Comparison between techniques based on charge characterisation and capillary suction time for assessing the dispersion characteristics of concentrated slurry

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Achieving a stable dispersion with high solid loading is pre-requisite in many conventional/emerging ceramic forming processes. Hence, assessing the quality of dispersion is one of the critical aspects to be considered during forming process to ensure the final product quality. There are several direct/indirect techniques to assess the quality of dispersion. Many are optical methods, which generally require dilution of the suspension, with consequent alteration of the equilibria. This complicates the system unless particular care is taken to compensate for the dilution process. Many times it has been observed that a dispersant, that provides good dispersion at low solids concentration will not necessarily provide good dispersion at high solids concentration.

This paper compares two indirect techniques, namely, particle charge detector (PCD) using the principle of 'Streaming Potential' and capillary suction time (CST) apparatus based on the principle of capillary suction pressure to study the effectiveness of a dispersant for maximum dispersibility. © *2004 Kluwer Academic Publishers*

1. Introduction

Dispersions in both aqueous and nonaqueous media are used in many products including ceramics, paints, pigments, printing inks, papers, adhesives, cosmetics, detergents, dyestuffs and pharmaceutical formulation [1]. The quality of products produced by wet processing is determined primarily by the state of the dispersion. Dispersion of the particles and the stability of the suspension, therefore, are key factors for the successful production of many industrial products. The degree of dispersion possible in any given system depends on the particle size. With decrease in particle size below 1 μm (colloidal range), the role of surfaces and interfacial phenomena dominates the properties of suspension due to availability of large surface area (10–300 m^2/g). Knowledge of these properties of the system is often desired to develop predictive strategies to control the state of dispersion and aggregation of powders.

A system of dispersed particles may be characterized by properties of the disperse phases, continuous phase, interfacial properties and the colloidal properties. An exhaustive list of these properties is given in Table I [2]. Although several methods are available to determine various properties under isolated conditions, difficulties remain for measurements in concentrated suspension [2]. If the particles are small enough i.e., colloidal in nature (<1 μm), they are kept in suspension by simple Brownian motion. However, due to the high surface area available, colloidal particles tend to

aggregate to reduce surface energy, thereby destabilizing the suspension. On the other hand for systems containing coarser particles (>1 μm), special attention is required to keep the systems in a highly dispersed state. Generally, the most practical way of maintaining a stable dispersion is through the use of chemical stabilizers called dispersants. Commonly, these dispersants are polyelectrolyte surfactants, which adsorb on the surface of the particles and modify the surface charges and thus also the electrostatic forces. The primary property of dispersants will be their ability to disperse fine particles and to stabilize the dispersion.

Dispersibility is defined as the ease with which particles are distributed in the continuous phase so that each particle is completely surrounded by the liquid phase and no longer makes permanent contact with any particles [3]. Generally, properties measured in dilute suspensions are co-related to predict the behaviour of concentrated suspensions. There exists a large variation in techniques for characterizing the stability of concentrated dispersion. It is a common practice to adjust both physical and chemical variables to obtain the desired stability and rheology of the suspensions. In practice, two techniques are primarily used, *sedimentation* and *rheology* measurements. Sedimentation technique is a relatively simple method using a series of measuring cylinders containing the dispersion in a homogeneous state. The settling rate is determined by monitoring the rate of descent of the upper interface with time and

TABLE I Parameters for characterizing a system of dispersed particles [2]

Systems	Properties
Disperse phase properties	Particle shape
	Size distribution
	Surface energy
	Homogeneity
Disperse phase	Solid particles, or liquid droplets, having above properties.
Continuous phase	Aqueous
	Non-aqueous
	Dissolved substances
Colloidal properties	Percent solid
	Stability
	Rheology
	Light scattering
	Electrical double layer
Interfacial properties	Zeta potential
	Adsorption density
	Thickness of adsorbed layer

provides information on the stability of the dispersion. A high value of settling rate corresponds to an unstable dispersion and vice-versa, except in concentrated systems where hindered settling occurs. Sediment volumes provide valuable information about the nature of dispersed particles. For example, aggregated/ flocculated particles form soft and loosely packed sediments and have large sediment volumes. However; stable suspensions will form compact sediments of smaller volume. Advanced imaging techniques such as computerized axial tomography (CAT) scans can also be used to get information about the structure and state of suspensions and flocs [4]. Techniques such as light scattering, absorbance measurements with spectrophotometers are generally used to study sedimentation rates. Although the method is easy to use and widely practiced, there are several limitations. For concentrated suspensions, the settling time under gravity could be very long, and secondary effects such as temperature fluctuations, and vibrations under normal laboratory conditions could complicate the tests, unless due precautions are taken to avoid such effects [2].

Rheological techniques are widely used to assess dispersion stability and provide useful information on the particles interactions with the dispersion medium. Rheology is the science about deformation and flow of matter and rheological measurements give information on chemical and physical properties of a suspension. The rheology of a suspension, in terms of viscosity, viscoelasticity, yield point etc. is often essential to understand the system. For many materials, the viscosity is both time and shear rate dependent, for example for highly concentrated suspensions of inorganic particles, viscosity decreases with increased shear rate (shear thinning properties) because of the break down of structures (created by inter-particle forces) and orientation effects in the flow direction. In a concentrated suspensions, the inter-particle distances reduce and cause a network structure to be built up due to inter-particle interactions. This type of structure can be studied by inducing a very small deformation and measuring the viscoelastic properties. These measurements, however, give indirect information on the stability of dispersions

and therefore, must be used in conjunction with sedimentation tests for maximum benefit [2].

The aim of this paper is to present two techniques, namely the particle charge detector commonly known as PCD and capillary suction time (CST) apparatus assessing the stability of dispersions. Both the techniques provide information on dispersion stability and also determine the optimum dosages of the dispersant required to have the best dispersion characteristics for a particular problem in hand.

2. Principle of operation of the instruments used

2.1. Particle charge detector (PCD)

The principle of operation of particle charge detector (PCD 03 pH) apparatus (Make: Mutek, Germany) is based on 'Streaming Potential' measurement. It essentially consists of a cylindrical test cell of Teflon and a displacement piston of the same material, which is made to oscillate in the cell with a constant frequency (Fig. 1). A definite narrow gap is kept between the test cell and displacement piston for their movement. If a suspension is placed in the measuring cell, solid particles in the suspension will adsorb at the plastic surface of the piston and on the cell walls under the action of van der Waals forces. The counter-ions remain comparatively free. The oscillating movement of the piston forces a flow of the liquid phase of the sample between the piston and the wall of the cell. As a result, the diffuse cloud of counter ions of the electrical double layer is partially separated from (sheared off) the particles and other reagents present in the liquid. This partial separation of charges induces the so-called "Streaming Potential," which the instrument measures directly (in terms of mV). When the measured streaming potential is zero mV, the particle suspension is in a neutral state called isoelectric point (iep) [5, 6]. When a measurable streaming potential exists, then the particle is either negatively or positively charged depending on the sign of the potential displayed. Titrating the sample with a standard polyelectrolyte of opposite charge until neutralisation can enable the quantitative estimation of the overall charge of the system. The PCD apparatus has been used together with a compatible standard automatic titrator (702 SM Titrino). On reaching the zero streaming potential, it stops automatically and the
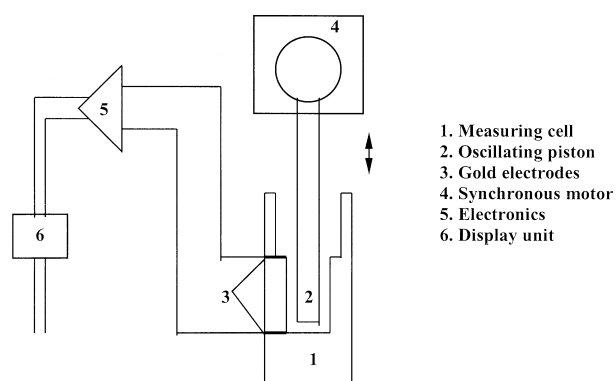

1. Measuring cell
2. Oscillating piston
3. Gold electrodes
4. Synchronous motor
5. Electronics
6. Display unit

Figure 1 Schematic diagram illustrating the assembly of PCD apparatus.
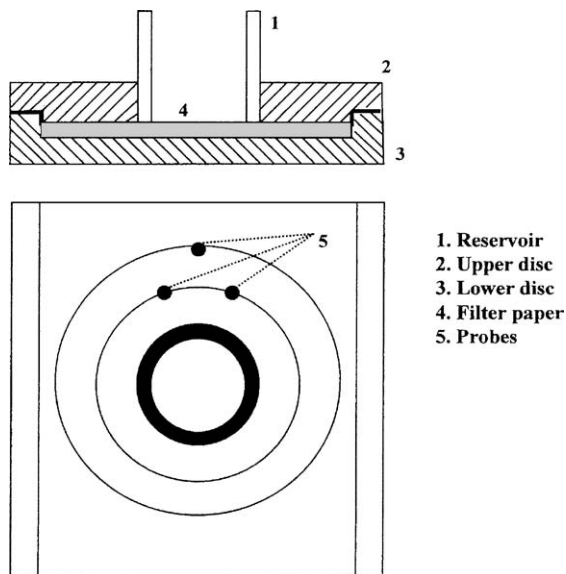
Figure 2 Schematic diagram of Capillary Suction Time (CST) apparatus.

1. Reservoir
2. Upper disc
3. Lower disc
4. Filter paper
5. Probes

exact volume of titrant consumed is read directly from the display. The specific surface charge, q in (μ eq/g) is calculated using the following formula.

$$q = \frac{V \cdot c \cdot 1000}{w} \qquad (1)$$

where V is volume of titrant consumed (ml), c is titrant concentration (= 0.001 N), 1000 is the calculation factor for the charge density, and w is the weight of the sample (in gm).

The total charge quantity (in C/g can be obtained by multiplying the specific charge (in eq/g) with the Faraday's constant (= 96485 C/eq).

In the current study, the 'Streaming Potential' measurement technique (PCD 03 pH made by: Mutek, Germany) has been used to determine the potential characteristics of a suspension at varying concentrations of dispersant. The optimum dispersed condition and dispersant amount for a defined solid content is derived from the maximum value of potential characteristics.

2.2. Capillary suction time (CST) apparatus

The operation of the CST apparatus is based on the principle of capillary suction pressure of a porous medium (Fig. 2). When a suspension is allowed to stand for some time, a sediment bed of certain height will be formed, depending on the state of dispersion/stability of the suspension. A stable suspension will take long time to form the sediment bed; also the bed will be compact due to the un-agglomerated nature of the dispersed particles in the suspension. On the other hand, an unstable suspension will form a loose and porous sediment bed rapidly. If a thin porous slab such as Whatman 17 filter paper is exposed to the bottom of such a sediment bed, dispersed medium (in the case of aqueous dispersion, water) will start to drain through the sediment bed into the porous medium (filter paper) and travel radially outward because of the capillary suction pressure of the porous medium. The rate of drainage will depend mainly on two factors: [1] the porosity of the bed, and [2] water holding capacity of the solids in suspension. The rate of drainage is proportional to the degree of porosity, i.e., for a low porosity bed; it will take longer time (i.e., slow rate) to drain the filtrate. Hence the rate of drainage will be lower for a stable suspension compared to an unstable one [7].

3. Experimental
3.1. Materials
The high pure α alumina (CT-3000 SG) obtained from ALCOA, India has been used for this investigation. The average particle size and the BET surface area of the powder used were 0.7 μm and 7.0 m²/g respectively. Dispersants and the reagents employed, were analytical grade and have been used without any further purification. Physical properties of the dispersants used are listed in Table II. In all the experiments doubly distilled water has been used for preparation of suspension. Unless otherwise stated, 5% (w/v) alumina suspension has been used for all the experiments.

3.2. Methods
3.2.1. Determination of potential characteristics
To determine the iso-electric point (iep) of alumina, (5% w/v) alumina suspension in distilled water was prepared and the suspension was transferred to the test cell of the particle charge detector and allowed to stabilize (indicated by a constant streaming potential on LCD). The potential determines charges quantitatively according to the Equation 1. Specific charges were measured with the addition of different additives by varying additive dosages and pH values, which were adjusted using HCl and NaOH. Specific charges were also determined from varying solid loading.

3.2.2. Measurement of capillary suction time
CST measurements have been carried out in TW 166 (make: Triton Electronics Ltd, UK), where a filter paper (acting as porous medium) was kept between two plates as shown in Fig. 2. The upper plate has a cylindrical hole through which a steel container snugly fits. The

TABLE II Physical properties of the dispersant

Organic dispersant	Ionicity	MW	Inorganic dispersant	Iconicity	MW
Tri-ammonium citrate	Anionic	243.2	Sodium silicate	Anionic	284.2
Darvan C	Anionic	10,000	Sodium tripolyphosphate	Anionic	336.0
Dispex N 40	Anionic	–	Calgon	Anionic	672.0

Suspension to be measured is kept in the container, and as the filtrate drains through the filter paper, the probes measure the outward movement of the wet and dry interface between two marked lines. CST measurements have been carried out with untreated alumina suspension, as well as with addition of dispersant. Measurements have also been carried out at different solid loadings. The data presented in the paper are average values of three measurements and variation was within ±1%.

3.2.3. Assessment of dispersibility using dispersion ratio (DR)

The assessment of the test of dispersion of alumina suspension has been made by comparing the dispersion ratio (DR) calculated from the CST data adopting the approach already described in detail elsewhere [7]. The method is based on the state of the suspension at the point of zero charge (pzc). The CST value for a dispersed suspension will be high compared to the value at its pzc. On either side of the pzc, the charged particle surface will experience electrostatic repulsion from the neighbouring particles keeping them in more dispersed condition. Similarly the use of dispersants imparts surface charge, which keeps the particles in suspension.

This variation in CST values with respect to the point of zero charge has been employed to assess the dispersibility of the particles. In this approach, the state of the suspension of a given solid concentration at any pH and dispersant/flocculant dosages is assessed on the basis of the state of the suspension at the respective point of zero charge. Since it is an established fact that aggregation is favoured at the point of zero charge due to the absence of a charged surface, the CST value at the pzc has been set as reference point. The dispersion characteristics are then expressed quantitatively in terms of a dispersion ratio (DR) according to the following relationship:

$$\text{Dispersion ratio (DR)} = \frac{\text{CST}_{\text{suspension}} - \text{CST}_{\text{liquid}}}{\text{CST}_{\text{suspension at pzc}} - \text{CST}_{\text{liquid}}}$$

A suspension with DR value above unity is in a state of dispersion whereas those with DR value less than 1 are in an aggregated state. The higher the value of DR above unity, the greater is the dispersibility. On the contrary, a value of DR below unity, indicates a higher degree of aggregation in the suspension.

4. Results and discussion
4.1. Stability maxima and optimum dispersant dosages for colloidal alumina

The variation of specific charge of alumina suspension with pH has been published elsewhere [8]. A charge reversal has been observed at pH 9.1, which is identified as the iso-electric point (iep) of pure alumina [8]. The addition of Darvan-C, has shifted the iep to pH 5.6. The effect of different dispersants (organic and inorganic) on the streaming potential has shown that the streaming potentials are negative on addition of all the disper-

sants [9]. The absolute magnitude of streaming potential increases with increasing dosage and then reaches a plateau region in all the cases. The initial increase in streaming potential occurs due to increase in specific charge adsorbed on the particle surface with increasing concentration of dispersant. Once the particle surface is covered completely, the unadsorbed excess additive remains in the solution. It may affect the viscosity of the solution without affecting the streaming potential. The inflection point in the curve gives the optimum dosage required for dispersion.

The alumina suspension without any additive has a pH value of 8.2–8.7 and the surface is slightly positively charged (0.01 C/g) in doubly distilled water. This is because the basic oxide Al_2O_3 consumes H^+ and increases pH, charging positively in pure water, according to the reaction:

$$[\text{M—O—H}]^{\text{o}} + \text{H}^+ \leftrightarrow [\text{M—O—H—H}]^+ \qquad (1)$$

A forced increase of pH triggers the reverse reaction and the surface gets negatively charged. The maximum value in negative PCD potential (and thus the surface charge) was observed for Dispex N-40. The dispersing ability in terms of PCD potential was found to be in the following order: Dispex N-40 > Darvan C > tribasic ammonium citrate for organic dispersants. The dispersive power of the inorganic dispersants were in the following order: Calgon > sodium tripoly phosphate > sodium silicate.

Fig. 3 shows the variation of specific charges with solid loading in presence and absence of dispersant. Increasing the solid loading in absence of any dispersant from 1.47 volume percent to 50 volume percent changes the surface charge from +0.02 C/g to −0.0098 C/g. It is clear from this curve that there is no appreciable change in surface charge with increasing solid loading, although an increase in pH value from 8–9 has been observed. In the presence of dispersant DAC at optimum dosages (105 ppm), the surface charge remains constant with increasing solid loading. It has been observed that pH also does not vary and remains constant at 8.7. However, the magnitude of surface charge in presence of DAC is shifted towards a more negative value.

4.2. Effect of pH on CST

Variation of CST values at different pH both in absence and presence of dispersant is shown in Fig. 4 [7]. The
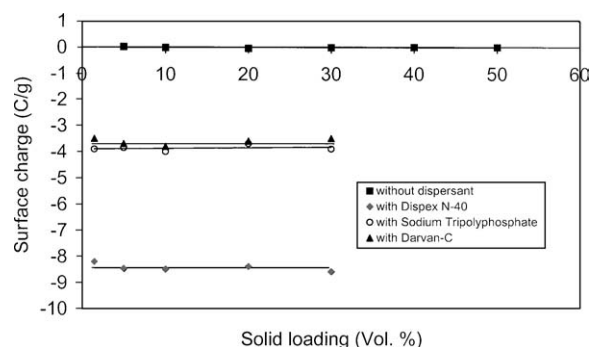
Figure 3 Effect of solid loading on surface charge of alumina powder.

TABLE III Dispersion ratio (DR) of alumina suspension (5.8 vol%) in presence of dispersants

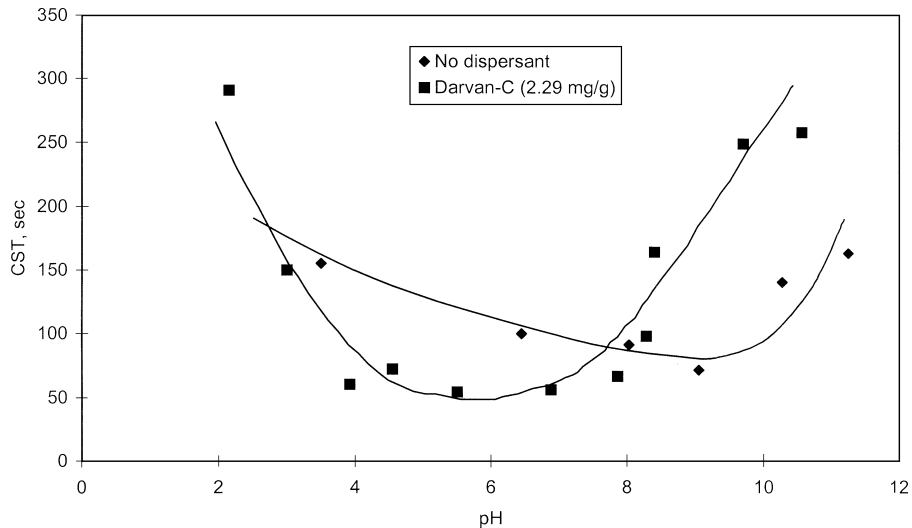| Dispersant	Optimum dosage (mg/g)	pH after dispersant addition	Streaming potential (mV)	CST (s)	Dispersion ratio (DR)
No dispersant	–	8.20	−42	221.8	1.05
Dispex N-40	6.36	9.21	−970	1023.5	4.99
Sodium tripolyphosphate	8.0	9.66	−912	1001.2	4.88
Calgon	12.0	8.85	−650	911.3	4.44
Triammonium citrate	8.0	8.20	−541	902.4	4.39
Darvan-C	6.36	8.18	−625	870.3	4.24

Figure 4 Effect of pH on CST of alumina suspension.

curve (a) depicts the variation in CST without addition of any dispersant. As expected, the lowest value of CST has been observed at the iep of alumina, where particles surfaces are uncharged and hence, agglomerated. Below and above the iep, the CST increases. Since surfaces are either positively charged (at acidic pH) or negatively charged (at alkaline pH), the suspension becomes electrostatically stabilized. On the other hand, addition of dispersant (Darvan C) shifts the iep to a lower value (minimum CST) as established earlier [8]. Optimum dosages of dispersant required can also be determined by measuring CST values of alumina suspension by varying the dispersant dosage which is in close agreement with the results obtained by PCD [7].

4.3. Comparison of dispersibility measured by PCD and CST

While comparing the results of PCD and dispersion ratio (DR), calculated with reference to the CST value at $pH_{(pzc)}$ [7], as given in Table III, it is clear from the data, that the best dispersibility can be achieved by using Dispex N-40 as it shows DR value of about 5.0. The second best is sodium tripolyphosphate and the third is Calgon. All these values indicate that DR value can be taken to assess the dispersibility of the suspension and would indicate the performance of any particular dispersant. It is seen that the CST value/DR ratio is high where the streaming potential is highly negative. The order of effectiveness of the different dispersants can be visualised and is in agreement with the results of streaming potential measured by particle charge de-

tector (PCD). It can therefore be seen that there is a definite relation between the streaming potential and CST values, i.e., higher the streaming potential, higher the CST value and capillary suction time gives a quantitative idea about the dispersion of the fine particles in a suspension.

5. Conclusions
The following are the conclusions drawn based on this investigation:

1. The PCD and CST techniques provide a convenient and reliable method for rapid estimation of the dispersion condition and optimum dispersant dosages required for stable suspension.
2. The qualitative estimation of dispersion ability of different dispersants can be made by PCD techniques.
3. CST technique not only indicates range of pH to be used for stable dispersion, but also the suitability of use of dispersants in certain pH ranges.
4. Dispersion ratio (DR) indicates the peformance of any dispersant added to a suspension. It gives a quick quantitative measure about the dispersibility of particles in the suspension.

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