1965, Mika 1970, Herbst and Mika 1970, Klimpel and Austin 1970, Austin 1971, Kapur 1972, Malgan and Fuerstenau 1976, Herbst et al. 1971, Fuerstenau et al. 1984, Meloy and Williams 1992 a and b).

Selection and breakage functions are lumped into a steady-state mill matrix. This steady-state mill matrix is multiplied (on the right side) by the feed matrix which describes the particle size distribution entering the mill. This multiplication yields the mill product matrix which describes the size distribution of the particles exiting the mill. In practice one creates the mill matrix by measuring the size distribution of the feed and product, then calculating the mill matrix by various methods. This is referred to as solving the Inverse Problem.

The dynamic (time-variant) PBM for simulating comminution with or without transport in grinding mills has also been solved assuming linearity (Fuerstenau et al. 1984, Herbst and Fuerstenau 1980, Klimpel 1970, Klimpel 1991, Kapur 1972). Considerable effort has been expended in also normalization of the selection and breakage rate functions (Arbiter and Bhrany 1960).

The selection and breakage functions are not lumped together as in the steady-state mill matrix. The dynamic PBM introduces more unknowns than the steady-state PBM, that is, the kinetic terms or breakage rate functions.

#### 2. Dynamic PBM model

#### BATCH

The batch dynamic PBM model, also based on

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conservation of mass in the mill, uncouples the breakage rate and selection functions and introduces time as a variable. In this paper the model is presented without the complication of transport. The  $k_i$  is the rate of breakage of particle size i in the mill, while the  $b_{ij}$  are the breakage selection functions for the breakage of particles from class j into class i. The dynamic conservation of mass equations describing the dynamic PBM model have been developed elsewhere (Herbst and Fuerstenau 1980). The primary dynamic PBM conservation of mass equations for five particle sizes follow:

$$p_1 = f_1 + \int (p_1 (-k_1)) dt$$
 (1)

$$p_2 = f_2 + \int (p_1 k_1 b_{21}) dt - \int (k_2 p_2) dt$$
 (2)

$$p_{3} = f_{3} + \int (p_{1} k_{1} b_{31}) dt + \int (p_{2} k_{2} b_{32}) dt - \int (k_{3} p_{3}) dt$$
(3)

$$p_{4} = f_{4} + \int (p_{1} k_{1} b_{41}) dt + \int (p_{2} k_{2} b_{42}) dt + \int (p_{3} k_{3} b_{43}) dt - \int (k_{4} p_{4}) dt$$
(4)

$$p_{5} = f_{5} + \int (p_{1} k_{1}k_{51} + p_{2}k_{2}b_{52} + p_{3}k_{3}b_{53} + p_{4}k_{4}b_{54}) dt - \int (k_{5}p_{5}) dt$$
(5)

The integrals are all evaluated from time zero to the grinding time,  $t_m$ . In addition to Equations 6-10, the following conservation expression yields additional equations.

$$\sum_{i=1}^{n} b_{ij} = 1.0 \quad \text{for each j}$$
 (6)

As with the steady-state PBM equation, the solution is degenerate or underspecified. For the Inverse Problem there are more unknowns than equations. In this paper two numerical solution approaches are compared. These are: 1) providing additional constraints on breakage selection functions or 2) performing the Arbiter-Bhrany (or other) normalization of the selection functions. Assumptions such as the Arbiter-Bhrany (1960) normalization equation regarding the  $b_{ij}$  and  $k_i$  may be used. However, additional constraints may be used. The dynamic PBM constraint equations are quiet logical and may be generated from:

$$1 \ge \mathbf{b}_{ij} \ge 0 \tag{7}$$

#### TRANSPORT

With the addition of transport, mixing and disper-

sion phenomena are added to the PBM model. For the Continuous Stirred Reactor Model (CSTR) of transport where V is the mill volume, Q is the mill volumetric flowrate, and  $\tau$  (retention time) is V/Q, one has the following equations for five particle classes:

$$\frac{d(VM_{1}(t))}{dt} = -k_{1}VM_{1}(t) - QM_{1}(t) + QM_{1F}(t)$$
(8)

$$\frac{d(VM_2(t))}{dt} = -k_2 VM_2(t) - QM_2(t) + QM_2(t) + QM_2(t) + b_{12}k_1 VM_1(t)$$
(9)

$$\frac{d(M_3(t))}{dt} = -k_3 M_3(t) - \tau M_3(t) + \tau M_{3F}(t) + b_{13} k_1 M_1(t) + b_{23} k_2 M_2(t)$$
(10)

$$\frac{d(M_4(t))}{dt} = -k_4 M_4(t) - \tau M_4(t) + \tau M_{4F}(t) + b_{14} k_1 M_1(t) + b_{24} k_2 M_2(t) + b_{34} k_3 M_3$$
(11)

$$\frac{d(M_{5}(t))}{dt} = -k_{5}M_{5}(t) - \tau M_{5}(t) + \tau M_{5F}(t) + b_{15}k_{1}M_{1}(t) + b_{25}k_{2}M_{2}(t) + b_{35}k_{3}M_{3}(t) + b_{45}k_{4}M_{1}(t)$$
(12)

In solving the transport PBM, the kinetic and breakage selection function data obtained from the batch dynamic PBM data is used in the above mill transport equations. The simultaneous, linear ordinary differential equations are solved with Laplace transform techniques. The Laplace transformed transfer functions for each particle class were developed. The inverse Laplace transform of the response was determined and the response in the time domain calculated.

#### 3. Solution method

The Levenberg-Marquardt (L-M) method was used to obtain both the steady-state and dynamic direct and Inverse Problem solutions to the PBM model (ANL 1980, Levenberg 1944, Marquardt 1963). Solution of the steady-state equations involves the solution of a set of constrained or unconstrained algebraic linear or non-linear equations. The dynamic PBM solution involves the solution of a set of constrained or unconstrained linear or non-linear integral equations.

The L-M method is a quasi-Newton method which is a variation on the gradient method. The method involves finding the zeros of a vector of functions.



In general, with these methods the simultaneous functions are approximated using a Taylor series. The equations are manipulated resulting in an explicit expression for new estimates of the x vector calculated from partial derivatives and the old x vector values. The procedure continues until there is no significant difference between estimated and old x vector values.

At each step in the actual procedure an error function is generated. The first partial derivatives of the error function with respect to the variables to be solved are determined in order to create a Jacobian matrix. The matrix equation solved is:

$$J s + f(x) = 0$$
 (13)

where J is the Jacobian matrix, s is the vector step to take to generate the next estimate of unknown variables, f(x) is the error function vector, and x is the vector of current estimates for unknown variables. For the first step, x is the vector of initial guesses. Subsequent x vectors are the sum of the previous x vectors and the s vector for that step. Computation of s was done by inverting the Jacobian at each step. For the sake of brevity, the algorithmic details of the technique are presented elsewhere (ANL 1980).

In solving the transport PBM, the batch constants are used in the mill transport equations. The set simultaneous, linear ordinary differential mill transport equations are solved using Laplace transform techniques.

#### 4. Discussion

#### BATCH

In order to assess the dynamic PBM, two examples were used. In the first example, actual grinding data was used (Klimpel 1970). Five particle classes experimentally representing standard sieve sizes were used. The following product  $P(t_m = 6)$  and feed composition F<sub>a</sub> used was for anthracite coal being ground for six minutes:

$$F_{a} = \begin{pmatrix} f_{1} & 0.250 \\ f_{2} & 0.300 \\ f_{3} &= 0.240 \\ f_{4} & 0.200 \\ f_{5} & 0.010 \\ \end{pmatrix}$$

$$P(t_{m} = 6) = \begin{pmatrix} f_{1} & 0.100 \\ f_{2} & 0.100 \\ f_{3} & 0.100 \\ f_{4} & 0.200 \\ f_{5} & 0.500 \\ \end{pmatrix}$$

In the first solution, inequality constraints were solved simultaneously with the conservation equations. The following solution was obtained for the batch PBM:

$$K_{ic} = \begin{matrix} k_1 & 0.250 \\ k_2 & 0.444 \\ k_3 &= 0.462 \\ k_4 & 0.148 \\ k_5 & 0.000 \end{matrix}$$

$$b_{11} \ b_{12} \ b_{13} \ b_{14} \ b_{15} & .000 \ .000 \ .000 \ .000 \ .000 \ .000 \\ b_{21} \ b_{22} \ b_{23} \ b_{24} \ b_{25} & .443 \ .000 \ .000 \ .000 \ .000 \\ B_c = \begin{matrix} b_{31} \ b_{32} \ b_{33} \ b_{34} \ b_{35} &= \ .197 \ .404 \ .000 \ .000 \ .000 \\ b_{41} \ b_{42} \ b_{43} \ b_{44} \ b_{45} & .000 \ .200 \ .449 \ .000$$

b<sub>51</sub> b<sub>52</sub> b<sub>53</sub> b<sub>54</sub> b<sub>55</sub>

In the second solution, the selection functions were normalized. The normalization procedure eliminates enough unknowns to permit solution. The normalization equations are:

$b_{41} = b_{52}$	(14)
-------------------	------

.359 .396 .551 1.00 .000

.000.000 .000 .000 .000 .000

$b_{42} = b_{53}$	(15)
-------------------	------

$$b_{31} = b_{42}$$
 (16)

$$b_{32} = b_{43} \tag{17}$$

$$b_{21} = b_{32}$$
 (18)

The following solution with the L-M algorithm was obtained:

K <sub>in</sub>	=		$f k_1 \ k_2 \ k_3 \ k_4 \ k_6$	=	0.250 0.428 0.551 0.237 0.000					
	b <sub>11</sub>	b <sub>12</sub>	b <sub>13</sub>	b <sub>14</sub>	b <sub>15</sub>	.000	.000	.000	.000	.000

	$b_{21}$	$b_{22}$	$b_{23}$	$b_{24}$	$b_{25}$		.380	.000	.000	.000	.000
$B_n =$	b <sub>31</sub>	$b_{32}$	b 33	b <sub>34</sub>	b 35	=	.620	.380	.000	.000	.000
	b <sub>41</sub>	$b_{42}$	$b_{43}$	b 44	$b_{45}$		.000	.620	.380	.000	.000
	b <sub>51</sub>	$b_{52}$	b <sub>53</sub>	b <sub>54</sub>	b <sub>55</sub>		.000	.000	.620	1.00	.000

The second physical example is similar.

	$f_1$		0.250
	$f_2$		0.300
=	$f_3$	=	0.240
	$f_4$		0.200
	$f_5$		0.010
	=	$= \begin{array}{c} f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \end{array}$	$\begin{array}{c} f_{1} \\ f_{2} \\ = \\ f_{3} \\ f_{4} \\ f_{5} \end{array}$



$$F(t_m = 6) = \begin{pmatrix} f_1 & 0.100 \\ f_2 & 0.300 \\ f_3 & = 0.100 \\ f_4 & 0.300 \\ f_5 & 0.200 \end{pmatrix}$$

In the first solution, inequality constraints were solved simultaneously with the conservation equations. The following solution was obtained:

$$\begin{array}{rcl} & k_1 & 0.250 \\ k_2 & 0.428 \\ K_{1c} & = & \begin{array}{c} k_3 & = & 0.324 \\ k_4 & 0.013 \\ k_5 & 0.000 \end{array} \\ \\ & & \\ B_c & = \begin{array}{c} b_{11} & b_{12} & b_{13} & b_{14} & b_{15} \\ b_{21} & b_{22} & b_{23} & b_{24} & b_{25} \\ b_{31} & b_{32} & b_{33} & b_{34} & b_{35} \end{array} = \begin{array}{c} .000 & .000 & .000 & .000 \\ .000 & .000 & .000 & .000 \\ .000 & .000 & .000 & .000 \\ .000 & .000 \\$$

In the second solution, the selection functions were normalized with the equations previously presented. The normalization procedure eliminates enough unknowns to permit solution.

The following solution with the L-M algorithm was obtained:

The existence of non-unique solutions to the dynamic PBM, which was just illustrated, is, of course, problematic for researchers and industry. A dilemma is created as to which solution is correct, whether it may be impossible to build up any type of a breakage selection and rate function knowledge base, and whether or not normalization is required at all.

When one compares the functionality of the kinetic and breakage rate functions obtained through the constrained and normalization approaches, one sees immediately the problems possible with a force fit -

the possible violation of conservation of mass constraints resulting in negative values.Examination of matrices K and B indicate that most deviation occurs in the smallest sizes.

It should be noted that if the normalization constraints are used for the selection breakage functions (B), errors may be created in the kinetic parameters to accommodate force fits to normalization assumptions.

The non-uniqueness of the solution, while a problem inherent in the solution approaches of PBMs wherever they are used, is a key problem with PBMs solution approaches.

Another related PBM issue is the assumption that the elements of M or B are invariant with respect to time, composition (size distribution), rheology, temperature, slurry density, etc. The effect of these factors has been measured (Fuerstenau et al. 1984, Klimpel 1991, Klimpel 1992, Tarshan 1992).

In wet grinding Meloy and Williams (1992 a and b) have shown that the steady-state  $m_{ij}$  must be functions of the mill conditions such as mill loading and/ or particle size distribution.

A new mill matrix must be developed for each grinding time interval – or for each size distribution in the mill. The supposition of time variant M and B elements contradicts the basic linearity assumption used to justify the constancy and interrelatedness of the breakage and selectivity functions used to generate mill matrices. Thus, one must question the use the Arbiter-Bhrany (1960) or other such relation-ships, because the assume the matrix elements are constant over time.

### TRANSPORT

When these two different dynamic batch solutions (normalized (n) and constrained (c)) above are used to predict the temporal of performance of an anthracite grinding network composed of one CSTR mill, the predictions diverge, particularly for the smaller sizes. The temporal plots of mass fraction of particle classes 1 and 2 are shown in Fig. 1 - 4. Two different retention times are shown for the first example in Fig. 1 through 4. This example is for a real anthracite system.

For the sake of brevity, only the dynamic transport equation solutions for the first two particle classes are reproduced here. These rather complicated equations were solved by forming the Laplace transforms of the simultaneous, linear PBM transport equations, solving the set of equations for the respective  $M_i(s)$ , and inverting the transformed equations to find the





Fig. 1 Temporal divergence, anthracite, particle size class  $m_1$ , long retention time



Fig. 3 Temporal divergence, anthracite, particle class  $M_1, \\ \mbox{ short retention time }$ 

response in the time domain.

The equations for  $M_1(t)$  and  $M_2(t)$  are as follows:

$$M_{1}(t) = \frac{M_{1F}\tau^{-1}}{(k_{1} + \tau^{-1})} (1 - e^{-(k_{1} + \tau^{-1})t})$$
(19)

$$M_{2}(t) = \frac{M_{2F}\tau^{\cdot 1}}{(k_{2} + \tau^{\cdot 1})} (1 - e^{-(k_{2} + \tau^{\cdot 1})t}) +$$

Obviously, examination of the figures reveals that predictions of time-varying performance of mills using different solution of dynamic PBM models leads to predictions which deviate at subsequent grinding times. This deviation is both startling and troublesome.

The effect of retention time in the mill is an important factor. At short retention times the mill contents raise quickly to their steady-state concentra-



Fig. 2 Temporal divergence, anthracite, particle class  $M_2$ , long retention time



Fig. 4 Temporal divergence, anthracite, particle class  $M_2$ , short retention time

tions. At long retention times the temporal divergence is more prevalent and pronounced. Unfortunately different initial batch solutions lead to different steady-state concentrations in the mill.

Other approaches or data fitting techniques to batch data over different time intervals would expect to have the same inaccuracies. Other approaches include fitting the transport PBM equations to the first two time intervals of the transport experimental data, developing time and concentration dependent kinetic and selection breakage functions, and doing a global least squares type regression to batch or transport data over all time periods. It is the belief of the authors that this tantamount to just placing inaccuracies in other areas.

However, even though it is possible that the constrained solution approach may make up for the lack of determinancy in the PBM model, it is no substitute for a better quanifiable understanding of the dependencies of mill concentration on kinetics and breakage rate functions.

The temporal plots of mass fraction of particle classes 1 and 2 for the second physical example are shown in Fig. 5 - 8. Two different retention times





-----  $m_1(t)$  constrained ------  $m_1(t)$  normalized

Fig. 5 Temporal divergence, particle class  $M_1,\, \text{long retention time}$ 



Fig. 7 Temporal divergence, particle class  $M_1$ , short retention time

are also shown for the example in **Fig.5** through **8** for mill concentrations for the first two particle classes. Results and trends are similar for the other three particle classes whose figures are not shown for the sake of brevity. The results for the second physical example are quiet similar to the first even though the normalization assumptions appear less valid.

Unfortunately, the problem demonstrated in this problem could be expected to be magnified in mill networks. Network dynamic nodal analysis and control strategies would likely be different for each case.

An interesting additional problem also arises during the course of dynamic mill simulation which make dynamic nodal analysis and control problematic. Predictions of time-varying performance of mills using different solution of dynamic PBM models will lead to different control and operating strategies.

#### 5. Conclusions

1 There is no unique solution to the batch dynamic PBM models. Different solutions were identified to yield the same product with the same feed







Fig. 8 Temporal divergence, particle class  $M_2, \, {\rm short} \, {\rm retention}$  tion time

matrix for actual anthracite grinding.

- 2 Solution of dynamic PBM models using normalization rather than mass balance constraints may not be necessary. In fact, normalization may lead to physically unrealistic solutions.
- 3 Predictions of the time-varying transport performodels lead to predictions which deviate at other solution approaches to dynamic PBM transport models leads to predictions which deviate at other grinding times for all CSTR retention times.
- 4 Because of the differences in the constrained and normalization solution approaches, dynamic mill simulation, dynamic nodal analysis and control become problematic.

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## An Effective Sem-Based Image Analysis System for Quantitative Mineralogy †

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#### Abstract

An effective image-analysis system for use in the study of particulate mineralogical material is described. The available commercial image-processing and image-analysis software systems do not usually include adequate algorithms for the effective analysis of multiphase mineralogical textures. Filtering algorithms are usually inadequate for the accurate removal of image noise without compromising the integrity of phase edges. Although most systems offer good algorithms for the analysis of binary images, algorithms for ternary and higher order images are almost non-existent and these are essential for the analysis of mineralogical material in the particulate state. Existing systems make no provision for effective stereological analysis of image data nor for the interpretation of microstructure using models based on stochastic and integral geometry.

This paper describes the development of an image analysis system based on an SEM equipped with secondary electron and back-scattered electron detectors, an image memory for the storage of digital images captured at slow scan speeds and a SUN workstation for image processing and image analysis. The algorithms and procedures described include a full range of linear-intercept analysis routines used in quantitative mineralogy.

#### 1. Introduction

Mineralogy has always been related to image analysis to a great extent. Luster, color and macroscopic texture are fundamental characteristics of visual nature that were probably used at the very birth of mineralogy as a science. The establishment of scientific mineralogy was possible due to the development of optical microscopy. The very first image-processing procedures in this field can be considered to be the use of filters and polarized light in order to modify the appearance of the individual minerals being viewed. Since then, image analysis and processing have evolved enormously. Technological progress in related fields like mineral processing and extractive metallurgy have, at the same time, drastically increased the demand for quantitative information from mineralogical specimens. This quantitative information must be accurate enough for the measured values to be used as parameters for simulation models, process design procedures and control strategies.

Some examples of particle population properties that can be measured by image analysis are particle size distribution, particle composition and particle composition distribution (the liberation spectrum), surface area per unit volume and interphase area per unit volume of phase, the last being a measure of mineralogical texture. Measurements must be made on cross sections of carefully mounted particle specimens because mineralogical materials are opaque. By cross-sectioning, the particles' internal microstructure is exposed for the so important textural characterization and liberation spectra measurement. Furthermore, the spatial interpretation of the one- or two-dimensional information extracted from such cross-sections can be accomplished by means of a variety of stereological procedures that have been developed in recent years.

Several stereological relationships are used in quantitative mineralogy. Those based on linear-intercept analysis are the most accurate and convenient and are very well understood theoretically. The measurement of the one-dimensional linear-intercept distribution is accomplished by superimposing a frame of linear probes on the image containing the features. If this procedure is repeated for several images from the same particle population, the distribution of linear-intercept lengths becomes smooth enough to be used as an unambiguous measure of that particular

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feature. Then the stereological relationships are used to convert it to the necessary three-dimensional information. This procedure is quite straightforward if perfect phase-discriminated images are available. In order to obtain such images, an effective image analysis system coupled with a set of image-processing routines is required.

A comprehensive set of image-processing routines for digitized images that can be used for quantitative mineralogy is presented for the first time in this paper. A detailed description of the stages involved between image acquisition and stereological transformation for real mineral particles from test ores is presented.

#### 2. Image analysis system

The generation of a good image is an essential precursor to any serious image-analysis work. When analyzing mineralogical structures, it is essential to start with an image that resolves all of the features of interest and provides sufficient contrast to distinguish separate phases that must be analyzed. Particular attention must be paid to feature edges and phase boundaries. These play an important role in the generation of accurate statistical analysis of multiphase materials.

There are essentially three methods that are commonly used for the generation of images: optical microscopy, scanning-electron microscopy, and SEM coupled with x-ray microanalysis. The imaging system of choice will depend on the problems and materials that need to be studied. Probably the most commonly used system is the SEM equipped with both backscattered and secondary electron detectors. The back-scattered electron detector is good for mineral phase identification because the intensity of the output is proportional to the average atomic mass in the region of the specimen under the electron beam. However, closely related minerals cannot be readily distinguished, and for complex mineralogies, x-ray microanalysis is essential for routine use.

#### 2.1 Image collection and digitalization

Digital image storage is essential for subsequent image analysis. Not all scanning-electron microscopes are equipped with digital storage and some digital interface may be required. Variable scan rates and digital frame averaging are useful facilities to incorporate in a digital interface.

The digital image should be capable of being displayed in real time so that the operator can adjust focus, magnification, background intensity and contrast. The intensity and contrast in the captured image are probably the most important parameters that can ensure effective phase discrimination. **Fig. 1** shows a back-scattered image of cross-sectioned sphaleritedolomite particles. This image is a weighted average of eight individually digitalized frames scanned at slow scanning speeds. Intensity and contrast have been adjusted to produce very good phase discrimination.

The peaks in the image intensity spectra should be well separated, and the required portion of the spectrum should fill the whole of the available digital intensity range. This should be done by adjustment of the microscope controls. Various digital histogramstretching algorithms that are often used to correct a poorly adjusted image are at best useless and more often introduce unwanted artifacts into the image and should be avoided. **Fig. 2** shows an example of a good histogram for a raw image containing three phases.

Background intensity variations should be corrected before any further image processing. Variations in background intensity are observed in most images. In the optical microscope these result from variations in illumination intensity and in the SEM from variations in detector collection efficiencies at different points on the sample surface. Various interactive algorithms are available to correct images for background intensity variations, but we have found that each detector configuration should be accurately mapped for background intensity variations. Additive correction is more effective than multiplicative correction. The background should always be adjusted to the same level in all images that will be processed automatically so that bias due to overall variations in image intensity can be avoided.

#### 2.2 Phase discrimination

Mineralogical analysis usually relies on accurate definition of mineral phases, and some preprocessing of the image is necessary to ensure proper phase discrimination. The elimination of the halo that will always surround the phases with higher grey values whenever more than two phases are discriminated is probably the most important image preprocessing operation that is required. This is called delineation filtering, and it converts the steep grey-level ramps that define the phase boundaries in a grey-level image into sharp steps so that the transition from one phase to the next is accomplished in a single pixel step. The effect of delineation is illustrated in **Fig. 3** and **4**. The insets show magnified portions of the main image so that single pixels are visible. The effect of





Fig. 1 A typical image of multiphase particulate material.



Fig. 2 Intensity histogram of an image showing good use of the entire available grey-level range.

the delineation filter is clearly visible. Delineation filtering will generally improve phase separation. The grey-level histogram after delineation is shown in **Fig. 5**, which can be compared with the histogram of the original image in **Fig. 2**. The significant improvement in phase separation is clearly evident. The removal of the halo effect is particularly important for mineral liberation studies. A halo will always register the feature as unliberated and will grossly distort any estimation of surface exposure of the mineral.

The delineation algorithm used is defined by

if 
$$(g_{max}-g_i \le g_i-g_{min}) g_i = g_{max}$$
  
else  $g_i = g_{min}$  (1)

where  $g_{max}$  and  $g_{min}$  are the largest and smallest grey levels in a roughly circular neighborhood of pixel i. In order to make the algorithm efficient, only those



Fig. 3 Image discriminated without prior delineation filtering. The halo at the interface between the bright phase and the dark background is visible. The inset is a magnification of the region inside the small square.



**Fig.4** Image that has been discriminated after delineation filtering. The halo has been eliminated. The removal of the halo is particularly important for mineral liberation studies.

pixels i are examined that have a two-dimensional gradient greater than a predetermined level. The choice of neighborhood size and gradient threshold should be established for each mineral and particle type. Once determined, these should be fixed for all subsequent analysis of the same material.

Correct phase discrimination usually cannot be achieved by grey-level thresholding alone. The fluctuations in grey level within a phase are usually too great and there will always be some pixels in each phase that are too high or too low so that they are allocated to the wrong phase by thresholding. Some additional information is usually required that can





Fig.5 Intensity histogram of an image showing good phase discrimination after delineation filtering.

characterize each phase unambiguously. The best characterization is undoubtedly an elemental composition at each pixel as can be determined by x-ray microanalysis. This is a comparatively expensive approach, and we have found other characterizations that work well. In a three-phase image, the bright phase can be characterized by thresholding the image at a level past the phase peak in the grey-value histogram. This produces a highly fragmented image of the bright phase as illustrated in Fig. 6. Any spurious regions that appear in the original discriminated image are very unlikely to produce any highlevel fragments so that selection of only those features in the discriminated image that are touched by at least one high-level fragment produces a very good binary image of the required phase. This procedure is significantly better than the use of any low-pass or median filter for the elimination of small spurious regions. Both of these filters make significant changes to the feature outlines, which in turn introduce unacceptable errors in the measured distribution of linear intercepts.

#### 2.3 Edge tracing and feature identification

Most image-analysis operations are performed on binary or ternary images. A wide range of logical and morphological operations is useful to analyze various aspects of the image. A few of the standard operations are essential for mineral liberation work. Since liberation is essentially a property of the particulate state, identification of individual features in the image that arise from separate particles is of crucial importance. The basis for feature identification is edge tracing. If the edge of a feature is traced, the feature is identified simply by filling all pixels within the edge, which for particles, will always be a closed region. An edge pixel of a feature must satisfy two requirements: the pixel must belong to the feature and must be connected to the background in at least one of the



**Fig.6** A "fingerprint" image of the bright phase in a 3-phase image. This is useful for the elimination of artifacts.

four orthogonal directions (4-contiguity). This definition requires a definition of the background. A 4-path in the image is any sequence of pixels in which each pixel is connected to its leader and to its follower in one of the four orthogonal directions. An 8-path in the image is any sequence of pixels in which each pixel is connected to its leader and to its follower in one of eight directions. The background of an image is the collection of all pixels that are connected to the image frame by at least one 4-path. The use of the 4-path rather than the 8-path prevents the background from penetrating the features across very narrow diagonal openings at the feature edges. These normally arise from slight imperfections in the greylevel thresholding at the feature edges and do not usually signify an actual small concavity on the particle surface. Several efficient edge-tracing algorithms are available, and these are easy to incorporate into an image-analysis package.

#### 3. Quantitative measurements

Image analysis involves the measurement of geometrical features in the image. These include area, perimeter, orientation, location and various derived geometrical properties.

#### 3.1 Measurement of linear features and area

The simplest geometrical measurements to make on a digitized image are linear lengths and areas. The area of a feature is simply equal to the total number of pixels that are required to represent the



feature multiplied by the area occupied by each pixel. The error introduced, because it is not possible to represent the curved boundary of a feature exactly by means of rectangular pixels, is small provided that the features are significantly larger than the pixel size. The length of a linear element is calculated from the coordinates of the pixels at each end of the segment using

length = 
$$((x_2 - x_1)^2 + (y_2 - y_1)^2)^{1/2}$$
 (2)

Because these measurements of area and length are not significantly affected by the digitalization of the image, they are preferred for quantitative work. However geometrical properties that cannot be measured entirely using linear segments and area are also often required and then the digitalization can have very significant consequences.

# **3.2** Quantitative measurement of perimeters – the fractal problem

The measurement of perimeter length of any feature in an image can often provide useful information. For example it may be used in equation (12) below to calculate the surface area per unit volume of a particular mineral or phase and, by restricting the measurements to perimeters that separate two specific phases, the interphase area between them in the three-dimensional structure can be obtained.

The measurement of perimeter is unfortunately subject to a great deal of uncertainty because it is dependent on the digital pixel size and the resolution at which the original image is generated. A feature edge is defined through a number of steps that must be taken to follow the feature boundary. Steps may be horizontal, vertical or diagonal. Each step progresses from one edge-pixel to a neighboring edge-pixel. The perimeter length of a feature in a digitized image is calculated as

perimeter length =

$$N_{h} \times C_{h} + N_{v} \times C_{v} + N_{d} (C_{h}^{2} + C_{v}^{2})^{1/2}$$
 (3)

where  $N_h$  and  $N_v$  and  $N_d$  are the number of steps in the horizontal, vertical and diagonal directions respectively, and  $C_h$  and  $C_v$  are the calibration factors in the horizontal and vertical directions respectively.

The ratio of diagonal to linear steps in the edge tends to increase as the pixel size decreases and the total number of pixels increases more than proportionately as the image is enlarged relative to the

pixel size. This is the fractal problem, and unfortunately, most surfaces in nature do not approach a limiting perimeter length as the image resolution increases indefinitely. As a result, it is not possible to make measurements of perimeter length by image analysis in any absolute sense. It is possible to make only comparative measurements of the perimeter of different features when they are imaged at the same magnification and resolution. An approximate procedure that can be used to correct the measured perimeter for the fractal effect has been developed and is quite successful when applied to the kind of images that are generated when mineralogical particles are studied. The procedure corrects the measured perimeter to a standard magnification (and therefore resolution) that is convenient for the job on hand. We usually refer back to the resolution at the smallest magnification used.

The empirical correction is developed as follows. A series of monosize particle samples are prepared from a population that shows no variation in distribution of particle shape with particle size. Such populations of particles are difficult to prepare, but a sample of material that has been prepared by crushing without undue handling and screening of the products is usually adequate. The monosize fractions are separated by careful screening between closely sized screens. The separate size fractions are mounted, sectioned and polished, and images are generated at a magnification that is proportional to the representative size of the sample. The average perimeter per unit are a  $(B_A)$  of each sample is plotted on log-log coordinates against the ratio of particle size of the sample  $(d_p)$  to the reference particle size  $(d_p^*)$ . Let M represent the magnification used to generate the image of particle size  $d_p$  and  $M^*$  the magnification used to generate the image for particle size  $d_p^*$ . Let  $C_{fr}(M)$  represent the fractal correction factor at magnification M defined so that the measured value of B<sub>A</sub> corrected for the fractal effect varies exactly as  $d_p^{-1}$ .

$$B_{A} (d_{p}) C_{fr}(M) \alpha \left(\frac{d_{p}}{d_{p}^{*}}\right)^{-1}$$
(4)

A typical set of measured values of  $B_A(d_p)$  is shown on log-log coordinates in **Fig. 7**. The slope of the line is -1.15 and the line is represented by

$$B_{A} (d_{p}) \alpha \left(\frac{d_{p}}{d_{p}^{*}}\right)^{-i}$$
(5)





Fig.7 Method for correcting measured perimeters for the fractal effect.

with i = 1.15. From equations (4) and (5)

$$C_{fr} (M) = \left(\frac{d_p}{d_p^*}\right)^{i-1}$$
(6)

Since the calibration experiment is performed with the magnification proportional to  $d_p^{-1}$ 

$$\frac{M}{M^*} = \frac{d_p^*}{d_p} \tag{7}$$

$$C_{\rm fr}(M) = \left(\frac{M}{M^*}\right)^{1-i}$$
(8)

Measured values of perimeter per unit area at any magnification can be corrected using the connection factor in equation (8) to reduce all measurements to the reference magnification.

#### 3.3 What is stereology and why is it needed?

In practice, stereology provides a body of methods that can be used to calculate some properties of threedimensional geometric structures using data obtained from two-dimensional sections of these structures. The ability to translate data from two dimensions to three is very important in applied mineralogy because of the frequent use of microscopic observations of minerals in polished or thin section. Some of the stereological procedures give exact results (within the scatter imposed by the need to sample materials for examination), while others are only approximations, but all provide quantitative rather than qualitative or merely descriptive information. It is this quantitative property of stereological methods that is most important in practice. While qualitative descriptions of mineralogical structures are of enormous utility to the mineralogist and have been used for more than a century, they are not entirely satisfactory for generating data that can be used in mineral processing.

The fact that it is always necessary to sample the material under study prior to examination and also because real mineralogical materials show considerable non-uniformity and indeterminacy in texture and structure, it is only possible to make measurements in a statistical sense, and stereological methods are statistical in nature. These methods supply information on the average geometrical properties throughout a structure but yield virtually no information on the geometrical properties of a single element in the structure. The problems that arise because of the indeterminate nature of mineralogical structures continue to attract a great deal of research interest.

In addition to the standard symbols, it will be necessary also to make use of concepts and notations from probability theory. We will use the following symbols.

#### p(x)dx =

fraction by number of elements having property x in the range (x, x + dx).

f(x)dx =

fraction by volume of elements having property x in the range (x, x + dx). This is also called the volume-weighted distribution and is sometimes written as  $f_v(x)$ .

The concept of conditional probability will be denoted by a vertical line so that

p(x|y)dx =

fraction by number of elements having property x in the range (x, x + dx) counted only from among those elements that are characterized by property y.

An important rule converts the conditional probabilities to total joint probabilities

$$p(x, y) = p(x|y) p(y)$$
 (9)

from which follows immediately

$$p(\mathbf{x}) = \int p(\mathbf{x}|\mathbf{y}) p(\mathbf{y}) d\mathbf{y}$$
(10)

The integral in equation (10) will always be taken over an appropriate range of the variable y.



# 3.4 Basic stereological relationships that are used in quantitative mineralogy

Perhaps the most well-known and widely used stereological conversion relationships are those that relate point, linear and areal fractions to volume fractions

$$V_V = A_A = L_L = P_P \tag{11}$$

These simple relationships illustrate very nicely the two basic stereological ideas: the conversion of quantitative information from zero to one to two to three dimensions and ability of stereology to yield precise three-dimensional quantities about a threedimensional geometrical structure from measurements made in lower dimensions. The lower dimensional measurements are usually significantly easier to make than the three-dimensional measurements. Often it is impossible, with current measuring instruments, to make the appropriate three-dimensional measurements. In fact, prior to the development of image analyzing computers in the 1970's, it was impossible to make accurate measurements in any dimension other than zero, and point counting was the only viable microscopic measuring technique.

The surface area of irregular 3-D geometrical elements can also be recovered from measurements in lower dimensional spaces using

$$S_v = \frac{4}{\pi} B_A \tag{12}$$

or

$$S_v = 2I_L \tag{13}$$

It must be emphasized at this point that equations (11), (12) and (13) are valid only when the values are averaged over many individual elements, and it is important to take the ratio of averages not the average of ratios. Thus when evaluating  $B_A$  for a mineralogical specimens,  $B_A$  is computed as the total perimeter of a particular phase measured over many typical fields of view divided by the total area of that phase in those same fields of view.

Equations (12) and (13) may be combined to give

$$B_{A} = \frac{\pi}{2} I_{L}$$
(14)

All quantities in equation (14) are measured in lower dimensional space and equation (13) can be used to check the consistency of measurements made during any sampling by image analysis. The last two equalities in equation (11) also provide convenient consistency checks that should always be applied. A particularly useful relationship exists between  $I_L$  and the mean intercept length,  $\mu$ , through the phase in question.

$$I_{L} = \frac{2}{\mu}$$
(15)

This is particularly useful because  $\mu$  is so easy to measure by image analysis. In equation (15),  $I_L$  is interpreted as the number of intersections with the surface of the phase per unit length of linear traverse through that phase.  $S_V$  is the surface area per unit volume of the phase and  $B_A$  the perimeter of the phase per unit sectioned area of the phase.

There are a number of other exact stereological formulas, but these are not often used in mineralogy and are not discussed here. Weibel's<sup>1)</sup> text provides comprehensive discussion of all the classical stereological procedures.

#### 3.5 Measurement of size and size distribution

One of the most fundamental geometrical properties of a geometrical structure is its size or the size of the component parts. However, whenever the geometrical structure is not made up entirely of regular geometrical shapes, it is not possible to give a precise definition of size. In addition, the concept of size is not stereologically invariant, and the size of an element of a structure will usually appear to be smaller the lower dimension of the space in which the observation is made. For example, a sphere that is observed in 3-D will give a size equal to its diameter, when observed in a two-dimensional space, the size will be assessed as the diameter of the circle, which is the intersection of the sphere with the two-dimensional sampling plane. This circle will have a diameter less than or, on rare occasions, equal to the diameter of the sphere. If the observation is made in a onedimensional space, the size will be assessed as the length of intersection of a line with the sphere. which will also be less than the diameter of the sphere except on the very rare occasion that the line probe passes exactly through the center of the sphere. A detailed description of how one and two-dimensional measurements on sections or projected areas of particles relates to their size distribution is given in King<sup>2)</sup>, 1982.

Because of the uncertainty associated with any definition of size when shape is not regular, the stereological conversion of size is shape dependent. For spherical elements, the size is unambiguously defined as the diameter of the sphere, and the average



is related to the average size measurement in 2-D and 1-D as follows.

$$\overline{D} = \frac{16}{9} \frac{\overline{d}^3}{\overline{d}^2}$$
(16)

$$\overline{D} = \frac{4}{3} - \frac{\overline{\ell}^2}{\overline{\ell}}^2$$
(17)

where D is the diameter of the sphere,  $\overline{d}^3$  and  $\overline{d}^2$  the average cubed and squared measured diameters of the circles observed in 2-D and  $\overline{\ell}^2$  the average of the squared chord length measured in 1-D.

When the individual elements are not all the same size, it is the distribution of sizes that is important, and for spherical particles the appropriate stereological transformations are

$$p(A) = 6\overline{A} \int_{\frac{\pi}{4}}^{\infty} \frac{p(A|D)}{\pi D^2} f_v(D) dD$$
(18)

with 
$$p(A|D) = \frac{1}{\pi D (\pi D^2 - A)^{1/2}}$$

$$p(d) = \frac{3\bar{d}^2}{2} \int_{d}^{\infty} p(d|D) \frac{f_v(D)}{D^3} dD$$
(19)

with 
$$p(d|D) = \frac{d/D}{D(1-(d|D)^2)^{1/2}}$$
  

$$p(\ell) = \frac{3\bar{\ell}}{2} \int_{\ell}^{\infty} \frac{p(\ell|D)}{D} f_v(D) dD$$
with  $p(\ell|D) = \frac{2\ell}{D^2}$ 
(20)

is used to transform the linear intercept distribution to the particle size distribution.

$$\mathbf{p}(\ell) = \overline{\ell} \int_{0}^{\infty} \mathbf{p}(\ell | \mathbf{D}) \frac{\mathbf{f}_{\mathbf{v}}(\mathbf{D})}{\overline{\ell}_{\mathbf{D}}} d\mathbf{D}$$
(21)

Here is  $\overline{\ell}_D$  is the average intercept length that would be observed in a sample having particles of only one size D and  $\overline{\ell}$  is the mean of the measured liner-intercept distribution. In equation (21)  $p(\ell)$ and  $p(\ell|D)$  are distributions by number or numberweighted distributions. In practice, the length-weighted distributions are usually preferred and using the relationship between the length and number-weighted distributions

$$p_{L}(\ell) = \frac{\ell p(\ell)}{\bar{\ell}}$$
(22)

$$p_{L}(\ell|D) = \frac{\ell p(\ell|D)}{\overline{\ell}_{D}}$$
(23)

equation (21) becomes

$$p_{L}(\ell) = \int_{0}^{\infty} p_{L}(\ell|D) f_{v}(D) dD.$$
 (24)

Equation (24) is usually used in the cumulative form

$$P_{L}(\ell) = \int_{0}^{\infty} P_{L}(\ell|D) f_{v}(D) dD$$
(25)

where

$$P_{L}(\ell) = \int_{0}^{\ell} p_{L}(\ell') d\ell'$$
(26)

Equation (25) is the preferred stereological technique for the measurement of size distribution by image analysis. Although equations (21) and (25) in reality express precisely the same information, the numerical solution of (25) appears to be slightly better behaved than that of equation (21).

The transformation equations (18), (19), (21), (24) and (25) are integral equations which are quite difficult to solve, and their solution has attracted a great deal of attention in the literature. Fortunately a reliable numerical procedure has been developed and solutions can now be generated with a great deal of confidence. Remember it is the left-hand sides of these equations that are measured, and the equations must be solved to obtain the volume-weighted distribution of sizes  $f_v(D)$  in three-dimensional space. In general p(d) is not meaningful when mineralogical materials are studied (since d is not defined for structures of indeterminate shape), and it is only the distribution of linear intercepts  $p(\ell)$  that has an unambiguous meaning and can be measured.

#### 3.6 Measurement of mineral liberation

A particularly important transformation in applied mineralogy is the conversion of apparent linear liberation of particulate mineralogical material to the threedimensional liberation spectrum. This is probably the most important image-analysis task for the application



of mineralogy to mineral processing. The only satisfactory stereological transformation is based on the measurement of the apparent linear-liberation spectrum.

$$p(g_{\ell}|D) = \int_{0}^{1} p(g_{\ell}|g) p(g|D) dg$$
 (27)

In equation (27) g<sub>i</sub> represents the linear grade measured on a particle transect and g is the volumetric grade of a particle. The solution of this integral equation is also quite difficult and requires some care. The same numerical procedure used for the particle size distribution inversion has been found to give accurate and quick results. This solution is described in Schneider et al.<sup>3)</sup>, 1991. With a reliable numerical solution in hand, equation (27) provides an effective and accurate stereological procedure for the measurement of mineral liberation. An alternative solution that uses just the moments of the distribution and forces the spectrum p(g) to correspond to a beta function is not very satisfactory for practical work and does not offer any advantage in convenience or ease of use. Although we do not yet know a great deal about the function  $p(g_{\ell}|g)$ , some useful approximations have been developed using computer-simulated two-phase particles. These have been confirmed to give accurate solutions for p(g) from measurements made on a variety of ores under conditions ranging from almost complete to almost no liberation. The function  $p(g_{\ell}|g)$ is definitely dependent on the mineralogical texture of the ore, and quantitative textural analysis will be required to discover the dependence on texture. It is the need to know this function that has prompted the study of mathematical models for texture using integral geometry techniques, as described in Barbery<sup>4)</sup>, 1991. This will be a major research area in the future. Accurate measurements of  $p(g_{\ell}|g)$ are being made at present using natural minerals after very careful and confirmed fractionation of the particle population using magnetic-fluid techniques.

Equation (27) is often used in the length-weighted form

$$p_{L}(g_{\ell}|D) = \frac{\int_{0}^{\infty} \ell p(g_{\ell}|D) d\ell}{\int_{0}^{\infty} \ell p(\ell) d\ell}$$
(28)

$$p_{L}(g_{\ell}|D) = \int_{0}^{1} p_{L}(g_{\ell}|g) p(g|D) dg$$
 (29)

To generate equation (29), the assumption that

$$\mathbf{p}(\ell|\mathbf{g}) = \mathbf{p}(\ell) \tag{30}$$

has been made. This reflects the assumption that particles of different grades generate similar linearintercept distributions, which is satisfactory, provided that either one of the phases does not exhibit specific shape characteristics when broken.

#### 4. Measurement of linear-intercept distribution

Equations (21), (25) and (29) provide the preferred stereological transformations for the measurement of particle size distribution and mineral-liberation spectrum. The equations are all based on the measurement of the appropriate linear-intercept distributions. Similar equations based on measured area distributions can easily be derived. Although several researchers favor the use of the area distributions, we have a strong preference for the linear-intercept distributions for a number of reasons: (1) The linear intercepts can be measured easily, quickly, accurately, and unambiguously using an image analyzer. (2) A very strong body of theory is available to relate linear-intercept distributions to mineralogical texture. (3) The linearintercept distributions in the phases of the unbroken ore are well defined and easily measured. The concept of the area distribution is not defined for most real mineralogical textures. (4) Areal analysis can be very seriously biased by features in the image that touch even if the contact is through a single pixel contact. Although several feature separation algorithms are available in the literature, none has been found to be reliable enough for automatic image analysis. (5) The correction for the image frame can be implemented with good precision for linear-intercept analysis but not for areal analysis.

# 4.1 Frame correction for linear-intercept analysis

The frame correction for linear-intercept analysis is implemented by defining a guard zone on the righthand side of the image as shown in **Fig. 8**. Only linear intercepts that start within the active zone to the left of the guard frame are recorded, and all intercepts that are not completed before striking the edge of the frame are rejected. This is illustrated in **Fig. 8**. The rejection of long intercepts will bias the data against longer intercepts and this bias must be corrected. The correction can be accurately made by





Fig.8 A guard frame can be used to eliminate the frame error when doing linear-intercept analysis. Linear intercepts shown as thin lines are rejected.

nothing that an intercept of length  $\ell$  will be unfairly rejected whenever it starts within a zone of width  $\ell$ +M-F. On the other hand, no intercepts of length less than F-M are rejected since these must start within the guard zone in order to strike the image frame. The number of intercepts of length greater than F-M must be corrected upwards by the ratio M/(F-\ell). If p'(\ell) is the measured linear-intercept distribution, the corrected distribution is given by

$$p(\ell)_{\text{corrected}} = p'(\ell) \frac{M}{F \cdot \ell} \text{ for } \ell > F \cdot M$$
  
= p'(\ell) for  $\ell \le F \cdot M$  (31)

#### 5. Data evaluation

A typical plot of the measured cumulative distribution of linear grades for pyrite in Witwatersrand pyritic quartzite is shown in Fig. 9. The particle size in the sample was  $-500\mu m + 425\mu m$ . The data is plotted in two ways: including and excluding the liberated intercepts at each end of the distribution. When the liberated intercepts are excluded, the distribution is called the internal distribution. The volumetric grade distribution was calculated from the linear grade distribution by the inversion of equation (29). The result is shown in Fig. 9. The result shows that 53% of the particles in the population are liberated quartzite with zero pyrite content and that there are no completely liberated pyrite particles in the population. The linear-grade distribution does of course show more liberation at each end of the distribution than is shown by the volume distribution. The inversion of equation (29) provides both the extreme liberated ends and the internal volumetric-



Fig.9 Experimental data illustrating the conversion of linergrade distribution to volumetric-grade distribution.

grade distribution directly and no ancillary estimation of the liberated extremes is required.

The technique used for the inversion of equation (29) is based on a finite difference approximation for measurements made on monosize particles

$$p_{Li} = \sum_{j=1}^{12} h_{ij} p_{vj}$$
 for i=1, 2, ... 12 (32)

- $p_{Li}$  = fraction by length of linear intercepts in linear grade class i
- p<sub>vj</sub> = fraction by number of particles having volumetric grade in class j
- h<sub>ii</sub> = corresponding finite kernel.

The numerical solution is usually obtained in the cumulative form

$$P_{Li} = \sum_{j=1}^{12} H_{ij} p_{vj}$$
 for i=1, 2, ... 12 (33)

The volumetric-grade distribution is found by minimizing the objective function

$$\phi = \sum_{i=1}^{12} \frac{|\hat{\mathbf{P}}_{Li} - \sum_{j=1}^{12} \mathbf{H}_{ij} \mathbf{p}_{vj}|}{|\hat{\mathbf{P}}_{Li}|}$$
(34)

subject to the constrains

$$p_{Vi} \ge 0$$

and

$$P_{V_{j-1}} \leq P_{v_j} \leq P_{V_{j+1}}$$



where  $\hat{P}_{Li}$  represents the measured cumulative lineargrade distribution up to and including class i.  $P_{vj}$  is the cumulative grade distribution up to and including class j.

Fig. 10 and 11 show an example of the practical application of this technique. A sample of particles of a dolomite-sphalerite ore in the narrow size range

710 to  $1000\mu$ m were very carefully fractionated using magnetic fluid techniques and the particles in the density interval 3.5 to 3.7 g/cc were carefully comminuted in an ultrasonic mill. The comminution products were mounted, sectioned, polished and imaged. The resulting linear-grade distributions are shown in **Fig. 10**, and the data converted to volumetric-grade



Fig. 10 Measured linear-grade distributions for progeny particles of various sizes generated by comminution of particles in the size range 710 to  $1000\mu$ m and in the narrow density range 3.5 to 3.7 g/cc.



Fig. 11 The volumetric-grade distribution corresponding to the data shown in Fig. 10.



distribution using the inversion procedure are shown in **Fig. 11**. The excellent detail in the calculated distributions is clearly visible, and the very significant differences between the linear and volumetric-grade distributions are clearly evident.

#### 6. Acknowledgement

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### 8. Notation and Symbols

It is convenient to use a symbolic notation for the many quantities that are measured directly or can be calculated or estimated from measurements on sections. The most important symbols that are in common use are given in **Table 1**. Whenever a symbol refers to a particular phase it is represented by means of a lower-case letter.

Definition	Symbol	Alternative Symbols	Dimension
1. Parameters of structure			
Volume (of component or structure)	V		m <sup>3</sup>
Surface area (of components)	S		m <sup>3</sup>
Length of linear feature in space	J	L	m
Mean curvature, integral	K	М, Н	m
Total (Gaussian) curvature, integral	G		$m^0$
Number of objects	N		$m^0$
Diameter (of spheres)	D		m
Caliper diameter	Н		m
Sheet thickness	τ	D	m
2. Parameter of profiles on section area			
Area of profiles	А		$m^2$
Boundary length of profiles (perimeter)	В	L, P, C	m
Transections of linear features	Q		$m^0$
Tangents to profile boundary	Т		$m^0$
Number of profiles	Ν	n	m <sup>0</sup>
Diameter (caliper) of profiles	d, h		m
Curvature of plane figure	С		
3. Parameter on test lines			
Length (total) of profiles on test line	L		m
Intersections with surface or profile boundary	Ι	P. N. C	$m^0$
Length of intercept or chord	l	L2, L3	m
Number of intercepts	n	N	$m^0$
4. Parameters on test point sets			
Point number on profiles or structure	Р		$m^0$
5. Parameters of test sets			
Test volume	VT		m <sup>3</sup>
Test area	AT		m <sup>2</sup>
Test line length	L		m
Test point number	$P_{\tau}$		$m^0$
Section (slice) thickness	ť	Т	m

	_		-			
<b>Fable</b>	1. I	list -	of	stereo	logical	symbols



Definition	Symbol	Alternative Symbols	Dimension
6. Densities in space			
Volume density	$V_{V}$		$m^0$
Surface density	$S_V$		m <sup>-1</sup>
Length density in space	Jv	$L_V$	m <sup>-2</sup>
Mean curvature density	K <sub>v</sub>	M <sub>V</sub>	m <sup>-2</sup>
Total curvature density	Gv	·	m <sup>-3</sup>
Numerical density	N <sub>V</sub>		m <sup>-3</sup>
7. Densities on test sets			
Areal density	A		$m^0$
Boundary length density	B		m <sup>-1</sup>
Transection density on area	Q		m <sup>-2</sup>
Numerical density of profiles on area	Ν <sub>Δ</sub>		m <sup>-2</sup>
Tangent density on area	Τ <sub>Δ</sub>		m <sup>-2</sup>
Intercept length density on line	L		m <sup>-1</sup>
Intersection density on line	I		m <sup>-1</sup>
Intercept number density	N		m <sup>-1</sup>
Point density	$P_{P}^{L}$		m <sup>0</sup>




# Numerical Analysis of Movement of Balls in a Vibration Mill in Relation with Its Grinding Rate<sup>†</sup>

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#### Abstract

Effects of grinding conditions and fractional ball filling on the behavior of balls and their collision characteristics in a vibration mill were investigated by image analysis with a video recorder as well as by a numerical calculation method. It was made clear that an increase in fractional ball filling causes an increase in frequency but a decrease in average intensity of ball collisions, and that it results in acceleration of the circulation speed of the balls in the reverse direction to that of circular vibration of the mill.

A good correlation independent of vibration conditions and fractional ball filling was obtained between the rate constant of grinding determined by grinding experiments with glass beads as a feed material and the effective breaking collision frequency of balls calculated by the simulation and defined as the frequency of ball collisions whose intensity is greater than the strength of feed particles. From these results, it was made clear that there is an optimum fractional ball filling, depending on the strength of the feed materials and vibration conditions of the mill, that maximizes the rate of grinding.

#### 1. Introduction

There are various types of ball-media mills which lately attract attention as ultrafine grinding mills. In order to elucidate the grinding mechanism of these mills, knowledge of movement of balls is fundamental and essential. Since many years ago, there have been published a number of experimental and theoretical studies on the ball movement in vibration mills<sup>1</sup>) which have about ten times higher grinding rate than tumbling ball mills, including the early work of Bachmann<sup>2)</sup>. As the recent analytical approaches, a group of balls were treated as an assemble by Kousaka et al.<sup>3)</sup>, the one-dimensional vibration of a few balls was analyzed by Inoue<sup>4)</sup>, the effects of vibration frequency and amplitude on the collision velocity and frequency of a single ball in one-dimension was studied by Kuwahara et al.<sup>5)</sup> and the motion of a single ball was analyzed in two dimensions by Suzuki et al.<sup>6)</sup> On the other hand, some attempts have been made in experimental ways with stress sensors buried in the inner wall of mill pots<sup>7</sup>) or with mechanical and electrical sensors fixed in the balls<sup>8)</sup> to measure the intensity and frequency of their collisions. However, there have been seen few reports which analyzed the movement of individual balls or measured the collision intensity and frequency of small balls in a vibration mill.

In practical use, vibration mills are operated usually with the fractional ball filling of 0.8 to  $0.9^{9, 10, 11}$ , which is quite larger than that of tumbling ball mills. Concerning the effects of fractinal ball filling, a number of reprots have been published with the discussions using a model of double actions<sup>12</sup>, on the relation with the circular speed<sup>13</sup> and on the effects of mill's shape<sup>14</sup>. However, the effects of fractional ball filling on the grinding properties as well as the movement and collisions of individual balls have not been cleared yet.

In the present study, it was attempted to simulate the movement of balls in a vibration mill by means of a numerical calculation method taking accout of the interactions between the individual discrete elements<sup>15, 16, 17, 18)</sup> and to compare the results with those obtained by experiments with a video tape recorder. In addition, the grinding performance was attempted to correlate with the intensity and frequency of ball collisions calculated from the simulation

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of ball movement. The focus was placed on the investigation of the effects of vibration amplitude, frequency and the fractional ball filling of a vibration mill on the grinding performance as well as the movement of balls.

## 2. Simulation by discrete element method

The balls in the pots of vibration mill with circular oscillation are put into violent motion by receiving kinetic energy through the collisions against the inner wall of pot or other surrounding balls. Since the drag terms by fluid in the equations of motion for the larger balls in the air are negligible, their movement is determined almost by the contact force from the mill pot and other balls as well as by the gravity force. In fact, the individual balls repeat the collisions many times in a short time period and besides the collisions are not completely elastic because of local plastic deformation and damage in the vicinity of the contact points. It was attempted here to simulate the movement of individual balls by use of discrete element method developed by Cundall et al.<sup>19)</sup>, applying modified calculation technique of circular elements proposed by Kiyama et al.<sup>15)</sup> as explained below briefly.

Assuming that each ball is a rigid sphere, the elastic and non-elastic characteristics at the ball collisions are expressed by modeling with elastic spring (stiffness k) and viscous dashpot (contact damping coefficient  $\eta$ ) as demonstrated in **Fig. 1**, leading to the following equation of motion for the balls in the two-dimensional pot.

$$m \frac{d^2 u_n}{dt^2} + \eta_n \frac{d u_n}{dt} + k_n u_n = 0 \qquad (1-1)$$

$$m \frac{d^2 u_s}{dt^2} + \eta_s \frac{d u_s}{dt} + k_s u_s = 0 \qquad (1-2)$$

$$I \frac{d^{2}\phi}{dt^{2}} + \eta_{s} r_{B}^{2} \frac{d\phi}{dt} + k_{s} r_{B}^{2} \phi = 0$$
 (2)

where u and  $\phi$  are translational and rotational displacements, the subscripts n and s denote the normal and tangential directions, and m,  $r_B$  and I are mass, radius and inertia moment of a ball respectively.

The position and the velocity of individual balls at a time t are obtained by the numerical integration of the above equations. The time increment  $\Delta t$  was set at  $1.0 \times 10^{-4}$  s from the practical viewpoint taking account of the condition of  $\Delta t < 2 \sqrt{m/k}$  as recommended by Cundall for the convergency and stability of the solution. The stiffness in the normal direction  $k_n = 1.45 \times 10^5$  N/m was adopted by the fitting based on the comparison of absolute velocity of balls with those determined by video pictures. The stiffness in the tangential direction ks was assumed to be a quarter of  $k_n$  as proposed by Kiyama et al. The contact damping coefficient  $\eta$  in both the normal and tangential directions were calculated from the following relation to maximize the damping of the abovementioned one-dimensional vibration equation.

$$\eta = 2\sqrt{\mathbf{m} \cdot \mathbf{k}} \tag{3}$$

As for the friction coefficient between balls, the value of 0.33 was used<sup>20)</sup>. The properties for collisions between the balls and the inner wall of mill pot were regarded the same as those between the balls.

#### 3. Experimental

The vibration mill used for the experiments (model MB-1.6 made by Chuo-Kakouki Ltd.) is quipped with a pair of pots which oscillate in circle around a horizontal axis. The vibration amplitude and the frequency were controlled with unbalance weights and an inverter respectively and set at 3.6, 4.5 and 5.2 mm



Fig. 1 Model of ball collision for numerical calculation of ball motion



for the former and 20, 25 and 30 Hz for the latter. A two-dimensional cell containing a single layer of balls was fixed onto the end of each mill pot as shown in **Fig. 2**. Balls with the diameter of 12.7 mm were used for the trials with the fractional ball filling from 0.6 to 0.95.



Fig. 2 Dimensions of mill pot (Top view)

The cover of the two-dimensional cell was made of transparent acrylic plate for the observation of ball movement inside the cell, which was taken by a video tape recorder using a synchronized stroboscope flashing at an interval of 60 1/s. The video pictures were superimposed on a display connected with a computer and the position of all the balls in the cell were memorized manually with a mouse for successive 20 picture frames. The velocity of balls was obtained as the distance between the positions of each ball in two successive frames divided by the time interval of 1/60 s. In addition, the circular movement of balls in the cell was noticed and its speed was determined from the time required for a single ball to make one turn by the slow motion video pictures.

In order to evaluate the results obtained by the simulation, grinding experiments were carried out with glass beads screened between 42 mesh (350  $\mu$ m) and 28 mesh (590 $\mu$ m) beforehand. The fractional feed filling of ball bed voidage was kept constant at 0.2. The ground fraction at each batch grinding was obtained from the weight passing 350 $\mu$ m screen.

# 4. Results and Discussion

# 4.1 Comparison of the calculated with the experimental

#### 1) Dispersion of balls

An example of the change of positions of balls calculated by the discrete element method is shown in **Fig. 3**. The values given on the right-hand bottom of each picture denote the time after the start of movement from the stably packed condition and the



Fig. 3 Example of change of balls' position in the mill pot



phase angle of the mill pot counted anti-clockwise from the bottom point. The straight line from the ball center and the circular arc from the point 90 degrees anti-clockwise from the bottom mean the translational and the rotational velocities of balls respectively. In order to investigate the appropriateness of the simulation, the dispersed states of balls calculated were compared with those obtained by observation with a video camera under various conditions of the vibration amplitude and frequency of the mill, in the radial (**Fig. 4**) and the tangential directions (**Fig. 5**).

These comparisons of ball number density show good agreement between the results obtained by simulation and experiments also under other vibrating conditions and fractional ball filling. As a general tendency, the ball number density near the inside wall is higher than that in the core. It is also clear from the figures that the ball number density is highest in the third quadrant and lowest in the first under all the vibrating conditions, though the balls are not well dispersed with the higher density near the pot bottom under the weaker vibrating conditions.

#### 2) Velocity

**Fig. 6** shows some examples of comparison of ball velocity obtained by simulation and observation with video pictures. Since the video pictures were taken at the interval of 1/60 s, the results by simulation which was carried out with a time interval of  $1 \times 10^{-4}$  s



Fig. 4 Distriubtions of ball number density (Radial direction)



Fig. 5 Distributions of ball number density (Tangential direction)





Fig. 6 Absolute velocity of balls

were modified corresponding to 1/60 s. The modified ball velocity agreed well with those determined by the observation at every condition of vibration.

Fig. 7 shows the change of average ball velocity with the fractional ball filling J, where the results by



Fig. 7 Effect of fractional ball filling on ball velocity

simulation and experiments agree well and a minimum velocity is seen around J = 0.8.

#### 3) Circulation speed

From observation of the movement of balls, it was noticed that the balls make circular movement as a whole in the mill pot and this was confirmed also by the simulation as shown in **Fig. 8**. This phenomenon of circulation of balls in the vibration mill, which would affects greatly the circulation of feed materials, has been long acknowledged qualitatively but its quantitative consideration has hardly been made.

**Fig. 9** shows the change of circulation speed of balls with the fractional ball filling under the standard vibrating condition of  $f = 25 \text{ s}^{-1}$  and 2a = 5.2 mm. Both the simulation and the observation with VTR indicate that the balls tend to circulate in the reverse direction against the circular oscillation of the mill pot and that there is a point where the direction of circulation changes.

Furthermore, another new knowledge has been obtained on the circulation of balls in the mill in relation with the friction coefficient of balls  $\mu$ . The results of circulation speed obtained by simulation with  $\mu = 0.33$  agreed well with those determined with VTR when the balls used repeatedly after washing and drying were applied for the tests. However, when entirely new balls were used for the experiments, the circulation speed was + 0.115  $\pi$  rad/s, while used balls showed - 0.314  $\pi$  rad/s under the same





Fig. 8 Comparison of circulation of balls obtained by simulation and observation with VTR at different fractional ball filling

condition. In order to clarify this phenomenon, the simulation was carried out with different frictional coefficients to calculate the circulation speed (**Fig. 10**). This figure shows clearly the tendency that the balls tend to circulate in the reverse direction against the mill's oscillation at each constant fractional ball filling, as the friction coefficient increases. It was confirmed that the friction coefficient of balls hardly affected the ball velocity, the intensity and frequency of ball collisions in spite of its considerable influence on the circulation movement of balls.

From the above results of dispersion state, velocity and circulation speed of balls, this simulation method seems highly useful to estimate the movement of balls in a vibration mill at different vibrating conditions and fractional ball filling.

## 4.2 Relations with the grinding rate

## 1) Effects of vibrating conditions

This numerical calculation method has a great advantage to provide with information of frequency and intensity of ball collisions, the measurement of which has hardly been possible conventionally. An example of distribution of ball collision intensity obtained by the simulation is shown in **Fig. 11**, where the intensity ranges mostly from 1 to 100 N at the fractional ball filling of 0.9 under the standard vibration condition.



Fig. 9 Effect of fractional ball filling on circulation speed of balls

The total number of collisions per unit time Z is given by the integration of  $Z_F$  with the collision intensity and amounted to 11,800 to 15,000 per second at the ball filling of 0.8 within the experimental range, which correspond to 220 to 280 collisions per ball in a second. As seen from **Fig. 12**, the total collision frequency does not change so much as vibration amplitude and frequency themselves in the experimental range of amplitude up to 5.2 mm.

On the other hand, the average collision intensity changes greatly depending on the vibration amplitude and frequency in the experimental range, though it tends to saturate above the amplitude of 7 to 8 mm (**Fig. 13**).

**Fig. 14** shows the relationship between the total collision frequency and vibration velocity, which are well correlated independent of the vibrating conditions. As seen in **Fig. 15**, however, the average collision intensity is not so well correlated with only the vibration intensity defined as  $K = a \omega^2/g$ .

Then, the effects of vibration amplitude and frequency on the total frequency and average intensity of ball collisions were examined keeping the vibration intensity constant as shown in **Figs. 16** and **17**. It is seen from these figures that under the normal operational range of amplitude and frequency both the total collision frequency and the average intensity increase with the increasing amplitude but that both of them decrease with the increasing vibration





Fig. 10 Dependence of circulation speed on coefficient of friction of balls obtained by simulation



Fig. 11 An example of distribution of ball collision intensity

frequency. These results agree well with the knowledge obtained from grinding experiments under the amplitude of 2.0 to 12.4 mm and frequency of 20 to  $50 \text{ s}^{-1}$  by Sasaki et al.<sup>21)</sup> that with a constant vibration intensity the grinding rate is raised with the increasing vibration amplitude but not by the increase of frequency.

# 2) Effects of fractional ball filling

In the present report, the relation of the grinding rate with the intensity and frequency of ball collisions



Fig. 12 Change of total ball collision frequency with vibration amplitude and frequency



Fig. 13 Change of average ball collision intensity with vibration amplitude and frequency



Fig. 14 Relationship between vibration velocity and total ball collision frequency

was investigated from the grinding experiments of glass beads at low feed filling, neglecting the effects





Fig. 15 Change of average ball collision intensity with vibration intensity.





Fig. 16 Effect of vibration amplitude on total collision frequency and average collision intensity at constant vibration intensity.



Fig. 17 Effect of vibration frequency on total collision frequency and average collision intensity at constant vibration intensity.

Fig. 18 Effect of fractional ball filling on average intensity and total frequency of ball collisions.

of feed on the movement of balls. **Fig. 18** shows the relationships of the average intensity and total frequency of ball collisions with the fractional ball filling J at different vibration frequencies obtained by the calculation. As seen from the figure, the total collision frequency increases but the average collision intensity decreases with the increasing J. Therefore it is probable that there should be an optimum fractional ball filling and vibrating conditions depending on the size and strength of feed particles.

The grinding experiments have been carried out with glass beads as feed under different vibrating conditions to study the effect of fractional ball filling on the grinding rate. **Fig. 19** shows the plot of residues in the product R over  $350\mu$ m, which is the minimum particle size in the feed, against the grinding time t on a semi-log paper. Assuming the following firstorder equation of disappearance

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -\mathbf{k}_1 \cdot \mathbf{R} \tag{4}$$

the rate constant of grinding  $k_1$  is determined from the gradient of lines in Fig. 19 as follows.

$$\log R = -\log e \cdot k_1 \cdot t \tag{5}$$

The plot of this  $k_1$  against the fractional ball filling J is shown for two vibrating conditions in **Fig. 20**, which indicates maximum values of grinding rate around J = 0.9.





Fig. 19 First-order plot for breakage of glass beads at various fractional ball filling.

On the other hand, the grinding rate has been conventionally evaluated using selection functions. The selection function for vibration ball mills S(x), which corresponds to the rate constant of grinding with feeds of narrow size distributions, has been discussed in the following equation from the statistical standpoint<sup>22, 23, 24)</sup>

$$S(\mathbf{x}) = c_{sp} \cdot P_n \cdot P_f \cdot Z$$
(6)

where  $P_n$  is the probability of nipping of a feed particle between balls,  $P_f$  the probability of a nipped particle being broken, Z ball collision frequency and  $c_{sp}$  a constant. It is assumed that  $P_f$  is determined by the relationship between the strength of feed particles and ball collision intensity. Consequently, the relationship between the rate constant of grinding obtained from the grinding experiments  $k_1$  and the ball collision frequency Z obtained by the simulation



Fig. 20 Effect of fractional ball filling on rate constant to grinding.

should differ depending on the vibrating conditions and the fractional ball filling.

In order to relate these factors, the following frequency of ball collisions effective to break a particle (hereafter called effective breaking collision frequency) was defined taking account of the distribution of ball collision intensity and breakage strength of a feed particle  $F_{cr}$  as follows :

$$Z_{cr}(F_{cr}) = \sum_{F \ge F_{cr}}^{F_{max}} Z_F$$
(7)

Figs. 21(a) and (b) show the change of effective breaking collision frequency with the fractional ball filling at different vibrating conditions. Although the total frequency of ball collisions at the stronger vibration (Fig. 21(a)) hardly differs from that at the weaker one (Fig. 21(b)), the frequency of ball collisions with the intensity larger than some decades of N radically decreases at the weaker vibration. In addition, the effective collision frequency shows its maximum around J = 0.9 in the similar way as the grinding rate does. The relation between the rate constant of grinding k1 determined by the experiments and the effective breaking collision frequency  $Z_{cr}$  obtained by the simulation for  $F_{cr}$ = 60 N from literature<sup>25)</sup> is shown in Fig. 22, which gives the following linear equation independent of the vibrating conditions and the fractional ball filling of the mill

$$\mathbf{k}_1 = \mathbf{c}_{\mathbf{k}\mathbf{z}} \cdot \mathbf{Z}_{\mathbf{c}\mathbf{r}} \tag{8}$$





Fig. 21 Effect of fractional ball filling on frequency of ball collisions with intensity greater than strength of feed particles.



Fig. 22 Relation between rate constant of grinding and frequency of ball collisions effective to crush feed particles. (Keys as for Fig. 19)

where  $c_{kz}$  is a constant related with the probability of particle nipping depending on the ball diameter and size of feed particles. From these results, it is concluded that the grinding rate could be estimated from the ball collision intensity obtained by the simulation of ball movement as well as the breakage strength of feed particles to some extent. It would be necessary, however, to take account of the effects of feed materials on the movement of balls as the fractional feed filling increases to influence it.

#### 5. Conclusions

The results obtained by the numerical calculation of movement of balls in a vibration mill using the discrete element method agreed well with those determined by the observation with a video tape recorder in terms of dispersion state, velocity and circulation speed of balls in the pot and it was found that this numerical calculation method is useful for describing the behavior of balls in the vibration mill.

Additionally, it has become possible by this numerical simulation to calculate the intensity and frequency of ball collisions, which have been difficult to measure directly and the following points have been made clear: (1) This numerical simulation describes the movement of balls well with the same parameters at different fractinal ball filling as well as vibrating conditions.

(2) The frequency of ball collisions is determined definitely by the vibration velocity proportional to the product of both vibration amplitude and frequency, although the average intensity of ball collisions is not determined definitely by neither vibration velocity nor vibration intensity.

(3) As the fractional ball filling increases, the frequency of ball collisions increases but their average intensity decreases.

(4) As the fractional ball filling increases, the balls tend to circulate in the reverse direction against the circular vibration of mill pot.



(5) The circulation of balls is influenced by the friction coefficient of balls  $\mu$ . With the larger  $\mu$ , the balls tend to circulate in the reverse direction against the circular vibration of the mill pot.

(6) At a costant vibration intensity, both intensity and frequency of ball collisions increase with the increasing vibration amplitude but decrease with the increasing vibration frequency under usual grinding conditions. This results obtained by the numerical calculation explains well the experimental results under the similar grinding conditions.

(7) A linear relation was found between the rate constant of grinding and the effective breaking collision frequency of balls defined as the ball collision frequency with intensity larger than the particle breakage strength, independent of the vibrating conditions and the fractional ball filling.

(8) The optimum fractinal ball filling to maximize the grinding rate was regarded as that to maximize the effective breaking collision frequency depending on both the feed particle strength and grinding conditions and was calculated to be around 0.9, which agreed well with the experimental results.

Although the numerical simulation here has been carried out for the 2-dimensional pot to realize the observation of the ball movement directly for the comparison of simulation with experimental data, the results would be possibly extended to the 3-dimensional cases to a great extent. This matter would be future subjects to be investigated together with the effects of other conditions such as the feed and surrounding fluid.

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# Nomenclature

а	= vibration amplitude of mill	[m]
C <sub>kz</sub>	= a constant in Eq. (8)	[-]
C <sub>sp</sub>	= a constant in Eq. (6)	[-]
e	= elastic drag	[N]
F	= average collision intensity	[N]
F <sub>cr</sub>	= strength of feed particles	[N]
f	= vibration frequency of mill	[s <sup>-1</sup> ]
g	= gravitational acceleration	[m·s⁻²]
Ι	= ball inertia moment	[kg·m²]

=	fractional ball filling of mill	[-]
=	vibration intensity of mill	
	$(\mathbf{K} = \mathbf{a}\omega^2/\mathbf{g})$	[-]
=	stiffness	[N·m <sup>-1</sup> ]
=	rate constant of grinding	[s <sup>-1</sup> ]
=	ball mass	[kg]
=	probability of being crushed	[-]
=	probability of being nipped	[-]
=	weight fraction remaining ung	coud[-]
=	ball radius	[m]
<u></u>	position in radial direction of	
	mill pot	[m]
=	selection function	[s <sup>-1</sup> ]
=	time	[s]
=	translational displacement of b	all [m]
=	vibration speed of mill	
	$(V = a \omega)$	[m·s <sup>-1</sup> ]
=	ball velocity	[m·s <sup>-1</sup> ]
=	total ball collision frequency	[s <sup>-1</sup> ]
=	ball collision frequency effective	'e
	to crush feed particles	[s <sup>-1</sup> ]
=	frequency of ball collisions wit	h
	intensity of F	[s <sup>-1</sup> ]
=	contact damping coefficient	[kg·s <sup>-1</sup> ]
=	circulation angle of balls	[rad]
=	friction coefficient	[-]
=	ball number density	[m <sup>-2</sup> ]
=	rotational displacement of ball	[rad]
-	angular velocity of vibration m	ill
	$(\omega = 2\pi f)$	[rad·s <sup>-1</sup> ]
	. ,	

#### < Subscripts >

J

K

k

r<sub>1</sub>

m P<sub>f</sub>

P<sub>n</sub>

R

r<sub>B</sub>

r<sub>m</sub>

S

t

u V

v<sub>A</sub>

Z Z<sub>cr</sub>

Z<sub>F</sub>

η

θ

μ

σ

φ

ω

s

w

B = ball

n = normal direction

= tangential direction

= wall of mill

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# The Experimental Stress – Strain Rate Relationship of Granular Materials †

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#### Abstract

The flow of granular materials is important in the field of material handling. However, there are many unknown factors associated with the analysis of these flows. Constitutive relations (stress and strain rate relations) are needed to describe the flow dynamics of granular materials. We experimentally obtained the constitutive relations of granular materials by using a chute-type shear apparatus. The chute in which the granular material is contained and covered by a top board, can be moved on straight rails, while the top board is loaded vertically and kept immobile. The shear stresses, normal stresses and strain rates measured by using the chute-type shear apparatus give the constitutive relations of the granular materials. The experimental results describe well the flow characteristics (e.g. the stress ratio of shear to normal stress is proportional to the strain rate, etc.) under the condition in which the friction forces between granular materials dominate.

#### 1. Introduction

In the handling of granular materials, flow is a phenomenon of great importance. However, compared with continuum such as water or air, very little is known at present about the flow mechanism of granular materials. This is, of course, because the handling of granular materials is much more complex compared with that of continuum but it is believed that one of the reasons for this is that flow dynamics have not been applied to granular materials as liquids. This is to say that the velocity and strain rate of granular materials, and also the relation between the stress and strain rate and such have not been correctly introduced into the dynamics of granular materials. Especially, in clarifying the flow of granular materials through flow dynamics, the constitutive relations (relation between stress and strain ratio etc.) must be clarified.

Experimental research in this connection has been conducted in the past but it is believed that a constitutive relation which properly expresses the flow of granular materials and which is simple and can be applied in practical uses has not yet been obtained. For example, the experiment by Savage et al<sup>1)</sup> in which shear flow is applied to a granular material inside an annular cell and the constitutive relation obtained involves the following problem. The annular cell used in their experiment is divided into a lower disk which rotates and an upper disk which is kept at rest to cause shearing while the range of the granular material layer moving at the same speed as the lower disk, namely the range which is not affected by shearing is defined by the condition  $\tau/\sigma < \tan \phi$  ( $\tau$ : shear stress,  $\sigma$ : vertical stress,  $\phi$ : internal frictional angle) and it is assumed that the velocity gradient in the area above this becomes linear. However it is difficult to determine the area of  $\tau/\sigma < \phi$  accurately since it is impossible to measure  $\tau/\sigma$  inside the apparatus. Moreover, with the annular cell continuously rotating and the granular material sealed therein, it is impossible to experimentally define the area which is not affected by the shearing effect. Since the existence of this area greatly affects the velocity gradient value inside the annular cell, it is difficult to obtain an accurate velocity gradient. Therefore, we prepared an apparatus consisting of a cell 3000 mm long and having a rectangular cross section (60 mm  $\times$  80 mm). This was packed with granular material and driven linearly and a shearing flow was induced in the material. The stress applied to the granular material and the velocity gradient were measured and from these results, the constitutive relation of the granular material was obtained. These show a non-linearity of the granular

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material flow characteristics. Furthermore, the various characteristics of the granular material would be clearly expressed.

# 2. Experiment apparatus and methods

Fig. 1 shows the apparatus that induces shear flow in a granular material and measures the shearing stress and strain rates. The container which is packed with granular material is 3000 mm long, 60 mm high, and 80 mm wide with a dolly provided under the container for free movement on rails in the lengthwise direction. A wire was tied to this apparatus and pulled by means of a motor which provides traction. For granular material specimens, circular pellets  $(D_p = 2.82 \text{ mm})$ , colored pellets  $(D_p = 2.87 \text{ mm})$ , and ceramic balls ( $D_p = 3.42$  mm) were used. The container was packed with granular material as shown in Fig. 1 then a top press board and weights (vertical load) were installed. The top press board of 2000 mm in length, 5 mm in thickness and 60 mm in width was provided with a support plate on its top surface to form a concave shape and prevent distortion of the press board. Also to prevent the press board from moving widthwise, smooth moving

wheels were attached at a height precluding contact with the particles to control the movement of the board. In addition, a top press board with a width of 78 mm was provided for use in experiments requiring observation from the side. The top press board was fastened to a load cell to prevent motion in the direction of overall movement of the container. The shear strength generated at the time of shear flow was measured and the shear stress was obtained. The measured results were recorded using a pen recorder. An example is shown in Fig. 2. Point (a) is the starting point and when the top press is set and the wire pulled, the load increases up to (b) due to the friction force between the granular materials. Feeding of the recording paper starts at (b) and the motor is started at (c). The load increases, yielding occurs at point (d), the container starts moving and shearing force is generated by the flow of granular material. When the motor is stopped at (e), the container stops, the shearing force due to the flow of granular material is relieved and the load decreases up to (f). When the top press board is removed at (f), the yield stress disappears and the force returns to (g). The value of the straight line (h) - (i) averaged over the loads between



Fig. 1 Chute type shear apparatus





Fig. 2 Typical chart recording of output from load cell used to determine shear stress generated in sheared granular material

(d) - (e) was used as the shearing force. Also the stress in the vertical direction applied on the shearing surface by the vertical load and weight of the press board was obtained. To measure the relation between stress and strain rates in the inner part of the granular material, a granular material similar to the specimen was attached to the upper and lower surfaces of the container and the press board which comes into contact with the granular material at a ratio approximating the packing ratio of the granular material. For the particles of the uppermost surface of the granular material layers packed in the container, namely for the granular material on the surface which generates shearing by contact with particles fixed to the press board, colored materials were arranged partially, the distance travelled and the travel time when the shearing force was generated were measured, and the strain rate in the fixed granular material was obtained. Fig. 3 shows



Fig. 3 Side view of granular material in chute

a schematic drawing of the condition seen from the side. The colored particles were arranged on one line

in the widthwise direction at a distance 1000 mm from the end of the container.

The distance through which the colored particles move varies depending on the position, between the vicinity of the side wall surface and near the center, and therefore the average was taken as the travelled distance. **Fig. 4** shows an example of measured



Fig. 4 Measured velocities of colored particles, used to determine the strain rate of a granular material

results of the velocity of colored particles when the container was driven at a velocity  $u_0$ . These were averaged and given as u to express the distance travelled by the colored particles.

The velocity of motion of the container from the start of the movement up to just before stopping measured by VTR is shown in **Fig. 5**. It can be seen that the time required for the velocity of the container to reach a value close to the steady-state value from 0 is very short compared with the whole time of the motion. Therefore, the error in the non-steady state container velocity before the steady container velocity is reached can be ignored. After reaching the steady state velocity, a fluctuation of about 10% in velocity can be seen but by averaging the total,  $u_0$  was obtained. An example is shown in **Fig. 5** by the dashed line.

When the motion velocity of the container is changed, the strain rate changes. Also the vertical stress is altered when different weights are placed on the press board. As the container of the granular material layer is transparent, the movement of the press board in the vertical direction was magnified through





Fig. 5 Measured velocity of chute

a VTR and observed from the side to see the changes occurring in the packed condition of the inner part of the granular material; The video camera was set up at a distance 1000 mm from the end of the container, in the same way as the arranged position of the colored particles.

## 3. Experimental results and observations

Experimental results for the relation between shearing stress and strain rate of circular pellets are shown in **Fig. 6**. The shearing stress  $\gamma$  is divided by the vertical stress P due to the vertical load to obtain a non-dimensional value. As shown in **Fig. 6**, the P value was changed 3 times and experiments were carried out. The strain rate  $\partial u/\partial y$  along the x axis is made non-dimensional using the particle diameter  $D_p$  and the gravitational acceleration g.

**Fig. 6** can be considered as a flow curve of the granular material (circular pellet) but the existence of the yield value is a characteristic differing from that of a Newtonian fluid. This is to say the flow curve of a granular material resembles that of a Bingham fluid. However it differs from a Bingham fluid in that  $\gamma/P$  is derived for the Y axis. If only  $\gamma$  is derived for the Y axis as in a Bingham fluid, the value of  $\gamma$  will depend greatly on the value of P but when combined as  $\gamma/P$ , data concentrates roughly in one place. Therefore, considering the results, it is thought that the combination  $\gamma/P$  is more reason-

able. However, as is obvious from **Fig. 6**, the  $\gamma/P$  value changes with the value P. Namely, with the increase of P, the  $\gamma/P$  value including the yield value increases greatly. As shown later in **Fig. 8**, along with the increase of P, the packing rate has increased and therefore it is believed that the packed condition in the inner part of the granular material becomes dense and that the  $\gamma/P$  value is increased. When  $\gamma$  is expressed by strain rate,  $\partial u/\partial y$  is affected by P and it is seen that the constitutive equation becomes non-linear.

Fig. 7 shows the experimental results of  $\gamma/P$ only in the case of P = 0.455 kPa. With the increase of strain rate,  $\gamma/P$  becomes non-linear. In granular materials, while the strain rate is low, the generation of shearing force is dominated by the friction force generated between the particles. When the strain rate becomes large, the force due to the collision of particles is added to this friction force, shearing force is generated and therefore the slope of the flow curve becomes steeper. However this phenomenon requires the condition that the packing rate is constant. Fig. 6 shows the results where all data including those of Fig. 7 are summarized but in Fig. 6, the change in the slope of the curve is not conspicuous. Consequently, it is thought that the packing rate inside the layer during flow has changed (decreased).

Therefore, the packing rate was obtained from the change in the layer height at rest, under no-load





Fig. 6 Ratio of shear to normal stresses as a function of strain rate for circular pellet

and under flow conditions. The results are shown in **Fig. 8**. In making this measurement, a 78 mm top press board which readily enabled observation of the changes in layer height from the side was used. Accompanying the increase in strain rate, the packing rate decreased slightly. This is because a dilatancy phenomenon occurs by including a shearing flow in the granular material layer and that the packing condition of granular material becomes coarse. Also when P becomes large, in some cases the packing rate exceeds 1 but this indicates that the packing rate has become dense due to the increase in load.

Fig. 9 shows the experimental results for the relation between shearing force and strain rate when colored pellets are used as specimen. Including the



Fig. 7 Ratio of shear to normal stresses as a function of strain rate for circular pellet (P = 0.455 kPa)



Fig. 8  $C/C_0$  as a function of strain rate for circular pellet

yield value, the  $\gamma/P$  values of the colored pellets are greater than those of circular pellets in their respective P values. Since the colored pellets are cylindrical in shape as opposed to the disk shape of circular pellets, the effect due to this difference in shape may be considered. Also in **Fig. 9**, the  $\gamma/P$  value is larger with a larger P value. This is perhaps caused by a dense packing condition resulting from the increase of P, in the same way as with circular pellets.

The results of  $\gamma/P$  where P = 0.455kPa are shown in **Fig. 10** and unlike **Fig. 9** which summarizes data of various P values, the linearity of  $\gamma/P$  is weak. It is thought that a decrease in the packing rate during flow is the cause.





Fig. 9 Ratio of shear to normal stresses as a function of strain rate for colored pellet

Fig. 11 shows measurement results of colored pellet packing rate, made in the same manner as those of Fig. 8. The results approximate those of Fig. 8 (results for circular pellets) with the packing condition becoming coarse with the increase of the strain rate. Also, a dense packing rate is seen with the increase of P.

**Fig. 12** shows the experimental results for the relation between shearing force and strain rate of ceramic balls. Regardless of the changes in P. the changes in  $\gamma/P$  are smaller compared with the other two types of specimens. As can be seen from **Fig. 14**, this is because the change in the initial packing rate due to the increase of P is smaller. Also, the yield value is the smallest among the three types of granular materials. As the ceramic balls are



Fig. 10 Ratio of shear to normal stresses as a function of strain rate for colored pellet (P = 0.455kPa)



Fig. 11 C/C<sub>0</sub> as a function of strain rate for colored pellet

almost perfect spheres, it is thought that compared with disk shaped or cylindrical shaped particles, they tend to move more easily and therefore have a smaller yield value.

Fig. 13 shows results of  $\gamma/P$  where P = 0.455kPa. Non-linearity of  $\gamma/P$  can hardly be seen. Also in Fig. 12, rather than the slope of the curve becoming steeper due to the increase in strain rate, the data shows that it becomes gentler. As can be seen from the measurement results of the packing rate given in Fig. 14, the reduction in the packing rate due to the increase in strain rate is more significant than for the other granular materials and this can be considered as the cause for the above. It is believed that since the ceramic balls are nearly spherical and have approximately the same diameter,





Fig. 12 Ratio of shear to normal stresses as a function of strain rate for ceramic ball

the dilatancy phenomenon becomes conspicuous at the time of flow induction and the reduction of the packing rate becomes greater compared with other specimens of granular materials. Consequently, it is thought that if the packing rate is perfectly constant, the non-linearity (the tendency of the slope of the flow curve to become greater) of  $\gamma/P$  in **Fig. 12** will also become obvious.

# 4. Conclusion

A shearing force was applied to a granular material by a linear movement and, shearing stress  $\tau$ , strain rate  $\partial u/\partial y$ , vertical stress P and packing ratio C/C<sub>0</sub> were measured. From the results of measurements for three types of granular materials, their constitutive relations were experimentally obtained. Consequently, it was found that generally, a primary relation exists between  $\tau/P$  and  $\partial u/\partial y$ . When P increases and packing becomes dense, the  $\gamma/P$  value including the yield value becomes large. Also it is thought that when the packing ratio is constant, the



Fig. 13 Ratio of shear to normal stresses as a function of strain rate for ceramic ball (P = 0.455kPa)



Fig. 14  $C/C_0$  as a function of strain rate for ceramic ball

 $\tau/P$  value as opposed to the  $\partial u/\partial v$  value becomes larger in a non-linear way but this tendency disappears when the packing condition becomes coarse due to the increase of  $\partial u/\partial y$ . Consequently, it was seen that the relation between  $\tau/P$  and  $\partial u/\partial y$  was extremely sensitive to small increases or decreases in the packing ratio. Also it was found that the yield value was smaller for spherical particles than for disk or cylindrically shaped particles. If an experimental constitutive equation can be obtained from these experiment results, and provided that relations between other vertical stress and strain rates can be obtained, then using these, it is possible to calculate the velocity distribution, stress distribution etc. over the entire area of hoppers from which granular materials flow out.

#### Nomenclature

С	: packing ratio at an arbitrary strain	rate of
	granular material	[-]
C <sub>0</sub>	: packing ratio at $P=0$ and $U_C=0$	[-]



D <sub>P</sub>	: mean diameter of granular mate	rial [mm]
g	: gravitational acceleration	$[mm/s^2]$
Р	: normal stress	[kPa]
u <sub>P</sub>	: velocity of the colored particle	[mm/s]
u <sub>c</sub>	: velocity of the chute	[mm/s]
$U_0$	: mean velocity of the chute	[mm/s]
х, у	: cartesian coordinates	[ - ]
au	: shear stress	[kPa]

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# Dispersion of Aggregate Particles by Acceleration in Air Stream †

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## Abstract

To clarify the dispersion mechanisms of aggregate particles in air, the dispersion of aggregate particles by acceleration in an air stream, which is a typical dispersion mechanism, was examined.

In the experiment, aggregate PSL (polystyrene latex) particles (primary spherical particle diameters are: 5.2 and  $2\mu$ m) were fed into an ejector, where aggregates were dispersed into smaller sizes by acceleration in a high-speed and high pressure (critical pressure higher than atmospheric pressure) air stream. Dispersed PSL particles were introduced into a sampling chamber and sampled on several slide glasses set on the bottom of the chamber by gravitational deposition. PSL particles thus sampled were observed with a microscope. This method allowed exact evaluation of the numbers of primary particles consisting of aggregates. It was suggested from the experiment that aggregate particles consisting of about  $5\mu$ m primary particles were almost entirely dispersed into primary particles by acceleration of the particles in the ejector.

The dispersion force acting on aggregate particles in an air stream at high Reynolds number was theoretically analyzed for a model aggregate particle and compared with the existing van der Waals adhesive force. It was found that the experimental results could be well explained by the theoretical comparison between the dispersion and adhesion forces.

# Introduction

The phenomenon of aggregate particle dispersion in an air stream is of importance in improving the performance of dry pulverization and classification processes of particles and also in analyzing the adhesion force between particles. Many studies using various types of dispersion apparatuses have been carried out in the past<sup>3, 5, 6, 8, 9</sup> but since those were made using polydisperse and non-spherical particles such as calciumcarbonate or carbon black, accurate evaluation of the experimental results was difficult.

In the present study, attention has been focused on dispersion by acceleration in an air stream which is a typical dispersion mechanism of aggregate particles. For the purpose of accurately grasping the dispersion mechanism and of searching for possibilities of obtaining high concentration PSL aerosol particles, an experiment was conducted to disperse relatively large (primary particle diameter of 2-5  $\mu$ m) dry PSL aggregate particles in a high-speed air stream and based on the obtained results, a theoretical study on dispersion by acceleration in an air stream was made.

In industrial processes, the demand for a stable generation of high concentration mono-disperse PSL particles is increasing for the evaluation of the collecting performance of dust collectors and for forming distance pieces for liquid crystal displays.

# 1. Theoretical study

# 1.1 Dispersion force acting on aggregate particles by an acceleration in air stream

Fig. 1 shows a model of an aggregate particle consisting of a large and a small particle. Particles A and B may each be an aggregate particle.  $F_d$ , which is the dispersion force when this aggregate particle is placed momentarily in a uniform fluid flow, is obtained. The equation of motion for the dispersion model<sup>3)</sup> of the authors reported previously is as shown below. Yuu et al carried out studies<sup>8)</sup> on this

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<sup>†</sup> This report was originally printed in Kagaku Kougaku Ronbunshu, 18, 233 (1992) in Japanese, before being translated into English with the permission of the editorial committee of the Soc. Chemical Engineers, Japan.





Fig. 1 Illustration of a model aggregate

model using the resistance which took into account the effect of adjacent spheres but for the sake of simplification, the model of the authors is used.

$$\frac{\pi}{6} d_{vA}^{3} \varrho_{pA} \frac{dv_{pA}}{dt} = R_{fA} - F_{d}$$
(1)

$$\frac{\pi}{6} d_{\rm vB}^{3} \varrho_{\rm pB} \frac{d\upsilon_{\rm pB}}{dt} = R_{\rm fB} + F_{\rm d}$$
<sup>(2)</sup>

Where subscript A and B relate to the two particles composing the particle aggregate shown in Fig. 1,



 $d_v$  is the volume equivalent diameter,  $\varrho_p$  is the density of the particle,  $v_p$  is the velocity of the particle,  $R_f$  is the fluid drag force, and  $F_d$  is the dispersion force acting on the particle. Since the two particles are adhered to each other,  $v_{pA} = v_{pB} = v_p$ , and  $\varrho_{pA} = \varrho_{pB} = \varrho_p$  are assumed and from these expressions, the dispersion force  $F_d$  is expressed

$$F_{\rm d} = \frac{R_{\rm fA} - D_{\rm v}{}^3 R_{\rm fB}}{D_{\rm v}{}^3 + 1} \quad (D_{\rm v} \equiv d_{\rm vA}/d_{\rm vB} \le 1)$$
(3)

Here, to apply up to a large Reynolds number ( $Re = d_v u_r \varrho_f / \mu$ , based on the particle diameter), the following expression<sup>6</sup>) is used for the drag force.

$$R_{\rm d} = \frac{\pi}{8} d_{\rm v}^2 \varrho_{\rm f} u_{\rm r}^2 (0.55 + \frac{4.8}{\sqrt{Re}})^{-2} \varkappa \\ (Re \le 10^4)$$
(4)

Where  $\varrho_f$  is the density of the fluid,  $u_r$  is the relative velocity between the particles and the fluid, and  $\varkappa$  is the dynamic shape factor mentioned in 1.3. Generally,  $\varkappa$  is used for the Stokes drag force but as shown by Eq. (4),  $\varkappa$ , if defined, can be applied at an high Reynolds number<sup>2</sup>).

By substituting Eq. (4) in Eq. (3), the dispersion force  $F_{\rm d}$  can be obtained using the following expression.

$$F_{d} = \{0.119 \varrho_{f} u_{r}^{2} d_{vB}^{2} D_{v}^{2} (\varkappa_{A} - D_{v} \varkappa_{B}) + 2.07 \sqrt{\mu} \varrho_{f} u_{r}^{3} d_{vB}^{3} D_{r} (\varkappa_{A} - D_{v}^{3/2} \varkappa_{B}) + 9.05 \mu u_{r} d_{vB} D_{v} (\varkappa_{A} - D_{v}^{2} \varkappa_{B}) / (D_{v}^{3} + 1)$$
(5)

#### 1.2 Fluid flow at the ejector

Eq. (5) consists factors relating to the fluid (relative velocity between particles and fluid  $u_r$ , density of fluid  $\varrho_f$  etc.) and factors relating to the particles (volume equivalent diameter  $d_v$ , dynamic shape factor  $\varkappa$ ) and therefore the former is studied first.

The velocity of the fluid never exceeds the sound velocity (critical velocity) and therefore when only the fluid velocity is considered, the dispersion force due to acceleration of the air stream cannot exceed the force equalling this. However, as can be seen from Eq. (5), for a Reynolds number which is larger than the Stokes' law, if the density of fluid increases, it is possible to increase the dispersion force. For example, as in the present experiment where an ejector is used to raise the critical pressure above the atmospheric pressure by delivering high pressure gas through a very narrow clearance, the density of the fluid increases in proportion to this critical pressure and therefore even if the flow velocity has reached the critical velocity (sound velocity), an even higher dispersion force can be achieved. Furthermore, the viscosity of fluid such as air or nitrogen hardly change with pressure changes and therefore are not considered here.

The ejector used in the present experiment consists of an annular section with a very narrow



clearance  $I_t$  (variable from 0 - 3 mm) and a throat section as shown in **Fig. 2**, and therefore it is readily possible to make the fluid immediately after ejection from the annular section attain a flow reaching the critical pressure and critical velocity by adjusting this  $I_t$  and the pressure  $P_1$  of feed gas (nitrogen in this present experiment). In this case, assuming that the annular section is a convergent nozzle and considering that the energy change in this section is not a completely adiabatic change but a polytropic change with wall surface friction, then the critical pressure and critical velocity can be obtained as follows:

$$P_{\rm m}/P_1 = \{2/(n+1)\}^{n/(n-1)}$$
(6)

$$u_{\rm m} = \phi_{\rm m} \sqrt{RT_1} \tag{7}$$

$$\phi_{\rm m} = \sqrt{2g\varkappa \ (n-1)/(\varkappa - 1) \ (n + 1)} \tag{8}$$

Where  $P_1$  is the pressure at the ejector,  $T_1$  is the absolute temperature of the inlet gas, R is the gas constant, g is the acceleration due to gravity, n is the index of polytropic change, and  $\varkappa$  is the ratio of constant pressure to constant volume heat capacity (about 1.4 in the case of nitrogen). If n can be obtained, the pressure  $P_m$  and flow velocity  $u_m$  can be derived.

Besides this, the formula in the case of an adiabatic flow are as follows:

$$P_{c}/P_{1} = \left\{ 2/\left(k + 1\right) \right\}^{k/(k-1)}$$
(9)

$$w_{\rm c} = \phi_{\rm c} \sqrt{RT_1} \tag{10}$$

$$\phi_{\rm c} = \sqrt{2gk(k+1)} \tag{11}$$

Assuming an index of polytropic change n = 1.3, from Eqs. (8) and (11), we get,

 $\phi_{\rm m}/\phi_{\rm c} = 0.88$ 

Since it is believed that this value of a well finished round hole nozzle may reach 0.95 - 0.975, 0.88 obtained with n = 1.3 is roughly a reasonable value for the present annular nozzle where the contact area between fluid and wall surface is large.

Therefore, when n = 1.3 is substituted in Eqs. (6) – (8), the critical pressure  $P_{\rm m}$  and critical velocity  $u_{\rm m}$  are obtained as follows:

$$P_{\rm m} = 0.546 P_1 \, [{\rm Pa, \ abs.}]$$
 (13)

$$u_{\rm m} = 16.1 \sqrt{T_1} \, [{\rm m/s}] \doteq 280 {\rm m/s}$$
 (14)

From this critical pressure  $P_{\rm m}$ , the density of the

fluid  $\varrho_{\rm f}$  can be obtained. Also the initial velocity of the particles at the ejector inlet is approximated as 0, and even supposing that it is 10 m/s, the relative velocity  $u_{\rm r}$  between the particles and the fluid does not change much and therefore  $u_{\rm r}$  is taken as the critical velocity  $u_{\rm m}$ . As can be seen from Eqs. (13) and (14), the critical velocity  $u_{\rm m}$  is constant. The critical pressure of the fluid, namely the density  $\varrho_{\rm f}$  changes with the fluid feed pressure  $P_1$  to the ejector, and by increasing  $P_1$ , the dispersion force in Eq. (5) can be made larger.

# **1.3** Structure and dispersion process of aggregate particles

The dynamic shape factor  $\varkappa$  and volume equivalent diameter  $d_v$  necessary for calculating the dispersion force are given by the following expression when aggregate particles are roughly composed of uniform spherical primary particles<sup>4</sup>).

$$\varkappa = 0.862 N^{1/3} \qquad (2 \le N \le 10) \tag{15}$$

$$d_{\rm v} = N^{1/3} d_{\rm p1} \tag{16}$$

Where N is the number of primary particles composing an aggregate, and  $d_{p1}$  is the primary particle diameter. However, Eq. (15) is for chainlike aggregate particles and this point shall be studied later. The values of both expressions are dependent on the number N of the primary particle and therefore, we shall next study the process by which aggregate particles actually disperse and to what extent the N aggregate particles disperse.

Fig. 3 shows the dispersion process of aggregate particles by acceleration of the air stream.



Fig. 3 Illustration of dispersion process of aggregate particles



When aggregate particles corresponding to particles A and B in **Fig. 1** are large, as can be seen from Eq. (5), a large dispersion force  $F_d$  arises and it is thought that dispersion proceeds immediately. That is to say the dispersion of large aggregate particles need not be considered in such a dispersion process and it is sufficient to focus attention only on fine aggregate particles with small primary particle numbers N. Therefore, we shall next study dispersion force and process of aggregate particles approaching a final state.

Table 1 shows the various values necessary for calculating the dispersion force  $F_{\rm d}$  acting on aggregate particles composed of 2 to 4 primary particles and the adhesion force acting between the particles at the time of separation. For the dynamic shape factor  $x_{\rm B}$ , Eq. (15) for calculating chainlike aggregate particles was used but due to the fact that there is no method for calculating the dynamic shape factor of small aggregate particles composed of several primary particles, and due to the fact that in this case, the fluid passes through the inside of aggregate particles, and even if their shape is cluster, it is assumed that they can be treated almost in the same manner as chainlike particles and therefore as an approximate, Eq. (15) was applied. Also the volume equivalent diameter  $d_{\rm v}$  was obtained using Eq. (16) except in the case where doublets disperse. If a doublet is composed of two dentical spheres, the dispersion force shown in Eq. (5) becomes  $F_{\rm d} = 0$  and doublets do not disperse. Therefore, in this table, the value of  $D_{\rm v}$  of a doublet (N = 2) assumed to have a difference of  $d_{\rm vA}/d_{\rm vB} = 0.9$  in the size of 2 particles is shown. The dispersion force is determined by the sort of particle resulting from the dispersion. When the value shown in this table and the fluid flow velocity and density are substituted in Eq. (5), the dispersion force  $F_{\rm d}$  is obtained.

On the other hand the value of the adhesion force between particles which maintains the aggregate shape is determined by the number of contact points shown in the table and whether dispersion will take place or not is determined by the difference between the values of this adhesion force and the above dispersion force  $F_d$ .

On the basis of the values shown in Table 1, calculation results of the dispersion force  $F_d$  and adhesion force between particles  $F_a$  under various conditions are shown in **Fig. 4. Fig. 4** (a) shows the calculation results of the dispersion force  $F_d$  when aggregate particles disperse into one primary particle and its remainder by nitrogen pressure ( $P_1$  in **Fig. 2**)  $1.1 \times 10^3$ kPa at the ejector inlet and the adhesion force  $F_a$  between particles (van der Waals force). From the figure, it can be seen that the dispersion

Number of primary	Before dispersion	After dispersion		$d_{\rm vA}$	$D_{\rm v}$ $d_{\rm vA}$	$\frac{\varkappa_{\rm B}}{= 0.862 N^{1/3}}$	Number of
N		А	В	$u_{\rm vB} = 1$ $u_{\rm pl}$	_ d <sub>vB</sub>		points
2	Particle A Particle B	•	0	$d_{\rm vA} = 0.9 d_{\rm vB}$ (assumed)	0.9	1	1
	٩	•	$\infty$	$d_{\rm vA} = d_{\rm p1}$	0.79	1.09	2
3	•∞	•	$\infty$	$d_{\rm vB} = 2^{1/3} d_{\rm p1}$			1
	٩	•	60	$d_{vA} = d_{p1}$ $d_{vB} = 3^{1/3} d_{p1}$	0.69	1.24	3
4	¢	•	8				2
	8	•	$\mathcal{S}$				1

 Table 1 Characteristics of model aggregate particles







Fig. 4 Calculated results of dispersion and adhesive forces

force  $F_{\rm d}$  becomes larger as the particle diameter  $d_{\rm vB}$  obtained from Eq. (16) becomes larger and as mentioned before, it can be understood that larger aggregate particles become more prone to disperse.

On the other hand, for the adhesion force between particles, freeze dried standard PSL particles free of impurities (made by Nippon Synthetic Rubber Co., Ltd.), are used in the experiment and also since the fluid is nitrogen gas absolutely free of moisture, it is assumed that the liquid bridging adhesion force is extremely small. The adhesion force  $F_a$  between particles is calculated using van der Waals force with the Hamaker constant of PSL particles of 1  $\times$ 10<sup>-19</sup> J as the average value of documented values<sup>1)</sup>  $6.2 - 16.8 \times 10^{-20}$  J and a separation distance between particles of 0.4  $n_m$ . As shown in Table 1, the adhesion force  $F_a$  between particles changes  $F_{a1}$ ,  $2F_{a1}$ ,  $3F_{a1}$ ..., depending on the number of particle contact points. If the dispersion force exceeds this adhesion force, the aggregate particles will disperse. For example, when an aggregate particle consisting of 4 primary particles of  $5\mu m$  disperses into 1 and 3 particles, it becomes  $d_{\rm vB} = 3^{1/3} \times 5\mu m = 7.2$  $\mu$ m as shown in **Table 1** and the dispersion force  $F_{\rm d}$  becomes 4.8  $\times$  10<sup>-7</sup>N according to **Fig. 4** (a). On the other hand, the adhesion force, even though it may involve a 3 point contact, becomes  $3.8 \times 10^{-7}$ N and it is expected that dispersion will most likely occur. When the primary particle diameter is  $2\mu$ m whereas the dispersion force for  $d_{vB} = 3^{1/3} \times 2\mu m =$  $2.9\mu$ m becomes  $F_d = 1.1 \times 10^{-7}$ N, and as the value of the adhesion force becomes  $F_a = 5 \times 10^{-8}$ N,  $1 \times 10^{-7}$ N,  $1.6 \times 10^{-7}$ N respectively larger for 1 point, 2 point and 3 point contacts, dispersion becomes more difficult.

Next, Fig. 4 (b) shows the calculation results



Fig. 4 Calculated results of dispersion and adhesive forces

when triplets consisting of 3 primary particles disperse into 1 and 2 particles. In this case, since aggregate particles are limited to triplets, the dispersion force is determined only by the fluid resistance. As mentioned before, the figure shows that the dispersion force is determined by the density  $\rho_f$  of the fluid when the fluid velocicty reaches critical velocity (280 m/s). From this figure also, it can be seen that primary  $5\mu$ m triplets can disperse and that when the primary particle diameter is  $2\mu$ m, dispersion becomes difficult.

When Stokes drag force acts on particles with diameters of  $2\mu m$  and  $5\mu m$ , the dispersion force is proportional to the particles diameter but at high



Reynolds number, the dispersion force (drag force acting on particles) becomes proportional to 1.5 - 2 power of the particle diameter and large aggregate particles become prone to dispersion.

#### 2. Experimental apparatus and methods

**Fig. 5** shows the experimental apparatus. The ejector (made by Nisshin Flour Milling Co., Ltd.) used for dispersion by acceleration of aggregate particles and provided various gas velocities by changing the clearance  $l_t$  and nitrogen pressure  $P_1$  (refer to **Fig. 2**).

The PLS particles used in the experiments were dry particles made by Nippon Synthetic Rubber Co., Ltd. by a freeze drying process having primary particle diameters of 5.2 and  $2\mu m$ . These PSL particles were fed through stainless capillary tube into the ejector and dispersed at the nozzle exit at critical pressure, critical velocity (sound velocity) nitrogen gas (maximum feed pressure  $1.1 \times 10^3$  kPa, abs., gas velocity 280 m/s), then introduced into a settling chamber (5  $\times$  10<sup>-2</sup>m<sup>3</sup>). When the inside of the chamber is roughly replaced by PSL aerosols, the nitrogen gas feed is stopped. A slide glass is placed at the bottom of the vessel in advance and after all particles have settled on the glass slide by gravitational sedimentation, about 1,000 particles is observed through an optical microscope. Since PSL particles with known primary particle diameters are directly viewed, the number of primary particles composing aggregates such as doublets and triplets can be clearly observed.



Fig. 5 Schematic diagram of experimental apparatus

## 3. Experimental results and discussion

Fig. 6 shows photomicrographs of PSL particles after dispersion. It can be seen that singlets, dou-



 $10 \mu m d_{pl} = 2 \mu m$ 

Fig. 6 Photomicrographs of dispersed PSL particles

blets, and triplets can be clearly observed.

**Fig. 7** shows the experimental results obtained in this way and the vertical axis represents the number ratio of the aggregate particles consisting of N primary particles (including N = 1) against the total particle number (singlets and total aggregate particle number) after dispersion.

**Fig. 7** (a) shows the experimental results using PSL particles with a primary particle diameters of  $5.2\mu$ m. At  $5 \times 10^2$  kPa and above, singlets (N = 1) representing 90% or more of the total were obtained. It was possible to generate height concentration PSL particles (about  $10^{12}$  particles/m<sup>3</sup>) through the PSL particles feed rate. The fact that





Fig. 7(a) Experimental results of PSL aggregate dispersion

PSL particles of 5.2µm almost all dispersed into primary particles is the same as the foreseen result in which the dispersion force exceeds the particle adhesion force and aggregate particles consisting of primary particles of  $5\mu m$  disperse into 1 primary particle and a remainder before in Fig. 4. Fig. 7 (b) shows the experimental results for PSL particles with a primary particle diameter of  $2\mu m$  where almost never disperse. The fact that almost all PSL particles with a primary particle diameter of  $5.2\mu m$ dispersed into primary particles, and the fact that PSL particles with a primary particle diameter of 2  $\mu$ m did not disperse so much agree with the theoretical results in Fig. 4 and it indicates that the dispersion force of aggregate particles by acceleration of an air stream can be expressed by Eq. (5). Also, the fact that doublets, except for singlets, are relatively numerous in the experimental results in Fig. 7 may be considered as verifying the fact that if doublets consist of two identical spheres, then the dispersion force shown in Eq. (5) becomes  $F_{\rm d} = 0$ and therefore they do not disperse.



Fig. 7 (b) Experimental results of PSL aggregate dispersion

# Conclusion

Using an ejector operating at a critical pressure higher than atmospheric pressure as the dispersion equipment and conducting dispersion experiments on PSL aggregate particles by acceleration in an air stream, the following results were obtained.

(1) PSL aggregate particles with a primary particle diameter of  $5.2\mu$ m subjected to acceleration under high pressure and a critical velocity at the nozzle outlet were almost all dispersed into primary particles but for primary particles with  $2\mu$ m diameter, it was found that dispersion by acceleration in air stream was difficult. The number concentration also depends on the particles feed rate but a fairly high concentration aerosol particles were obtained.

Consequently, for aggregate particles with a primary particle diameters of about  $5\mu$ m or larger, it was proved that an ejector using air stream acceleration operated under a critical pressure higher than atmospheric pressure can be used as a mono-



disperse, high concentration aerosol generator.

(2) The dispersion results obtained from the above experiment has been fairly well explained by comparing the theoretical dispersion force acting on model aggregate particles for which the dynamic shape factor was introduced with the theoretical values of the adhesion force between particles using the existing van der Waals force.

# Nomenclature

Α	=	Hamaker constant	[ <b>J</b> ]
$D_{\rm v}$	=	diameter ratio (= $d_{vA}/d_{vB}$ )	[-]
$d_{\rm v}$	=	volume equivalent diameter	[m]
$d_{p1}$	=	primary particle diameter	[m]
$\dot{F_{a}}$	=	adhesion force	[N]
$F_{d}$	=	dispersion force	[N]
g	=	acceleration due to gravity	[m•s <sup>-2</sup> ]
h		separation distance between	two
		spherical primary particles	[m]
k	=	ratio of constant pressure to	constant
		volume heat capacity	[-]
1	=	clearance shown in Fig. 2	[m]
Ν	=	number of primary particles	[-]
n	=	index of polytropic change	[-]
P <sub>c</sub>	=	critical pressure at adiabatic	flow [Pa]
$P_{\rm m}$	=	critical pressure at friction fl	ow [Pa]
$P_1$	=	pressure at ejector inlet	[Pa]
R	-	gas constant [	J•K <sup>-1</sup> •mol <sup>-1</sup> ]
R <sub>f</sub>	=	drag force	[N]
$T_1$	=	temperature at ejector inlet	[K]
t	=	time	[s]
u <sub>c</sub>	=	critical velocity at adiabatic f	low $[m \cdot s^{-1}]$
u <sub>m</sub>	=	critical velocity at friction flo	w [m•s <sup>-1</sup> ]
u <sub>r</sub>	=	relative velocity	[m•s <sup>-1</sup> ]
<b>v</b> <sub>p</sub>	=	particle velocity	[m•s <sup>-1</sup> ]
х	_	dynamic shape factor	[-]
μ	=	viscosity of fluid	[Pa•s]
$\varrho_{\rm p}$	=	density of particle	[kg•m <sup>-3</sup> ]
Qf	=	density of fluid	[kg•m <sup>-3</sup> ]
$\phi_{ m c}$	=	value given in Eq. (11)	$[m^{1/2} \bullet s^{-1}]$
$\phi_{\mathrm{m}}$	=	value given in Eq. (8)	$[m^{1/2} \bullet s^{-1}]$

## Subscripts

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A = particle A shown in Fig. 1
B = particle B shown in Fig. 1
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# Initial Collection Efficiency of Electret Filter and Its Durability for Solid and Liquid Particles †

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# Abstract

Expressions to describe the initial collection efficiency of electret filters for both charged and neutral particles were derived covering a wide range of Coulombic force and induced force parameters including the interceptional effect. The prediction equations were in good agreement with the experimental data. Further, the electret charge stability in humid air and in exposure to liquid and solid particles was studied by measuring the time dependency of the particle penetration. It was found that the electret charge is quite stable in humid air but that it is gradually attenuated when exposed to organic droplets because the collected organic droplets spread over the fibers and weaken the electric field around them.

#### Introduction

An electret filter consists of semi-permanently charged fibers and has a higher collection efficiency compared to its mechanical counterpart due to strong electrostatic attraction between particles and fibers.

The initial collection efficiency of an electret filter with a uniform charge distribution on each fiber was theoretically studied by Natanson<sup>6)</sup> and Pich<sup>7)</sup>. For the electret fiber with a charge distribution as shown in **Fig. 1**, Brown<sup>3)</sup> derived expressions for the col-



Fig. 1 Schematic illustration of charge distribution on an electret fiber.

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lection efficiency due to Coulombic and induced forces, and Pich<sup>8)</sup> proposed a prediction equation for the Coulombic force including the interceptional effect. However, Brown's prediction equation did not include the interceptional effect for a large interception parameter, which is important in the filtration of relatively large particles with fine electret fiber, while Pich's equation did not specify the range of the interception parameter for which his equation is applicable, although there is a critical interception parameter below which the interception effect is negligible.

This paper proposes useful prediction equations which cover the practical range of Coulombic and induced force parameter accounting for the interceptional effect. Further, since the stability of the electret charge is of great consideration for practical use, the charge stability was studied when an electret filter is exposed to organic mist and dust particles as well as to particle-free humid air.

#### 1. Initial collection efficiency

#### 1.1 Charged particles

For an electret filter with a dipole charge as shown in **Fig. 1**, Brown introduced a particle stream function and theoretically obtained the following expression of single fiber collection efficiency for charged particles when the interception effect is negligible.

$$\bar{\eta}_{\rm c} = 0.59 h_{\rm k}^{-0.17} K_{\rm c}^{0.83} \tag{1}$$



Where  $h_K$  is the hydrodynamic factor given by Eq. (2) for the Kuwabara flow<sup>5)</sup>, and  $K_C$  the Coulombic force parameter defined by Eq. (3).

$$h_{k} = -0.51n\alpha + \alpha - \alpha^{2} - 0.75$$
 (2)

$$K_{c} = \frac{C_{c}n_{p}e\overline{\sigma}}{6\varepsilon_{0} (1 + \varepsilon_{f}) \mu d_{p}u}$$
(3)

In electret filtration as opposed to mechanical filtration, the limiting trajectory of particles is such that the particles pass through a point at which their velocity is zero. Therefore, a particle with a limiting trajectory is transported toward the fiber surface in a direction normal to the fiber from the zero-velocity point and then collides with the surface where it is finally collected. Consequently, interception plays no role when a particle's radius is smaller than the distance between the zero-velocity point and the fiber surface. This implies the existence of a critical value for the interception parameter below which interception does not affect the single fiber collection efficiency. Brown showed that, for the collection of charged fibers, this critical interception parameter depends upon the orientation angle of the electret dipole  $\gamma$  and that interception is completely negligible for R < (K<sub>C</sub>h<sub>K</sub>/2) while for R < (K<sub>C</sub>h<sub>K</sub>)<sup>1/2</sup> it is important at some value of the angle  $\gamma$ .

Pich *et al.*<sup>8)</sup> derived the following expression for the Coulombic and interception single fiber efficiency at a fiber orientation  $\gamma$ , by assuming that a particle with a limiting trajectory has a zero tangential velocity at a half particle diameter away from the fiber surface.

$$\eta_{\rm CR} = \{\eta_{\rm R} + \frac{{\rm K_C}^2}{(1 + {\rm R})^2} - \frac{2\eta_{\rm R}{\rm K_C}}{1 + {\rm R}}\,\cos\gamma\}^{1/2} \qquad (4)$$

where  $\eta_R$  is the interception efficiency which is given for the Kuwabara flow as follows.

$$\eta_{\rm R} = \frac{1}{2h_{\rm K}} \left\{ \frac{1}{1 + {\rm R}} - (1 + {\rm R}) + 2 (1 + {\rm R}) \ln (1 + {\rm R}) \right\}$$
(5)

Further, they obtained the average single fiber efficiency by integrating the above equation over all dipole orientations assuming that a dipole orientation is random in the filter.

$$\overline{\eta}_{CR} = \eta_R + \left\{ \frac{1}{1 + R} - \frac{\eta_R}{(1 + R) \eta_R + K_C} \right\} K_C$$
(6)



Fig. 2 Comparison of Coulombic force-interception collection efficiencies of a single electret fiber predicted by Brown and Pich *et al.* 

Fig. 2 compares the Coulombic single fiber efficiency obtained by the particle trajectory calculation according to Brown's paper (R = 0,  $\gamma = \pi/2$ ,  $\alpha$ = 0.05) with that obtained by Eq. (4). Since Pich's equation does not account for the existence of a critical interception parameter, there is a contradiction in that the single fiber efficiency is higher for a smaller interception parameter in a large K<sub>C</sub> region. Fig. 2 shows that the single fiber efficiency curve obtained by Brown's procedure is an envelope of the curves calculated by Eq. (4). The critical interception parameter R<sub>C</sub> which was calculated by the authors according to Brown's procedure is shown in Fig. 3 as a function of  $K_C$  and  $\gamma$ , and the values of K<sub>C</sub> which give the critical interception parameter of  $R_C = 0.05, 0.1, 0.2, 0.5$  at  $\gamma = \pi/2$  are plotted by



Fig. 3 Critical interception parameter for Coulombic force particle collection.



solid circles in **Fig. 2**. It can be seen that the curve obtained by the Brown's procedure is tangent to the curves predicted by Pich's equation at points of solid circles. Therefore, Pich's equation Eq. (4) is valid only for  $R > R_C$  while for  $R < R_C$  it is necessary to apply Brown's procedure to calculate the single fiber efficiency.

**Fig. 2** is a comparison for the dipole orientation  $\gamma = \pi/2$ . However, because the orientation of a dipole charge in an electret filter is random, it is necessary to use a single fiber efficiency averaged over all the orientations of the dipole charge to calculate the filter efficiency. **Fig. 4** compares the



Fig. 4 Comparison of average Coulombic force-interception collection efficiencies of a single electret fiber predicted by Brown and Pich et al.

average single fiber efficiencies predicted by Eqs. (1) and (6). In this figure, since the applicable range of the Coulombic force parameter of Eq. (1) is not clearly given by Brown, the single fiber efficiency was recalculated by the authors for  $0.01 < K_C <$ 5 at  $\alpha = 0.05$ . Unlike Fig. 2, the curve predicted by Brown's procedure is not an exact envelope of Pich's curves in Fig. 4. For the average single fiber efficiency, it is futile to consider the critical interception parameter because it varies with the dipole charge orientation. Nevertheless, the single fiber efficiencies at the Coulombic force parameter which gives the critical interception parameter at  $\gamma$ =  $\pi/2$  (shown by solid circles) are fairly close to those predicted by the Brown's curve. Therefore, in the prediction of the single fiber efficiency, to calculate the filter efficiency, we may use the critical interception parameters at  $\gamma = \pi/2$  as the limit of the applicable range of Eq. (6). Consequently, since the critical interception parameter at  $\gamma = \pi/2$  shown in Fig. 3 is approximated by  $R_C = 0.66 (K_C h_K)^{0.64}$ ,

for  $R > R_C$ , Eq. (6) may be used for the average single fiber efficiency, and for  $R < R_C$ , the following equations which are approximations of the equation of Brown's curve shown in Fig. 4 must be used.

$$\overline{\eta}_{\rm C} = 0.78 {\rm K}_{\rm C} ; 10^{-3} < {\rm K}_{\rm C} < 10^{-1}$$
  
$$\overline{\eta}_{\rm C} = 0.59 {\rm h}_{\rm K}^{-0.17} {\rm K}_{\rm C}^{0.83} ; 0.1 < {\rm K}_{\rm C} < 10$$
(7)

#### 1.2 Neutral particles

Neutral particles are polarized by the electret charge and collected on the electret fibers as a result of the attractive force existing between the charge induced on the particles and the electret charge. The induced force is a function of only the distance between a particle and the electret fiber and does not depend on the dipole charge orientation. Therefore, the limiting trajectory always ends at the rear stagnation point of the fiber ( $\theta = 0$ ). By making use of this, Brown analytically obtained a point on the  $\theta = 0$  axis at which the particle velocity is zero, and numerically traced the particle trajectory backwards to obtain the original position of particles upstream the fiber.

The prediction equation derived by Brown for neutral particles is given by the following equation.

$$\bar{\eta}_{\text{In}} = 0.54 h_{\text{K}}^{-0.60} \, \text{K}_{\text{In}}^{0.40} \text{ for } 1 < \text{K}_{\text{In}} < 100$$
 (8)

where  $K_{In}$  is the induced force parameter defined by

$$K_{In} = \frac{(\mathcal{E}_{P} - 1) C_{C} \pi^{2} \overline{\sigma}^{2} d_{P}^{2}}{6 (\mathcal{E}_{P} + 2) \mathcal{E}_{0} (1 + \mathcal{E}_{f})^{2} \mu d_{f} u}$$
(9)

Likewise for charged particles, there exists a critical interception parameter in the collection of neutral particles. The critical interception parameter given by Brown is as follows.

$$R_{\rm C} = (h_{\rm K} K_{\rm In})^{1/2} \tag{10}$$

We recalculated the single fiber efficiency using Brown's procedure for a small  $K_{In}$  region accounting for the interceptional effect and the results were compared with the curves predicted by Eq. (8) and Natanson's equation ( $\eta_{In} = \pi K_{In}$ ). The present calculation results of the single fiber efficiency for R = 0 coincide with Natanson's in a small  $K_{In}$  region and with Brown's for  $K_{In} > 1$ . Incidentally, the values for  $K_{In}$  at which the present results of single fiber efficiency with interception equal to those



without interception (R = 0), correspond to those predicted by Eq. (10). The single fiber collection efficiency due to the induced force at R = 0 can be expressed by the following equation.

$$\begin{aligned} \eta_{\rm In} &= 1.48 K_{\rm In}^{-0.93} ; 10^{-4} < K_{\rm In} < 10^{-2} \\ \eta_{\rm In} &= 0.51 h_{\rm K}^{-0.35} K_{\rm In}^{0.73} ; 10^{-2} < K_{\rm In} < 1 \\ \eta_{\rm In} &= 0.54 h_{\rm K}^{-0.60} K_{\rm In}^{0.40} ; 1 < K_{\rm In} < 100 \end{aligned}$$
(11)



Fig. 5 Collection efficiencies of a single electret fiber due to induced force.

#### 1.3 Comparison with the experimental data

To confirm the validity of the prediction equations derived above, measurements of the collection efficiencies of electret filters were carried out by using the experimental set-up shown in **Fig. 6**. Liquid



Fig. 6 Experimental setup for the measurement of particle penetration through electret filters.

particles of DOS (Dioctylsebacate) were used as a test aerosol. DOS droplets were generated by a evaporation and condensation type aerosol generator<sup>4</sup>) and classified into monodisperse particles with a DMA (differential mobility analyzer). Following the classification of the particles by size, their charging state was regulated by a combination of a bipolar charger, a unipolar charger<sup>9)</sup>, the DMA and a parallel plate condenser to obtain uncharged, multicharged, and uncharged particles. The test filters used in the experiments were electret filters consisting of polypropyene fibers with a diameter of  $1.3 \mu m$ , a filter thickness of 0.71 mm and a packing fraction of 0.0612.

Fig. 7 shows the influence of the fiber and particle



Fig. 7 Effect of particle and fiber charges on particle penetration.

charges on particle penetration. The particle penetration of uncharged particles through an uncharged filter (designated by  $P_M$  in Fig. 7) was obtained by using an uncharged filter having the same filter property as an electret filter. When neutral particles are collected by an uncharged filter, the particle penetration curve is convex against the particle diameter because interception is dominant for large particles while there is a Brownian diffusion for small particles. When the filter is charged, the induced force acts on the neutral particles, and thus the particles' penetration decreases with increasing particle diameter. When both filter and particles are charged, the Coulombic force is responsible for the collection of small particles and the induced force for that of large particles, resulting in low particle penetration in an entire particle size region. By assuming the additivity of the collection efficiencies due to the two individual mechanisms, the single fiber





Fig. 8 Comparison of predicted induced force single fiber collection efficiency with experimental data.

collection efficiency due to the induced force was calculated using Eq. (12) and is plotted against the induced force parameter  $K_{In}$  in Fig. 8.

$$\eta_{\text{In}} = \eta_{\text{In}M} - \eta_{\text{M}}$$
$$= -\frac{\pi}{4} \frac{1 - \alpha}{\alpha} \frac{d_{\text{f}}}{L} \ln \frac{P_{\text{In}M}}{P_{\text{M}}}$$
(12)

In Fig. 8, since the charge on the electret filter used in the present work is unknown (actually, the measurement of the electret charge was attempted by Baumgartner *et al.*<sup>2)</sup>, however, it is very difficult to obtain the average charge for an electret fiber with a charge distributed along the fiber length), the electret charge is assumed to be  $\bar{\sigma} = 5.1 \mu C/m^2$ in order to satisfy the theoretical equation Eq. (11). Although the data scatter in the region of small K<sub>In</sub>, most of the data fit a single curve as predicted by Eq. (11), indicating that Eq. (11) is applicable for the prediction of the single fiber efficiency due to the induced force.

**Fig. 9** shows the single fiber efficiency due to the Coulombic force as a function of the Coulombic force parameter. The single fiber efficiency was calculated using Eq. (13) by assuming the additivity of single fiber efficiencies due to the induced force and the Coulombic force.

$$\eta_{\rm C} = \eta_{\rm InCM} - \eta_{\rm InM}$$
$$= -\frac{\pi}{4} \frac{1-\alpha}{\alpha} \frac{d_{\rm f}}{L} \ln \frac{P_{\rm InCM}}{P_{\rm InM}}$$
(13)

Since the electret charge is not measurable as in the



Fig. 9 Comparison of predicted Coulombic force single fiber collection efficiency with experimental data.

case for the induced force parameter, the value of  $\bar{\sigma} = 5.1 \mu C/m^2$  which was obtained from the data for neutral particles was used to calculated the Coulombic force parameter. It can be seen from **Fig. 9** that experimental data are well expressed by Eq. (7).

What follows from the comparison between experimental data and the prediction equations is that the assumed value for the electret charge  $\bar{\sigma} = 5.1 \,\mu\text{C/m}^2$  is true and that these prediction equations are valid for use to obtain the average single fiber efficiencies due to the induced force and the Coulombic force.

#### 2. Stability of electret charge

As shown in the preceding section, the electret filters have a very high initial collection efficiency compared to the conventional mechanical filters because the induced force and/or Coulombic force as well as the mechanical collection mechanisms, such as interception and Brownian diffusion, act on the particles. However, since the electret charge is not infinitely permanent, the problem arises on how long the initial collection efficiency is maintained for practical use. In the following sections, the electret charge stability is discussed when it is exposed to humid air and liquid and solid particles.

# 2.1 Influence of humidity

Because electret filters have a dipole charge on the fibers, the charge may be neutralized by a charge



transfer through the fiber or along the fiber surface. If the charge disappears by the surface charge transfer or is neutralized by the adsorption of ions on the fiber surface, humidity may greatly affect the charge decay characteristic of the electret filter. **Fig. 10** 



Fig. 10 Influence of humidity on particle penetration through electret filter.

shows the time course of particle penetration through the electret filter when the electret filter is exposed to particles-free humid air. As shown in the figure, the particle penetration remains constant for over a month, indicating that the electret charge is quite stable in humid air. Therefore, it can be said that the charge decay due to surface or volume conduction of dipole charges is negligible.

# 2.2 Influence of captured particles

Baumgartner and Löffler<sup>1)</sup> reported that particles collected in an electret filter lead to two opposing effects; i.e., an increase in collection efficiency due to the increased interception effect by the captured particles, and a collection efficiency decrease due to neutralization of the electret charge. Since the extent of these effects changes with the fiber size and the morphology of the particles accumulated in the filter as well as the particle load on the filter, particle penetration varies in a complex manner with the particle load. Fig. 11 compares the time dependency of penetration of charged liquid particles with that of charged solid particles. 0.1 µm DOS particles and 0.1 µm iron alum particles classified by the DMA were used as a test aerosol. Since the fiber size of the electret filter is as small as 1.3 µm, particle penetration of solid particles gradually increases with the particle load since the increased interception effect counterbalances the decrease of the electret charge. On the other hand, the penetration of liquid particles decreases with the particle load because captured droplets spread over the fibers contributing to a weakening of the electric field around the fiber without increasing the interceptional effect.



Fig. 11 Comparison of time dependencies of particle penetration and pressure drop through electret filter during the filtration of liquid and solid particles.

The difference in the morphology of the particles accumulated in the electret filter is also inferred from the pressure drop change with the particle load, *i.e.*, the solid particles clog the filter pores thus increasing the filter pressure drop, whereas the pressure drop is almost constant when liquid particles are filtered.

The reason for the particle penetration increase in the charged liquid particle filtration may be attributed to the neutralization of the electret charge by the opposite particle charge and the weakening of the electric field around the fibers due to the fiber surface being covered with a liquid layer. The influence of the latter on the electret filtration can be found by measuring the penetration of neutral droplets. **Fig. 12** 



Fig. 12 Comparison of time dependencies of particle penetration through electret filter for uncharged and charged droplets (particle concentration at filter inlet  $C_i = 3 \times 10^{.9} - 2 \times 10^{.8} \text{ kg/m}^3$  for uncharged droplets and  $C_i = 5 \times 10^{.3} - 6 \times 10^{.8} \text{ kg/m}^3$  for charged droplets).



compares the penetrations of neutral and uni-charge droplets through an electret filter. This figure shows that there exists a gradual increase in the penetration of neutral particles although it is not as significant as that of uni-charged particles. Therefore, even for neutral droplets, a decrease in collection efficiency occurs due to the fiber surface being covered with a liquid laver.

Fig. 13 shows the comparison of single fiber effi-



Fig. 13 Single fiber collection efficiencies of uncharged and charged droplets as a function of particles accumulated in the filter.

ciencies for neutral and uni-charged droplets. The abscissa in the figure is the amount of particles collected in the filter calculated using the following equation.

$$m = \frac{1}{L} \int_{0}^{C_{i}ut} Ed (C_{i}ut)$$
(14)

As can be seen from the figure, the single fiber efficiency for neutral particles decreases with particle accumulation and becomes equal to that of uncharged fibers at about  $m = 0.5 \text{ kg/m}^3$ . From the data for neutral particles, the charge on the electret fiber with particle accumulation was estimated by using Eq. (11), and this charge was used to calculate the single fiber efficiency for charged particles. The predicted change in single fiber efficiency for charged particles is also shown in Fig. 13. The predicted single fiber efficiency curve expresses the trend of experimental data fairly well, suggesting that the covering of the fiber surface with a liquid layer is the main cause of penetration increase even for charged droplets.

#### Conclusion

Prediction equations of electret fiber collection efficiency were derived for a relatively small electrostatic interaction between particles and electret fibers accounting for the interception effect, and compared with the experimental data. Further, the stability of the electret charge was experimentally studied when the electret filter was exposed to liquid and solid particles as well as to particle-free humid air. Consequently, it was found that the electret charge is fairly stable in humid air, but that the collection efficiency for liquid droplets gradually decreases with the particle load on the filter because captured droplets covered the fiber surface and thus weakened the electrical field around the fibers. Since the covering of the electret fiber surface with a liquid layer is dependent on the wetting property of the liquid, special attention is required in the electret filtration of organic droplets.

## Nomenclature

C <sub>C</sub>	=	Cunningham's slip correction	
		factor	[ - ]
$d_{f}$	=	Fiber diameter	[m]
$d_{\rm P}$	=	Particle diameter	[m]
E	=	Collection efficiency of filter	[ – ]
e	=	Elementary charge	[C]
h <sub>K</sub>	=	Hydrodynamic factor	[-]
K <sub>C</sub>	=	Coulombic force parameter	
		defined by Eq. (3)	[-]
K <sub>In</sub>	=	Induced force parameter	
		defined by Eq. (9)	[-]
L	=	Filter thickness	[m]
m	=	Accumulated mass of particles [k	g/m <sup>3</sup> ]
n <sub>P</sub>	=	Number of charges on a particle	[ - ]
Р	=	Particle penetration through filter	[ – ]
R	=	Interception parameter ( = $d_P/d_f$ )	[ - ]
R <sub>C</sub>	=	Critical interception parameter	[ - ]
r	=	Radial distance	[m]
t	=	Filtration time	[s]
u	=	Filtration velocity	[m/s]
α	=	Packing density of fibers	[ - ]
$\gamma$	=	Angle of dipole charge to airflow	[-]
8 <sub>0</sub>	=	Space permittivity $[C^2/(1)]$	Nm <sup>2</sup> )]
ε <sub>f</sub>	=	Dielectric constant of fiber	[ - ]
8 <sub>P</sub>	=	Dielectric constant of particle	[-]
η	=	Single fiber collection efficiency	[ - ]
$\overline{\eta}$	=	Average single fiber collection	
		efficiency	[-]



θ	=	Angle measured from rear	
		stagnation point	[ - ]
$\phi$	=	Angle measured from positive	
		pole of dipole charge	[ – ]
μ	=	Dynamic viscosity of air	[Pa.s]
σ	=	Charge density of fiber	$[C/m^2]$
σ	=	Average charge density of fiber	
		$(=2 \sigma_0/\pi)$	$[C/m^2]$
$\sigma_0$	=	Maximum charge density of fiber	$[C/m^2]$

# Subscripts

- C : Coulombic force
- In : Induced force
- i : Inlet
- M : Mechanical
- R : Interception

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# Study of Static Pressures of Granular Materials in a Silo Using the Distinct Element Method †

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#### Abstract

The pressure inside a silo, especially the dynamic pressure during discharge is a very important factor in its structural design. However, numerical simulations of this problem have seldom been performed because of its complicated behaviors. In this report, the distinct element method (DEM) which is suitable for discontinuous media is used for the analysis of the static state of granular materials in silos, and the possibility of its use to analyze the silo problem is considered. Also, the characteristic distribution of pressures on walls is studied using the DEM simulation, and the influence of friction coefficients and particle arrangement is examined. The result of this study is that the pressure distributions obtained from the DEM simulation are similar to the theoretical or experimental ones. This result of static analysis is used for the initial condition of dynamic analysis, and it is expected to be used to simulate the complicated behaviors of granular materials during discharge in silos.

#### 1. Introduction

The materials stored in a silo such as coal, grain, and flour are usually treated as powders or granular materials. The behavior of such materials resemble that of fluids, but doesn't comply with the rules of fluid mechanics or those of solid mechanics. Thus, this complicated behavior in a silo was mainly studied experimentally<sup>1), 2)</sup>, and the theory for its structural design is derived from experiments and observations or is based on the classical theory of Rankine. The design basis for a silo in most countries is founded on Janssen's formula for the static state, while for the dynamic case the incremental coefficient added to the static pressure is considered. In this way the behavior in a silo is understood experimentally but not theoretically. It is very difficult to simulate the behavior of the particles in a silo, although the inside pressure, especially the dynamic pressure during discharge, is a very important factor in its structural design.

On the other hand, the Distinct Element Method (DEM in short) is a numerical method used to simulate the assembly of discrete rigid bodies such

as rock mass. The DEM is often used in the civil engineering field, for example the failure of rock slopes, the stability of rock caverns, the dynamic behavior of sands, and so on. For the problem of silos, Kiyama et al<sup>3)</sup>. applied it to a simple model, but the number of its particles was too small to describe the complicated behavior in a silo. Recently, the development of computers has made great strides, and massive calculations can now be performed much faster than 10 years ago. Therefore a large scale model composed of 10,000 circular elements can be calculated on the DEM.

This report shows the analytical result for granular material in a silo using the DEM, and its possibility for use to simulate large numbers of elements is considered. Based on the analytical results, the relationship between the properties of granular material and the static pressures towards the walls in a silo is studied.

#### 2. Distinct Element Method

The DEM is a numerical method proposed by Cundall in 1971<sup>4)</sup>, and is very useful for the simulation of the complicated behavior of discontinuous media. Its main advantage is that it can be used for the large dynamic deformation problem continuously from static state to dynamic failure. It is usually applied for the problem of rock mass failure and the analysis of particle motions.

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The solution technique of the DEM is relatively simple. It is based on a few assumptions (see Fig. 1) and while the numerical integration of the equation of motion is performed, equilibrium conditions are considered in algorithms by which calculated unbalanced forces are reduced step by step. One of the difficulties is that the time increment for each calculation step must be defined so small that a very long execution time is required to analyze the behavior of materials in real time. In order to reduce the execution time, my program<sup>5)</sup> has been improved on the following two aspects. 1) The old program contains many rearrangements of variables and external file I/Os in order to reduce the necessary main memory capacity, but recently a large memory capacity can be used as a result of the extensional region of FORTRAN and the enhancement of computers themselves. Therefore, in the new program, the variables are directly set to their dimensions, and external file I/Os are concentrated. 2) To reduce the time of the searching process for the contacts between particles, adjacent particles are memorized between two boxing processes, which are also useful techniques of searching for contacts introduced by Cundall.

Owing to the development of computers and the improvement of the program mentioned above, it is possible to solve a case involving 10,000 particles,

while it was formerly limited to 1,000 elements. However, in order to deal with a real situation for powder technology the number of particles which must be handled would be at least 10 times higher.

#### 3. Influence of friction coefficient

The dynamic pressure during discharge is usually several times higher than the static pressure, and is one of the main problems in a silo design. In this report, as a reasonable initial state of the discharge analysis, the static state in a silo is simulated using the DEM, and the static pressures acting towards the side walls and the bottom are examined from the viewpoint of the properties of the particles.

Silos are grouped into two classes as shallow and deep bins according to the ratio of their diameter to height and to the static angle of repose of the materials inside them. The pressure acting towards the side wall of shallow bins is relatively in good agreement with the pressure based on Rankine's theory, and that of deep silos can be calculated using Janssen's formula.

In this chapter, a model of randomly arranged particles (see **Fig. 2**) is simulated, and the friction coefficient is used as a parameter having several values. In order to compare the analytical results,



Fig. 1 General principle of distinct element method





Fig. 2 Static state of particles and contact forces on walls (comparison of friction coefficients)

the variation of the wall pressure with respect to the value of the friction coefficient are examined in the DEM analysis.

#### 3.1 Analytical Model and Material Properties

The model used in this chapter is visualized as a 2-dimensional test model measuring 40 cm in width and 50 cm in height. Within this area 5000 particles of 6mm-diameter are arranged at random. **Table 1** shows the material properties of the particles which are defined as constant except for the friction coefficient. The friction coefficient between two particles is defined as being the same as that between a particle and wall in this analysis, and 4 values, 0.3, 0.5, 0.7, and 0.9, are used. The sequence of this analysis is as follows. First, the particles are arbitrarily arranged in the analytical area with small spaces between them. Second, the gravity force is applied to each particle, and the

ſable	1	Input	parameters
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Symbol	Unit	Value
k <sub>n</sub>	N/m	$1.0 \times 10^4$
k <sub>s</sub>	N/m	$1.0 \times 10^4$
β	sec	$5.0 \times 10^{-5}$
μ		0.3, 0.5,0.7, 0.9
γ	kg/m <sup>3</sup>	$2.0 \times 10^{3}$

calculation is continued until the motion of the particles is sufficiently converged. However, it is very difficult to control the motion of the particles perfectly by the algorithm of the DEM, therefore in practice the total calculation is performed up to 10000 steps with a time increment of  $5.0 \times 10^{-5}$  sec.

#### 3.2 Results of Analysis and Discussion

The final state of each friction coefficient is shown in **Fig. 2**. In this figure circles show the particles themselves, and short lines indicate the contact forces between the particles and the wall. The filled circles are merely the marks at each 10 cm interval.

When the friction coefficient is high the highest position of the particles is slightly higher. The difference is smaller than a 6 mm diameter particle between the friction coefficients 0.3 and 0.9. The direction of the contact force for the larger coefficient is not normal to the wall because of the greater tangential force than that for the smaller coefficient. The maximum contact force given on the top left of the figure is not significantly different, and it acts on the bottom. Therefore, it is assumed that the contact force acting towards the bottom is not seriously affected by the variation of the friction coefficient in this condition.

The contact forces acting towards the wall tend to decrease at higher locations of the particles but in the case of the adjacent forces the relationship is sometimes different. Therefore, in order to examine the distribution of the pressures towards the walls, the contact forces are integrated at each 4 to 5 cm-width interval and the distributions are shown in **Figs. 3** and **4**. **Fig. 3** shows the pressure dis-



tribution towards the side walls, and **Fig. 4** shows that towards the bottom. The pressures seem to be appropriate considering the dashed line in **Fig. 4** 





Fig. 4 Pressure towards bottom in static state (comparison of friction coefficients)

which shows the calculated pressure exerted by the weight of all the particles. The pressures towards the bottom are lower near the side walls, and this tendency is similar to that in practical or experimental conditions.

As the pressure distribution towards the upper part of the side walls has a nearly triangular form, it is proportional to the depth and the dispersion is small. Contrariwise, the lower part shows a large variation of the pressures and the distribution has a form other than triangular. Each case is shown with its corresponding result and the difference between the cases of each friction coefficient is not large. The straight lines in Fig. 3 represent the Rankine's active pressure for the friction coefficient 0.3, and if the coefficient is larger, the Rankine's pressure must be smaller. However, the results obtained from the DEM analysis are larger than the Rankine's pressure, therefore the pressure calculated using Janssen's formula must be smaller than indicated by these straight lines. The forms of the pressure distributions resemble those of a deep bin, therefore the analytical results must be compared with the Janssen's. However, a greater difference between theory and analysis would be shown even if the result of the DEM is compared with the Janssen's.

The map of the contact forces is shown as short lines in **Fig. 5**. The forces describe a random spidery figure because of the concentration of the forces by the local arching phenomenon, and the stress concentration on the walls shown in **Fig. 3** is also related to the arching. In the case of particles arranged arbitrarily, the stress distribution is strongly influenced by their arrangement. It is considered that when the size of the particles is relatively large with respect to the bin, the distribution of the



Fig. 5 Distribution of contact forces (friction coefficient  $\mu = 0.5$ )

forces in the bin is not homogeneous and the arrangement of the particles is closely related to the concentration of the stress. Also, the stress reduction at the corner of the model shows the influence of the friction between particles and walls. It can be said that the arrangement of the particles and the friction force at the walls are important factors which affect the stress distribution.

#### 4. Influence of the arrangement of particles

The result of the last chapter indicates that the influence of the arrangement of the particles on the pressure is relatively large, and the partial concentration of the contact forces leads to an unbalanced stress distribution. In this chapter a slightly different arrangement of the particles from the previous analysis is examined, when the other conditions are kept constant. Regularly arranged models are also introduced to clearly demonstrate the influence of the arrangement.

#### 4.1 Random Arrangement

The material properties and the conditions of the analysis except the arrangement of the particles are the same as in the case of the friction coefficient 0.7 in Chap. 3. The arrangements before the calculation are changed and the vertical distance of the particles is set 0.01 mm and 0.1 mm higher in two



cases, so that the appearances of the models are almost identical.

The lateral pressure distributions on the side walls are shown in **Fig. 6** and the vertical pressure distributions on the bottom are shown in **Fig. 7**. The



Fig. 7 Pressure towards bottom in static state (comparison of arrangements of particles)

total distributions are not significantly different, but the difference between each case is as large as those of Figs. 3 and 4. The map of the contact forces does not appear so different (see Fig. 8), but there are some differences in the connectivities of the forces, and they are the cause of the variation of the pressure distribution. The maximum values of the contact forces are not equal, and that of Case 1 which is the result of the last chapter is close to the maximum value in Fig. 5 for the friction coefficient 0.5, and the form of map also resembles that of Fig. 5, but not the other two cases. From these results it can be observed that the pressures towards the walls are very sensitive to the arrangement of the particles, and when the arrangements of the particles are similar, the result of the analysis does not vary significantly even if the friction coefficients differ.

#### 4.2 Regular Arrangement

It has been shown that the arrangement of the particles is a very important factor affecting the pressure distribution on the wall. Therefore, a regular arrangement model was analyzed in order to compare it with the random arrangement model. Here, regular means that the particles are horizontally and equidistantly arranged with no empty space. The model is composed of 4960 particles which are alternately arranged as 54/55 particles per line, and the other conditions of the analysis are the same as for the random model except the friction coefficient which takes values of 0.3, 0.5, and 0.7.

The pressure distributions on the walls and the bottom are shown in Figs. 9 and 10. The pressures



Fig. 8 Distribution of contact forces  $-\mu = 0.7$  (comparison of arrangements of particles)







Fig. 10 Pressure towards bottom in static state (particles arranged regularly)

in these figures vary according to the friction coefficient. The form with the friction coefficient 0.3 resembles the Rankine's pressure except near the bottom, and those with 0.5 and 0.7 are similar to Janssen's. However, the values in three cases tend to the Rankine's pressure with the coefficient 0.3, therefore in the case of shallow bins the result of the DEM analysis is similar to that of the traditional theory, but in the case of deep bins the DEM results in larger pressures that derived from experience.

As mentioned above, it is assumed that the interaction between the particles is mainly slip when the friction coefficient is small, and when it is larger, the interaction gradually changes to include toppling. As in the traditional theory in which the interaction is assumed to be only slip, the result of the DEM is different from the theoretical one. On the other hand, the pressure towards the bottom is relatively constant with the exception of the reduction near the side walls, and the extent of this reduction depends on the friction coefficient. These phenomena indicate that the friction forces between the particles and the side walls are closely related to the reduction of the pressure near the lower corners. Otherwise, the forces between the particles may have arbitrary directions, but the direction of the forces acting on the wall is almost normal to the wall. Therefore the pressures near the lower corners are lower than at other parts of the wall. These two reasons are believed to be the explanation for the reduction of the pressures.

The distributions of the contact forces in **Fig. 11** are relatively homogeneous and the maximum value is smaller than in the case of the random arrangement. This fact shows that the local concentration of the stress is caused by the localization of the arrangement or a vacancy in the rows. However, in real situations the diameter of the particles is much smaller, and the influence of the arrangement seems to be smaller.



Fig. 11 Distribution of contact forces (particles arranged regularly)



#### 5. Influence of the diameter of particles

The pressures in a silo calculated using the DEM analysis are fairly varied depending on the particle arrangement. However, the size of the particles in this report compared to the size of the silo is much larger than the particles in real silos, and this deviation must be of strong influence on the distribution of the pressures. Therefore, in this chapter a model of small particles having almost half the area of the previous models is used in order to evaluate the effect of the size of the particles. The diameter of the particles is taken as D = 4 mm, and the number of the particles as N = 10000. Therefore, the total mass of the model is not so different from that of the previous model in which D = 6 mm and N =5000. The other analytical conditions are the same as for the previous models with the exception of the time increment which is defined as  $2.0 \times 10^{-5}$ sec (see Table 2).

The map of the contact forces in Fig. 12 shows the local concentration as in the cases of D = 6 mm,

Table	2	Input	parameters
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Symbol	Unit	Value
k <sub>n</sub>	N/m	$1.0 \times 10^4$
k <sub>s</sub>	N/m	$1.0 \times 10^4$
β	sec	$2.0 \times 10^{-5}$
μ		0.7
γ	kg/m <sup>3</sup>	$2.0 \times 10^{3}$



Fig. 12 Distribution of contact forces (D = 4 mm, N = 10000)

and naturally the distribution is composed of smaller units, thus it appears to be more homogeneous that in the cases of the larger particles. Also, the maximum contact force which is assumed to be a parameter of the degree of local concentration is relatively small.

The pressures towards the side walls and the bottom are shown in **Figs. 13** and **14**. The curves



Fig. 14 Pressure towards bottom in static state (D = 4 mm, N = 10000)

in Fig. 13 show a well-balanced and smooth form compared to those in Fig. 6. The pressure itself is larger than that of Janssen's formula, but the distribution is similar to the other results. The form of the curve in Fig. 14 is uneven like that in Fig. 7, but the standard deviation for D = 4 mm in Table 3 is smaller than that for D = 6 mm.

As mentioned above, when the diameter of the particles is smaller, the result becomes more homogeneous and well-balanced. However, in practical situations the diameter of the particles is much smaller and their number is huge. From such a point of view in order to analyze a practical problem using the DEM, a massive and high-speed program is required, and the diameter of each particle which is



D	4 mm	6 mm				
		Case 1	Case 2	Case 3		
$M_v$	5940	6310	6360	6790		
S <sub>d</sub>	1180	1900	1590	1910		
A <sub>v</sub>	6160		6930			

 Table 3
 Mean value and standard deviation of bottom pressures

related to the size of the whole model must be reasonably determined or a regular arrangement must be properly used with the appropriate properties.

#### 6. Conclusions

The behavior of granular materials in a silo, especially the pressure distribution on the walls, is studied using the DEM simulation. From this study it is concluded that:

- 1) The form of the distribution curve of the pressure towards the side walls is identical to that of the traditional theory. However, the value obtained by simulation is larger than the theoretical one, and one reason for this deviation is believed to be the fact that the rotation motion is not considered in the theory.
- 2) When the particles are arranged at random, the simulation is significantly influenced by the variations of the arrangement, and especially the size of the particles is so large with respect to the bin that a vacancy in the rows causes stress concentration. This is also one reason for the irregular form of the pressure distribution on the walls.
- 3) When the size of the particles is smaller, the pressure distribution becomes more homogeneous. However, to deal with the real size of particles is very difficult due to the limitations of the capability of computers.

4) The pressure on the walls decreases near the lower corner of the bin, and it is considered that the friction force between the particles and the wall causes this phenomenon. However, the effect of this phenomenon on the total behavior must be examined.

As mentioned above, the static state in a silo can be simulated using the DEM, even with some remaining problems. Taking this static state as a reference, the simulation of the discharge can be analyzed, and the complicated behavior during the discharge could be explained using the DEM analysis.

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#### Nomenclature

k <sub>n</sub>	: coefficient of normal spring	[N/m]
k <sub>s</sub>	: coefficient of shear spring	[N/m]
η	: coefficient of proportional dampi	ng[sec]
μ	: coefficient of friction	[-]
γ	: unit weight	[kg/m <sup>3</sup> ]
D	: diameter of particles	[mm]
Ν	: number of particles	[-]
M <sub>v</sub>	: mean value of pressures	$[N/m^2]$
S <sub>d</sub>	: standard deviation of pressures	$[N/m^2]$
A <sub>v</sub>	: averaged theoretical value of pr	essures
		[N/m <sup>2</sup> ]



# Dry Submicron Classification by a Small Blow Down Cyclone †

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#### Abstract

At present, dry powders are classified using mainly a vortex centrifuge or sieving equipment, in which the lowest 50% cut size is still greater than one micrometer. Impactor-type classifiers are capable of operating in the submicron range, but have low throughput and high energy consumption.

Our new free vortex cyclones are capable of producing excellent sharp classification of dry powders in submicron cut sizes, especially with the use of a 5% to 15% blow-down flow rate from the dust collector chamber. A specified cyclone has been experimentally studied under various operating conditions using several kinds of test powders.

#### 1. Introduction

Many types of particle size classifiers have been developed for the industrial market, but there is no submicron-cut sizer in practical use except impactors. However, the impactor has practical problems involving very low throughput and high energy consumption.

Our modified cyclone type can classify dry powders of submicron cut size with both large throughput and low energy consumption. The classification performance has been much improved with the use of a blow-down system, which sucks part of the gas flow from the cyclone dust catcher box.<sup>1), 2), 3)</sup>

Experimental results are given under several conditions in this report.

#### 2. Experimental Apparatus and Operating Procedure

Fig. 1 represents our typical cyclone which has an outer diameter of 70 mm $\phi$ , and Fig. 2 is skematic diagram of an experimental set-up.

The two-stage cyclone system (Type II) has been tested in order to obtain improved performances

with the blow-down flow of the 1st cyclone. The one stage cyclone system is called Type I.

The experimental procedure is as follows:

The cyclone inlet flow rate is kept constant, and a test powder is fed into the cyclone inlet pipe at a constant rate. The ratio of the blow down flow rate to the inlet flow rate is maintained constant. The test powder is almost completely dispersed upstream the cyclone inlet by means of an air jet disperser. Downstream the cyclone classifier, coarse classified powder is collected into the cyclone dust box, fine powder is also collected on a paper filter, and blowdown powder is collected on another filter.

The collected yield  $\eta$  of the fine powder is calculated using the following equation (1) where  $W_C$  is the mass of the coarse powder collected at the cyclone,  $W_B$  is the mass of the blow-down powder at the blow-down filter, and  $W_F$  is the mass of the fine powder at the main filter. In the case of a 2 stage cyclone system,  $W_C$  is the combined mass caught by both cyclones.

The partial separation efficiency  $\Delta \eta$  is also calculated using equation (2), considering both the collected mass fraction and the measured particle size distribution of each collected powder. The mass and size distribution of the feed powder are calculated based on the sum of each collected mass and their mass fraction (ratio), and not directly from the feed powder.

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Fig. 1  $\phi$ 70 mm Cyclone with bottom cone

$$\eta = \frac{W_F}{W_C + W_B + W_F}$$
(1)

$$\Delta \eta = \frac{\Delta W_{\rm C} + \Delta W_{\rm B}}{\Delta W_{\rm C} + \Delta W_{\rm B} + \Delta W_{\rm F}} \tag{2}$$

where " $\Delta$ " represents the incremental mass of collected powders for every small corresponding size range.

The classification performance is also evaluated using the following equations (3) and (4) as the sharpness indexes.

$$\chi_1 = D_{P25}/D_{p75} < 1 \tag{3}$$

$$\chi_2 = D_{p10}/D_{p90} < 1 \tag{4}$$

where  $D_{pX}$  represents the particle size at the partial separation efficiency  $\Delta \eta = x\%$ .

The particle size distributions are measured mainly by a laser diffraction type (Maicrotrac SPA), and occasionally by a X-ray sedimentation type (Sedigraph 5000).

The test powders include two types of Calcium Carbonate (JIS-Z 8901•No. 17, and #2000), Kanto-Loam (JIS-Z8901•No. 11) and Alumina (#8000).

#### 3. Experimental Results and Comments

The effects of the blow-down flow rate of the partial separation efficiencies of the two stage cyclone system are remarkable as shown in both Fig. 3 and Fig. 4. However, the yield of fine powder decreases with the increase in blow-down follow rate.

**Fig. 4** represents an interesting effect of the inlet flow velocity on the classification efficiency. A high velocity results in a deteriorated performance for the case without blow-down and in a good performance for 15% blow-down.

**Fig. 5** illustrates the effect of different powders on the efficiency of a single stage cyclone. The powder characteristics affect the performance. However, the blow-down flow improves the classification sharpness in all cases.

Fig. 6 represents the difference between the particle size distributions obtained with the 2 stage cyclone system (Type II) and with the single cyclone system (Type I). The inlet velocities are kept at 20 m/s for Type II and 30 m/s for Type I, in order to obtain almost similar pressure losses in these two cyclone systems. The 2 stage type produces smaller particle size of the fine powder, with a nearly similar yield. However, the inlet air flow rate of the 2 stage is about 2/3 the flow rate of the single stage in this experiment, therefore the 2 stage energy consumption is also about 2/3 that of the single stage. If the powder concentration of both inlet flows is the same, the powder throughput of the 2 stage is again about 2/3 of the single stage throughput. In these experiments the powder concentration is fairly low (about 20 g/m<sup>3</sup>), and can be increased up





Fig. 2 Experimental Cyclone Systems (Type I and Type II)



Fig. 3 Effect of the 1st Cyclone Blow Down Rate on Partial separation Efficiency of Two Stage Normal Cyclone System (CaCO<sub>3</sub> #2000, Type II)



Fig. 4 Effect of the 1st Cyclone Inlet Velocity on Partial Separation Efficiency of Two Stage Normal Cyclone System with and without Blow Down Rate 15% (CaCO<sub>3</sub> #2000, Type II)



Fig. 5 Partial Separation Efficiency of  $\phi70$  cyclone Classifier (Type I)



Fig. 6 Particle Size Distributions of Calcium Carbonate Classified by  $\phi$ 70 Cyclone Classifier (Type I) and 2 Stage  $\phi$ 70 Cyclone Classifier (Type II)



to 100 g/m<sup>3</sup>, based on our past experiences.

Fig. 7 gives similar results for the 2 stage system, and shows a better performance compared to the single stage of Fig. 5.

**Fig. 8** represents the classification efficiency difference obtained by two types of measuring instruments of particle size distributions for an experiment. The X-ray sedimentation method (Sedigraph) gives usually narrow distributions and better classification results compared to the laser diffraction method (Microtrac). Therefore, these performance evaluations should be done using similar types of instruments for particle size characterizations.

Fig. 9 represents the effect of a bottom cone at the inlet of the cyclone dust chamber or at the bottom of the cyclone body. It is desirable for a cyclone to be equipped with a bottom cone in order to prevent reentrainment of the collected fine powder.

**Table 1** gives the entire experimental results including the fine powder yield and the classification sharpness indexes.

Incidentally, the partial separation efficiencies  $\Delta \eta$  involving the blow down flow decrease to zero, instead of the blow down flow rate ratio. The latter case has been obtained in many experimental conditions of wet type cyclones. The reason for this is not clear, but might be due to strong flow turbulence and reentrainment of fine powder at the cyclone bottom.

#### 4. Conclusion

The experimental results of a sub-micron particle size classification by a modified blow-down cyclone are as follows:

- (1) The effects of blow-down flow from a cyclone dust chamber are remarkable, and its performance is as good as that of forced vortex type classifiers for a few micrometers cut size. However, the yield of fine powders drops lower than that with the original type, and a small amount of over one micrometer size particles still remains in the classified fine powder.
- (2) The effect of blow-down flow is larger at higher inlet velocity than at lower velocity. This may be due to the use of the blow-down flow to prevent reentrainment of coarse particles in a cyclone.
- (3) The classification performance varies with the powder characteristics for the same operating conditions.



**Fig.7** Partial Separation Efficiency of 2 Stage φ70 Cyclone Classifier (Type II)



Fig. 8 Partial Separation Efficiency of 2 Stage φ70 Cycle Classifier (Type II) Measured by Different Methods



Fig. 9 Partial Separation Efficiency of \$\phi\$70 Cyclone Classifier with and without Bottom Cone and Blow Down Rate 15% (CaCO<sub>3</sub> JIS No. 17) (Type I)



Sample Powder	Cyclone Diameter and Type	Inlet Velocity (m/s)	Blow	Sharpness Indexes		Cut Size	Yield of Fine
			Down Rate (%)	$\varkappa_1$	×2	D <sub>p50</sub> (μm)	Powder $(\eta\%)$
		25	0	0.22	0.11	0.61	9.3
CaCO <sub>3</sub>	$70\phi \times 70\phi$	25	5	0.38	0.19	0.36	6.2
<b>#</b> 2000	Two Stage	25	10	0.74	0.22	0.35	5.1
		25	15	0.84	0.29	0.35	4.1
		19	0	0.26	0.14	0.33	9.9
		19	15	0.75	0.20	0.34	6.3
CaCO <sub>3</sub>	$70\phi \times 70\phi$	22	0	0.25	0.13	0.41	9.0
#2000	Two Stage	22	15	0.77	0.22	0.34	5.2
		25	0	0.22	0.11	0.61	9.3
		25	15	0.84	0.29	0.35	4.1
		30	0	0.50	0.25	0.41	6.3
Kanto Loam		30	5	0.60	0.25	0.41	6.7
JIS No. 11	70 <b>φ</b>	30	10	0.69	0.32	0.37	5.7
$(D_{p50} = 2.4 \ \mu m)$		30	15	0.73	0.37	0.38	4.4
F		30	20	0.66	0.26	0.37	4.5
	70φ	30	0	0.37	0.19	0.43	6.4
CaCO	70 <b>φ</b>	30	15	0.97	0.79	0.32	2.0
JIS No. 17	$70\phi \times 70\phi$	20	0	0.72	0.30	0.35	6.2
	Two Stage	20	15	0.97	0.75	0.33	2.6
41.0	70ø	30	15	0.77	0.41	0.24	4.1
-π <sub>2</sub> Ο <sub>3</sub> -# 8000	$70\phi \times 70\phi$						
# 0000	Two Stage	20	15	0.74	0.39	0.15	3.7

Table 1 Experimental Results of Cyclone Classifiers

- (4) The performance of a 2 stage cyclone system (<u>Type II</u>) is substantially higher compared to that of a single stage system with the same pressure loss of the system, though the throughput is about two third that of the single stage.
- (5) Performance evaluation depends on the type of instrument used for the measurements of particle size distributions.
- (6) The use of a bottom cone at the inlet of a cyclone dust chamber seems desirable for the maintenance of a good performance.

#### Nomenclature

D <sub>P</sub>	: particle diameter	[µm]
Хi	: classification sharpness indexes	(-)
	[i =	= 1 or 2]
η	: collection efficiency of fine part	icles
		[%]
$\Delta \eta$	: partial separation efficiency	[%]

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# Analysis of the Powder Composite Process by a Mechanical Method †

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#### Abstract

Recently, composite particles covered with different kinds of fine particles have been fabricated using various mechanical methods in a dry phase. However, the quantitative analysis of the composite process has not yet been conducted systematically.

In this paper, a mechanical processing method called MECHANOFUSION was used to investigate the composite process of glass beads and titanium dioxide fine particles. As a first trial, the ratio of fine particles fixed onto core particles and the BET specific surface area of the processed particles were measured as a function of the processing time.

Consequently, the composite process was described as the following two steps: The first is the adhering step whereby fine particles adhere to the core particles' surface, and the second is the compacting step of the fine particle layers. Furthermore, it was found that the BET specific surface area of the processed powder was correlated with the energy consumption per weight of material in the apparatus.

#### 1. Introduction

Recently, attempts to fix fine particles onto the surface of particles to produce the so-called composite particles is being actively pursued in the field of powder technology.

A number of processing methods have been proposed<sup>1)</sup> but the dry type mechanical method<sup>2)</sup> proposed by Koishi et al. is known to be simple and to possess high applicability. Motivated by this success, a number of methods using fine grinding machines<sup>3)</sup> have been developed in succession<sup>2)</sup>. Also there are a number of reports<sup>3-5)</sup> which claim that the production of composite particles in a variety of combinations including plastics, metals, ceramics and such has become possible and numerous studies on the characterization<sup>6-7)</sup> and application<sup>8-10)</sup> of the obtained particles are documented.

Thus, studies in these areas are being actively pursued but presently, not many studies of the composite process are being carried out by actual machines<sup>11, 12</sup>. It is believed that the main reason for this lies in the difficulty to perform a quantitative analysis of the obtained composite particles. In fact, much of the analysis of characterization and composite process phenomenon is conducted mainly by electron microscopes.

In this present study, one of the actual machines, the Mechanofusion system<sup>4)</sup> (manufactured by Hosokawa Micron Corp.) was used to observe the characterization of composite particles from their structure and an attempt was made to analyze the observations using a simple and quantitative method. Then on the basis of the results, the particle composite process was analyzed. Furthermore, the relation between the operation conditions of the apparatus and the composite process was studied.

#### 2. Experiment

The outline of the experimental apparatus is shown in **Fig. 1**. The main part consists of a rotating chamber and a semi-cylindrical arm head fixed with a certain clearance against the inner surface of the chamber. Powder loaded into the chamber is compressed onto the inner surface by centrifugal force and receives the complicated forces such as compression, shearing and rolling between the arm head and the inner surface of the chamber. The powder

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<sup>†</sup> This report was originally printed in J. Soc. Powder Technology, Japan, 29, 434-439 (1992) in Japanese, before being translated into English with the permission of the editorial committee of the Soc. Powder Technology, Japan.





Fig. 1 Experimental apparatus for fabricating composite particles (MECHANOFUSION SYSTEM, Hosokawa Micron Corp.)

subjected to this action is scraped off from the inner surface by the scraper and again subjected to the above action. It is thought that the composite particles are obtained by repeating this action during processing. In the experiment, AM-20F shown in **Table 1** was used but the other three types of facili-

Table 1	Specifications	of	experimental	apparatus
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Туре	Chamber diameter: D (mm)	Motor power (kW)	Volume ratio of powder processed (-)
AM-15F	150	1.5	1
AM-20F	200	3.7	3
AM-35F	340	3.7-7.5	16
AM-80F	800	11-30	233

ties were also used for the data mentioned later.

In setting the experimental conditions, the combination of particles and the mixing ratio are defined from the aspect of the materials while for the operation conditions, rotation speed of the apparatus, atmosphere, temperature and such are determined. Here, for the purpose of analyzing the composite process, the ratio of the core particles diameter to that of the fine particles was set<sup>2)</sup> at a large value which is said to be effective to fabricate composite particles. Therefore, the powder specimens mentioned in Table 2 were used.

The glass beads used in the basic experiment are spherical test specimens of GMB-20 powders with uniform particle diameters. PMMA is of spherical shape while silicon sand is of irregular shape. For the fine particles which were fixed onto the surface of the core particles, rutile type titanium dioxide (produced by Teika Co., MT-150W) was used. The core particle size was measured by the laser analysis method (Microtrac) and the average particle size was expressed as 50% diameter of the volume basis. The average diameter of the titanium dioxide is catalog value. The weight ratio of titanium dioxide to the glass beads was set at 0.03. As for the rotation speed, 3 conditions were set to prevent crushing of the glass beads. The present experiments were all conducted in normal atmosphere and no external heating or cooling of the apparatus was provided.

In the experiment, the core particles and the fine particles were weighed for the specified ratio, and a total of 500 grams of the particles was loaded in the chamber and rotated at the set speed for the specific time. The motor power during operation was measured and by subtracting the value at idling, a value corresponding to the power acting on the powder was obtained. The temperature of the chamber during operation was obtained through a thermocouple embedded in the arm head. In the case of processing glass beads and titanium dioxide, the chamber temperature did not exceed 361K.

First, to observe the fixed ratio (R) of titanium dioxide onto the glass beads with the lapse of processing time, a simplified method using the apparatus shown in **Fig. 2** was employed. After mixing 5 grams of the processed powder in methyl alcohol for 1 minute, the powder was dispersed for 1 minute by ultrasonic waves (300 W). Then the powder was passed through a micro-sieve (mesh 10  $\pm$  1  $\mu$ m, Tsutsui Rikagaku Kikai Co.) by sound wave oscillation for 90 minutes while adding methyl alcohol. The residue left on the sieve was dried for 24 hours

	Glass beads	РММА	Silica sand	TiO <sub>2</sub>
Specific gravity (kg/m <sup>3</sup> )	$4.2 \times 10^3$	$1.2 \times 10^3$	$2.7 \times 10^{3}$	$4.3 \times 10^3$
Mean particle diameter $d_{p50}$ (µm)	23	12	26	0.015
Specific surface area (m <sup>2</sup> /kg)	$0.062 \times 10^{3^{**}}$	$0.42 \times 10^{3^{**}}$	$0.59 \times 10^{3^*}$	$97.9 \times 10^{3^*}$

Table 2. Properties of powder materials used

\*BET \*\*calculated





Fig. 2 Experimental apparatus for measuring the ratio of fine particles fixed onto the surface of core particles

in a constant temperature bath (393K), the titanium dioxide residue was weighed, and from this, R was calculated. The validity of this method was confirmed by making use of the methyl alcohol into which 0.15 gram of titanium dioxide and 4.85 gram of glass beads are dispersed. In this case, R was -0.015 under the above processing condition. It proves the error is little in this method. Furthermore, R will change with the dispersion conditions of the processed powder. However, from the viewpoint of discussing the composite process, the experiments were conducted under the above mentioned constant conditions.

#### 3. Experimental results

Fig. 3 shows the relationship between the fixed ratio R onto the surface of glass beads and the processing time t. Here, when we look at the effect



Fig. 3 Change of the ratio of fine particles fixed onto the surface of core particles with processing time (glass beads -  $TiO_2$ )

of rotation speed, the spread of data is observed at 500 rpm, but R increases with processing time and becomes constant at about 0.9 in 5 minutes or more. With rotation speed exceeding 750, R reaches 1.0

in 5 minutes. Fig. 4 shows SEM photos of composite powder after processing for 120 minutes at 500 and 1000 rpm and for both, it can be observed



Fig. 4 SEM pictures of glass beads- $TiO_2$  composite particles (a) N = 500 r.p.m., 120 min process, (b) (c) N = 1000 r.p.m., 120 min process

that titanium dioxide has fixed onto the surface of the glass beads to form composite particles.

From the above, the relationship between the ratio R and the processing time t is described by the following two steps: The first one is a step in which fine particles adhere onto the core particle. The second one is a step in which R becomes constant. The former step is seen earlier as rotation speed increases.

Next, in an attempt to observe how the structure of the particles changes in the above composite process, the BET specific surface area was measured. An automatic specific surface measuring apparatus Model 2200-01 manufactured by Shimadzu Corp. was used and  $N_2$  was used as the absorption gas. To obtain information limited to composite particles, those of R = 1, namely samples processed at 750 rpm and 1000 rpm were used.

Fig. 5 shows the relationship between the specific surface area  $S_w$  of the processed powder and the processing time t. Here,  $S_w$  at t = 0 was obtained by calculating it from the values in **Table 2**. From the **Fig. 5**, it can be seen that  $S_w$  decreases, tracing an S curve with the lapse of time. As for the effect of rotation speed, it is seen that the  $S_w$  value is smaller at 1000 rpm than that at 750 rpm. Looking at **Fig. 4** (c) to study the cause for the decrease of  $S_w$ , it can be observed that titanium dioxide is present in a compacted condition. Consequently, it is thought that the reduction in specific surface area is caused by the compaction of the titanium dioxide layer onto the glass bead surface. From the above, in the area where R becomes constant, the





Fig. 5 Change of BET surface area of composite particles with processing time (glass beads -TiO<sub>2</sub>)

specific surface area decreases as the processing time becomes longer, and the surface layer of core particle tends to be compacted.

A similar phenomenon is also observed when the core particles are substituted with PMMA. For the series shown in **Fig. 6**, it has not been firmly confirmed that the fixed ratio of fine particles onto core particles is 1. However, a trend similar to that



Fig. 6 Change of BET surface area with processing time (PMMA-TiO<sub>2</sub>)

of Fig. 5 is seen. Fig. 7 shows electron microscope photos of processed particles with processing times of 5 minutes and 480 minutes. It is observed that the compacting density of the titanium dioxode layer increases with the reduction of the specific surface. From the above example, it is thought that the phenomenon explained in Fig. 5 is quite general. Also since the specific surface in Fig. 6 becomes roughly constant with an extended processing time, it is assumed that a similar trend will be seen in the case of Fig. 5 when processing is conducted for a long time.



Fig. 7 Electron microscope pictures of PMMA-TiO<sub>2</sub> composite particles, (a) (b): 5 min process, (c) (d): 480 min process, (a) (c): SEM, (b) (d): TEM pictures of section areas, ×10,000

#### 4. Discussions

A model of the composite process of particles using the present apparatus and the above experimental results and observations can be expressed as shown in **Fig. 8**. Namely it is thought that the



Fig. 8 Composite processes of core particles and fine particles by MECHANOFUSION processing

composite process, taking into account Figs. 3, 5, and 6, can be expressed by the following two steps.

I: 
$$R \nearrow$$
,  $S_w \searrow$   
II:  $R = 1$ ,  $S_w \searrow$ 



Here, I is considered to be the step where fine particles adhere onto the surface of the core particle and as a result, R increases with the lapse of time while contrarily  $S_w$  tends to decrease. On the other hand, in II, the adhering of fine particles onto the core particle surface ends and only  $S_w$  decreases which is considered to be a compacting process of the fine particle layer on the core particle surface. As already known, this model, was analyzed as bulk material. Therefore, it is thought that a study of its distribution is also necessary in the future.

For practical purposes, it is important to know the relationship between the composite process and the operation conditions of the apparatus. Here we will focus on the case where all fine particles fix onto the core particle (R = 1) which is an important area from the viewpoint of practical use. Looking at **Fig. 5**, it can be seen that the specific surface area S<sub>w</sub> becomes smaller as the processing time t increases and also as rotation speed is increased. This implies that S<sub>w</sub> becomes smaller as the energy supplied to the powder becomes higher. As a trial, if the x axis represents the energy E applied to a powder unit mass, we obtain **Fig. 9** and it shows



Fig. 9 Relationship between BET surface area of composite particles and energy consumption (glass beads-TiO<sub>2</sub>)

that the data is expressed by one curve independent from rotation speed. Therefore, in the area where R = 1, the setting of the operation conditions is made by considering E.

Fig. 10, shows data which were re-arranged by the present method. In the experiments, the 4 types of different sizes, shown in **Table 1** were used. The properties of silica used as the core particles are shown in **Table 2**. Here, the fixing ratio R of titanium dioxide onto silica surface was not measured. However, it is interesting to note that



Fig. 10 Relationship between BET surface area and energy consumption of four kinds of apparatus indicated in Table 1 (silica sand-TiO<sub>2</sub>)

the data can be arranged on one curve without referring to the size of the apparatus and its operation conditions. This implies that the scale-up of the apparatus can be done by the relation shown in **Fig. 10**. It is necessary to have further studies hereafter on this point, including the measurement of R values.

#### 5. Conclusions

Using an actual machine and expressing the particle composite process by the fixing ratio of fine particles onto core particles and by the specific surface area of the processed powder quantitatively, the following conclusions were obtained.

(1) The particle composite process obtained with Mechanofusion apparatus was described by the following two steps: the step where fine particle adheres onto the core particle surface and the step where the fine particles compact onto the core particle surface.

(2) The composite process was correlated with the energy applied to a powder unit mass.

#### Acknowledgement

We wish to express our gratitude to Dr. Masafumi Arakawa, formally professor of Kyoto Inst. of Tech. for his valuable suggestions in summarizing this paper and to Dr. Takamasa Hanaichi of the Medical Dept. of Nagoya University for his guidance in photography with electron microscopes.



#### Nomenclature

D	: chamber	diameter	of	experimental	apparatus
					[mm]

 $d_{p50}$  : average particle size [ $\mu$ m]

- E : Energy consumption per unit weight of material in the apparatus [J/kg]
- N : revolution of the chamber [rpm]
- n : weight content of  $TiO_2$  fine particles [-]
- R : ratio of fine particles fixed onto the surface of core particles [-]
- $S_w \quad : \mbox{ BET surface area of processed particles} \\ [m^2/kg] \label{eq:sw}$
- T<sub>max</sub> : maximum temperature of the arm head of the apparatus during operation [K]
- t : processing time [min]

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#### The Symposium on Powder Technology

"The 27th Symposium on Powder Technology" sponsored by the Council of Powder Technology (Japan), now an annual event, was held on August 26, 1993 at the Foundation of Osaka Science and Technology Center.

The symposium focused on "granulation", an old and yet a new technology under the main theme, "Granulation and Grain Designing". Lectures were given on various granulation technologies, their basics, applications, and problems from academic standpoints as well as from standpoints of users and makers. Enthusiastic discussions followed the instructive lectures, making the event a grand success.

Starting from this year, a commemorative lecture by the one receiving "the KONA Award" presented by the Hosokawa Powder Technology Foundation is to be given and a special lecture was given by this year's awardee, Professor Hisakazu Sunada of the Meijo University.







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#### Addendum

In the paper entitled "Slot Flow Metering Fundamental Investigations, Pilot-ScaleTests and Industrial Prototype" by B.J. Harris, J.F. Davidson and C.E. Davies in KONA No. 10 (1992), p 106, the following table 1 was missing.

Table 1.	Experimental results	of Davies and Foye	$(1991)^1$ ,	Davies et al (1992)	<sup>2</sup> and Harris et al.	$(1992)^3$ .
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Material	Bulk density (kgm <sup>-3</sup> )	Particle size (µm)	$K_{e}^{*}$ (kgs <sup>-1</sup> m <sup>-5/2</sup> )	k* (-)	C* (-)
Rape <sup>1</sup>	601	1900	857	2.4	0.64
Casein <sup>1</sup>	576	350	509	4.8	0.40
Urea <sup>2</sup>	734	3130	826	2.4	0.51
Sand A <sup>3</sup>	1450	155			
Sand B <sup>3</sup>	1400	233		0.12	0.43
Sand C <sup>3</sup>	1500	518			



Academic publication	concerning powder	technology in Jap	an (1992)
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# Journal of the Society of Powder Technology, Japan Vol. 29 (1992)

Title	Author(s)	Page	
• Dust Adhesion to a Cyclone Wall at an Elevated Temperature	S. Mizukami, J. Hirose and H. Murata	4- 10	
• The Dispersion Mechanism of a Mixer-Type Disperser	K. Gotoh, M. Takahashi and H. Masuda	11- 17	
• The Performance of Granular Bed Filters with Dust Loading	H. Mori, N. Kimura and S. Toyama	18- 25	
• Arch Formation of Limestone Carried in Cargo Holds of a Self-unloading Ship and Variation of the Flow Properties with Time	H. Tsunakawa and T. Nagata	26 - 31	
• Study on Static Pressures on Granular Materials in a Silo Using the Distinct Element Method	J. Yoshida	86 - 94	
• A consideration of the Rate of the Solid State Reaction Followed by a Solid Solution Phase in a Unidirectional Diffusion system	A. Shimizu, Y. Hao and H. Sasaki	95 - 101	
• The Limit of Grinding of Alumina Powder in Water by a Planetary Ball Mill	T. Yokoyama, T. Kubota and G. Jimbo	102-109	
• Particle-Reentrainment from a Fine-Powder Layer by an Accelerated Air-Flow	S. Matsusaka, Y. Nakamura and H. Masuda	110 - 115	
• Preparation of Semiconductive In <sub>2</sub> O <sub>3</sub> -SnO <sub>2</sub> Fine Powder by Mechano-Chemical Reaction	H. Shiomi, S. Akit and M. Nakamura	162 - 167	
• The process of Ultra-Fine Grinding of Titania Accompanied by Simultaneous Surface Treatment in a Media-agitating Mill	K. Uchida, K. Kamiya, N. Asoh and F. Ikazaki	168-172	
• Wet Coating of Fine Particles on PSL Particles by Heterocoagulation	T. Niida, Y. Kousaka, M. Tsugoshi, Y. Nishie and Y. Endo	173 – 179	
• The Effect of Powder Treatment Conditions on the Thermal Conductivity of Nylon Coated AlN	J. Takada and H. Shingu	180-184	
• The Surface-treatment of Boron Nitride and its Surface Properties	N. Suzuki, N. Baba, H. Naoi, T. Koitabashi, A. Endo and H. Utsugi	185 - 189	
• A New Powder-Supply Method Using a Hopper with a Vibrating Coil Spring	M. Saito	248 - 253	
• Infiltration of Chloride Reduced Particles within a Ceramic Packing as a Method of Forming Inclined Concentration Layers	H. Mori, E. Ishikawa, W. Yi, M. Nakamura and S. Toyama	254 - 260	
• Study on Influence of Friction Coefficients on the Behavior of Granular Materials in Silo During Discharge Using the Distinct Element Method	J. Yoshida	261 - 268	
• Change in the Impeller Torque with the Progress of Spherical Agglomeration in an Agitated Vessel	H. Takase, K. Sanami and M. Sugimoto	269-275	
• Tensile Fracture Behavior of a Powder Bed Consolidated with a Low Normal Stress	M. Hirota, S. Yagi, H. Miura, M. Suzuki and T. Oshima	338 - 343	



Title	Author (s)	Page
• Suspension Conveying of the Particles at High Solid-gas Loading Ratios and High Conveying Pressures	M. Futamura	344 – 350
• Dry Submicron Classification by a Small Blow Down Cyclone	K. Iinoya, T. Fuyuki, Y. Yamada, H. Hisakuni and E. Sue	351 - 355
• Effects of Inner Structures on Gravity Flow and Stress in Shaft Furnaces	S. Mizukami	356 - 361
• The Coating of Fluidizing Particles by Atomization of Fine Powder Suspension	H. Kage, T. Yoshida, H. Matsui and Y. Matsuno	422 - 427
• On-line Monitoring for Agglomeration in Organic Liquid	T. Hirajima, W. Guinto, M. Tsunekawa, K. Tadano, I. Nakajima and M. Nakamura	428 – 433
• Analysis of the Powder Composite Process by a Mechanical Method	M. Naito, M. Yoshikawa, T. Tanaka and A. Kondo	434 - 439
• The Effect of the Surface Modification of Particles on the Contact Potential Difference Between a Powder Bed and Metal	H. Yoshida, T. Fukuzono, H. Ami, Y. Iguchi and H. Masuda	504 - 510
• The Effect of Vibration on the Behavior of an Ultra Fine Powder in a Spouted Bed	K. Ushiki, J. Kawase, R. Utsumi and T. Hata	511 - 517
• The Effect of Heating Temperature, Heating Time and Coal Rank on the Apparent Viscosity of Coal-Hydrogenated Anthracene Oil Slurry	T. Sakaki, M. Shibata and H. Hirosue	518 – 523
• Numerical Simulations with Potential Flow for Anisokinetic Sampling Errors and Particle Concentration Distributions in a Sampling Nozzle	M. Samata	584 — 592
• The Effect of Sodium Hexametaphosphate on the Grinding of Alumina Particles	K. Matsumoto, H. Shimizu, H. Matsuoka and T. Tanaka	593 - 597
• Fine Particle Separation by Probability in a Wet Process	Z. Tanaka, T. Kaneko and T. Takahashi	598 - 602
• The Effect of Air Velocity on the Flow Characteristics of the Pneumatic Conveying of Granular Materials	M. Futamura	603 - 609
• The Pressure Fluctuation and the Formation of a Lamination Layer during the Uniaxial Compression of Ultrafine Particles	M. Mizuno and G. Jimbo	662 – 668
<ul> <li>Investigation of the Shape Separation Performance of a Rotating Conical Disk based on the Rolling Frictional Characteristics of Irregular Particles         <ul> <li>The Effect of the Feed Rate on Separation Efficiency –</li> </ul> </li> </ul>	K. Yamamoto, M. Makino and M. Sugimoto	669 — 675
• The Continuous Kneading of Metal Particles and Its Evaluation	Y. Mido, H. Suzuki, K. Sakamoto and K. Terashita	676 - 681
• Surface States of Aluminum Nitride Powder and Its Waterproof Treatment	K. Sugiyama, H. Takahashi, S. Konno, S. Tanaka, T. Matsuda, M. Uenishi and Y. Hashizume	682 - 687



Title	Author (s)	Page
• Wet Size Classification for Fine Particles in Centrifuges	Z. Tanaka, T. Miya and T. Takahashi	750 - 754
<ul> <li>Silica Coating at the Nano-Meter Level on an α-Alumina Fine Powder</li> </ul>	M. Sando, A. Towata and A. Tsuge	755 – 761
<ul> <li>Packing of Binary Particulate Mixture with a Continuous Composition Profile by Using a Filtration Method</li> </ul>	M. Iwata, W. D. Yi, M. Nakamura and S. Toyama	762 – 768
<ul> <li>The Compressive Crushing of Brittle Materials in a Powder Bed.</li> <li>The Effect of Feed Size on the Production of Fine Particles –</li> </ul>	Y. Kanda, T. Oyamada, R. Nakayama and T. Matsuo	824 - 830
• New Method for the Preparation of Polyamide Coated Aluminum Nitride Powder	J. Takada	831 - 837
<ul> <li>Study of the Shape Separation of Fine Particles Using Fluid Fields         <ul> <li>Dynamic Properties of Irregular Shaped Particles in Wet Cyclones –</li> </ul> </li> </ul>	S. Endoh, H. Ohya, C. Ikeda, K. Masuda, S. Suzuki and H. Iwata	838 – 844
• Influence of Distributor Types on the Fluidizing Characteristics of a Tapered- Fluidized Bed	Y. Okada, T. Ohwaki, Y. Ishibashi, Y. Taguchi, H. Ozawa, R. Yamazaki and G. Jimbo	886 – 890
• Granulation in a Tapered-Fluidized Bed and Its Dominant Factors	Y. Okada, T. Ohwaki, K. Uesugi, Y. Taguchi, H. Ozawa, T. Suzuki, R. Yamazaki and G. Jimbo	891 – 896
• A New method for the Measurement of Powder Characteristics Based on the Reentrainment Phenomena	H. Masuda, S. Matsusaka and K. Imamura	897 – 905

## Funsai (The Micromeritics) No. 36 (1992)

Title	Autor(s)	Page
• Model Simulation of Ball Motion in a Tumbling Ball Mill Under High and Low Gravity	H. Hashimoto and R. Watanabe	4-11
• Formation of Fine Particles of Slightly Soluble Medicines by Dry Ball-Milling	A. Ikegawa and E. Yoshino	12 - 19
• Sintering of Superconducting Fine Particles in the Bi-Ca-Sr-Cu-O System Prepared by Spray Pyrolysis	K. Okuyama, M. Shimada, N. Tohge and M. Adachi	20- 29
• Enhancement of Solid Acid Strength and Stabilization of Constituent Particles of Zirconias and Other Oxides Through Coordination with Inorganic Anions	K. Mukaida, M. Sato, A. Iijima, H. Ando and N. Anbo	30 - 36
• Effect of Powder Roll Mixing to Cyclodextrin Molecular Complexation	Y. Nozawa, M. Kishimoto and M. Takeda	37-44

.



# Kagaku Kogaku Ronbunshu Vol. 18 (1992)

Title	Author(s)	Page
<ul> <li>Effect of Fractional Ball Filling of a Vibration Mill on the Rate of Grinding – Results of Numerical Analysis of Ball Motion –</li> </ul>	T. Yokoyama, H. Usui G. Jimbo and K. Tamura	78 - 86
<ul> <li>Calculation of Stress Distributions in a Powder Bed as a Plane Strain Field and Verification by Experiment         <ul> <li>The Effect of Friction Factor –</li> </ul> </li> </ul>	S. Yuu, E. Karube and S. Fujimoto	94 - 100
• Direct Numerical Simulation of Three- Dimensional Navier Stokes Equations for Free Jet and Experimental Verification	S. Yuu, Y. Kawaseki and T. Nagasue	101-107
• Stabilization of Flow of Pellets Based on Computer Simulation of a Matallurgical Reaction in a Shaft Furnace	S. Mizukami and S. Toyama	205-211
• Dispersion of Aggregate Particles by Acceleration in Air Stream	Y. Kousaka, Y. Endo, T. Horiuchi and T. Niida	233 - 239
• Initial Collection Efficiency of Electret Filter and its Durability for Solid and Liquid Particles	Y. Otani, H. Emi and J. Mori	240 - 247
• Flow Characteristics of Discharge Flow Region in a Stirred Vessel with Aeration	K. Ogawa, S. Yoshikawa and H. Shiode	495 - 501
• Feedback Properties of the Rolling Schedule	I. Tamura, H. Nishitani and E. Kunugita	502 - 509
• Measurement of Velocity Profiles of Fluid in a Liquid Spouted Bed by Using a Laser Doppler Velocimeter	F. Ogino, M. Kamata and K. Shimokawa	510 - 514
• Visualization of Particle Motion in a Liquid Spouted Bed by Using Neutron Radiography	F. Ogino, M. Kamata, K. Shimokawa, K. Mishima, S. Fujine, K. Yoneda, K. Kanda and T. Tsujimoto	515 – 520
• Effects of Fluid Viscosity on Ball Movement and the Initial Rate of Wet Grinding of a Vibration Ball Mill	T. Yokoyama, H. Usui and G. Jimbo	616 - 621
• Formation of Composite Latex Particles by Deposition of Amphoteric Particles	K. Higashitani, T. Yamamura, Y. Isshiki, A. Kage and A. Kondo	637 - 642
• Estimation of Particle Velocity in Moving Beds based on a Flow Model for Bulk Solids	H. Takahashi and Y. Honda	849 - 855
• Flow and Segregation of Binary Mixture of Particles of Different Shape in a Rotating Horizontal Cylinder	M. Furuuchi, T. Honda, H. Harifuchi and K. Gotoh	935 – 941
<ul> <li>Theoretical Analysic of Liquid Bridge Formation Between Two Particles         <ul> <li>Bridge Formation by I deal Pure Water –</li> </ul> </li> </ul>	Y. Kousaka, Y. Endo and Y. Nishie	942 - 949
<ul> <li>Liquid Bridge Formation between Two Particles         <ul> <li>Bridge formation by water containing soluble impurity –</li> </ul> </li> </ul>	Y. Endo, Y. Kousaka and Y. Nishie	950 - 955

#### **New Product News**

Hosokawa Micron Corporation introduces two new products.



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The FINETRON is a newly developed, high performance screw feeder fitted with a mechanism to vibrate the screw itself in the axial direction, as well as a special agitator swinging inside the hopper bottom.

#### **Special features**

- Offers a very accurate feeding.
- Minimises pulsations of feeding.
- Applicable even for adhesive or short fiber materials which are difficult to feed by other types of feeders.
- Can cope with a wide range of feeding capacities.
- Easy to clean and disassemble.
- Can be combined with weighing equipment for a more accurate feeding system on a loss-in-weight basis.

FT-10	FT-15	FT – 20	FT-25	FT-40	FT - 50	FT-75	FT - 100
0.6	1.3	4.0	11	43	110	360	960
to	to	to	to	to	to	to	to
3.6	7.8	24	66	258	660	2160	5760
	FT-10 0.6 to 3.6	FT-10         FT-15           0.6         1.3           to         to           3.6         7.8	$\begin{array}{c cccc} FT-10 & FT-15 & FT-20 \\ \hline 0.6 & 1.3 & 4.0 \\ to & to & to \\ 3.6 & 7.8 & 24 \\ \end{array}$	$\begin{array}{c ccccc} FT-10 & FT-15 & FT-20 & FT-25 \\ \hline 0.6 & 1.3 & 4.0 & 11 \\ to & to & to & to \\ 3.6 & 7.8 & 24 & 66 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

# **HOSOKAWA MICRON**

LEADERS IN POWDER PROCESSING, THERMAL PROCESSING, ENVIRONMENTAL PROTECTION AND PLASTIC PROCESSING.

Hosokawa Micron responds to global needs through emphasis on materials science and engineering. The Group is an international provider of equipment and systems for powder processing, thermal processing, environmental protection, and plastics processing. The Group maintains facilities for research, engineering, manufacturing, and service in each of the world's major industrial markets.

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