A surface charge characterization device using sedimentation potential for single and mixed particle systems

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1. Introduction

Surface charge is considered as one of the most important properties of fine particulate systems [1–4]. To identify dispersion and aggregation mechanisms, surface charge indicated by zeta potential is frequently measured in a wide range of industries, from pharmaceuticals to mineral processing. Among various approaches to characterize surface charge, the sedimentation potential method has been less popular compared to others, partly because of the lack of time efficient and integrated measurement techniques that can be easily automated. The sedimentation potential method has some advantages: it is applicable to more concentrated systems compared to electrophoresis; and other data related to system dispersion or aggregation, including visual clues, can be collected simultaneously. These attributes are of interest in our studies on characterizing mineral processing systems.

The purpose of this paper is to introduce a surface charge characterization system based on sedimentation potential. We start with the theory of measurement to help place the apparatus design in context. Determinations on single minerals are verified by comparison with electrophoresis, and the method is then extended to binary systems.

2. Theory

2.1. Sedimentation and zeta potential

Sedimentation potential is the potential difference that arises when charged particles settle in a force field (usually gravity). Charge destabilization created by the fluid drag surrounding each falling particle induces numerous dipoles in the suspension. These individual dipoles sum to produce the macroscopic potential difference between two points in a column. This phenomenon was first discovered by Dorn [5] in 1878 and is often called the “Dorn effect” [6,7].

For spherical, nonconducting, monodisperse suspensions with negligible particle–particle interaction and surface conduction, sedimentation potential can be related to zeta potential by the Smoluchowski equation [8] (see Nomenclature):

\[ E_s = \frac{\varepsilon \varepsilon_0 \delta (\rho - \rho_0 )}{\eta \lambda} \xi \]  

This equation assumes that the double layer thickness \( 1/\kappa \) is small relative to the particle radius \( a \), i.e., \( a \kappa \gg 1 \), and \( E_s \) can be expressed as follows:

\[ E_s = \frac{(E_B)_h - (E_0)_h}{H} \]  

where, \( E_B \) is a function of temperature, pH and electrode geometry. Electrical and particle hydrodynamic interactions become a consideration at high concentrations (\( \phi > 1.8\% \) v/v [9]) and the Smoluchowski equation needs to be modified. Taking both electrical and hydrodynamic interactions into account, Levine et al. [10]...
derived the following equation based on the Kuwabara cell model [11]:

\[ E_{s(mod)} = \frac{9\varepsilon_{0}\varepsilon_{r}\phi/2\lambda a^2}{\gamma(xa, \phi)} \]  

(3)

where \( \gamma(xa, \phi) \) is a function of \( xa \) and \( \phi \).

For specific conditions, Eq. (3) can be solved analytically. For example, when \( xa \rightarrow 0 \), Eq. (3) simplifies to:

\[ E_{s(mod)} = E_s(20\phi + 1) \left( 1 - \frac{9\phi^{1/3}}{5} + \phi - \frac{\phi^2}{5} \right) \]  

(4)

From Eq. (4) as \( \phi \rightarrow 0 \), \( E_{s(mod)} \rightarrow E_s \) which implies no correction to the Smoluchowski equation is necessary when the suspension is sufficiently dilute.

In addition to measuring \( E_s \), Eq. (1) indicates that \( \phi \) and \( \eta \), the volume fraction of solid and suspension viscosity between the two points, respectively, are required.

2.2. Particle volume fraction: Maxwell’s conductivity model

Maxwell’s model [12] relates the conductivity in heterogeneous media to the volume fraction of the constituent phases. This model was used in the present work to calculate the unsteady volume fraction of particles between the two electrodes during settling. The model can be expressed as follows:

\[ \frac{K_s}{K_L} = \frac{1 + 2\beta \phi}{1 - \beta \phi} \]  

(5)

\[ \beta = \frac{K_0 - K_L}{K_P + 2K_L} \]  

(6)

One of the major assumptions is that the model neglects interaction with particles which means no disturbance in the surrounding electric field. Although the model is thus theoretically restricted to low concentration of dispersed phase, it has been used successfully in many concentrated systems [13–15], including mineral processing [16,17]. For insulating particles where \( K_p \ll K_L \), Eq. (5) can be written in the following form [18]:

\[ \frac{K_s}{K_L} = \frac{1 - \phi}{1 + \phi/2} \]  

(7)

from which, the following can be derived:

\[ \phi = \frac{1 - \delta}{1 + \delta/2} \]  

(8)

\[ \delta = \frac{(R_0)}{(K_L)} \]  

(9)

Resistance readings were converted to specific conductivity, \( \lambda \), using the following relationship:

\[ \lambda = \frac{H}{K_p A} \]  

(10)

2.3. Viscosity of suspension

Einstein’s equation for viscosity of dilute suspension of non-interfering spherical particles was used to calculate suspension viscosity in the present work. The analytical expression is [19]:

\[ \eta = \eta_0(1 + 2.5\phi) \]  

(11)

Eq. (11) was experimentally verified by Eirich et al. [20] and found to work well up to 4% \( \phi \) solid concentration.

3. Apparatus

3.1. Background

After Dorn’s discovery, a few attempts were made to determine zeta potential of suspensions using the sedimentation potential technique. In the early works [21,22] the slurries were prepared in a separate container and then allowed to fall through the settling tube and the arising potential difference was measured using two electrodes set a distance apart in the tube. In recent work, Ozaki et al. [23] introduced a rotating column for sedimentation potential measurement to eliminate drift and/or lack of symmetry of the measuring electrodes. These methods either assumed the volume fraction or calculated it assuming uniform particle flow during settling. Marlow and Rowell [9], using turbidity, were the first to report any in situ volume fraction measurement. Conductivity of the medium and pH were measured separately to calculate zeta potential as a function of pH.

The present work describes an integrated technique with in-process measurement of all the system variables. The method is tested on high purity alumina and silica samples.

3.2. Cell and accessories

The general setup is shown in Fig. 1. The glass tube was 2.5 cm inner diameter of modular design to give various lengths. Two pairs of Ag/AgCl electrodes (Warner Instruments Inc.) were mounted through stopcocks, each electrode in the pair set 20 cm apart. The Ag/AgCl electrode pairs were connected to two separate channels of a Keithley 7700 20-channel, differential multiplexer embedded in a Keithley 2700 Integra series multimeter. One pair of electrodes was used for potential difference measurement and the other for resistance measurement. Due to the high resistance of the suspension, the resistance measuring electrodes polarized and gave inaccurate readings. To eliminate the problem a flip switch was inserted between the source (multimeter) and the resistance measuring electrodes. The switch was used to alternate current flow direction after each measurement to reduce charge build-up on the
electrodes. Slow polarization of potential measuring electrodes is also possible. The influence can be minimized by keeping updated information of background potential and subtracting from the suspension potential. The pH electrode (Cole–Parmer) inserted into the tube via a CG−350-03 glass joint was connected to another channel through an Oakton 510 benchtop pH meter. A vacuum pump was connected at the top of the tube to draw the electrolyte inside the column.

A program developed using Matlab R2008a carried out instrument control, data acquisition and data processing. This allows sufficient flexibility to operators to design measurement sequences. It helps easy and quick post-processing of data by calculating the variables of interest. Interfacing was performed using VXIPnP driver with serial communication and SCPI (Standard Commands for Programmable Instrumentation) command format was used to control the multimeter.

4. Experimental

4.1. Single mineral systems

4.1.1. Samples

The alumina sample was obtained from Sigma–Aldrich (CAS no. 1344−28−1) and was >99% pure. It was dry screened to isolate the target size of 25−37 μm. Silica was obtained from Opta minerals (BARCO 32) and was >99.5% pure with reported average size of 0.34 mm. The sample was pulverized then dry screened to retrieve the target size of 53−75 μm. A size analysis was performed using Horiba LA 920 (laser scattering principle) and the results are given in Table 1. The sizes were selected by experimentation to give sufficient settling time for reliable potential measurements. Chemical and physical properties of the particles are given in Table 2.

4.1.2. Procedure

Samples were washed thoroughly with deionised water (prepared by reverse osmosis) and suspensions were prepared in a beaker by adding a known weight of sample to 500 mL deionised water. Background electrolyte was 10−3 M KCl (corresponding to Eq. (4)). The suspension, 2% v/v in both cases, was conditioned over a magnetic stirrer for 30 min. For pH adjustment HCl and KOH were used.

After conditioning, the particles were allowed to settle in the beaker. The electrolyte supernatant was drawn into the column using the vacuum pump up to a pre-determined level and then the bottom valve on the tube was closed. The setup was left for 10 min to condition the electrodes before background potential was recorded. The potential difference and the resistance were measured and stored as the background values. The particles were transferred to the tube via a funnel through the top opening. The column was 77 cm long for these experiments.

After introducing the particles, the potential difference, resistance and pH readings were taken successively. Measurements were taken one after another to avoid possible interference. From resistance readings, volume fraction and specific conductivity were calculated. Potential difference sensed by the pH meter was converted to pH values using the linear relationship (1 pH ≈ 59 mV and 0 mV at pH 7). The suspensions were then drained to the beaker, the electrodes and column were cleaned with deionised water and the procedure repeated at a new pH.

4.2. Mixed mineral systems

4.2.1. Procedure

The objective was to correlate the components of a mixed system with their surface properties and to reveal any surface modification by particle interaction using SiO2/Al2O3 as a model. Sufficient particle size difference and length of the column were used for the minerals to separate under gravity settling. The test sets are given in Table 3. The pH was set above the iso-electric-point of both minerals to favour dispersion.

Three 500 mL beakers were used. In two of the beakers, 500 mL suspension was prepared using 20 g alumina or 20 g silica with 10−3 M KCl as background electrolyte. (The source of the powder samples and their preparation procedures are the same as above.) The third beaker was filled with 500 mL background electrolyte. The pH of all three was adjusted to ca. 11. The beakers were conditioned over a magnetic stirrer for 30 min.

To improve mineral separation the column length was increased by 30 cm. After conditioning, the column was filled with the electrolyte from the third beaker and left for 10 min to condition the electrodes before background potential was recorded. The supernatant of the alumina and silica suspensions (i.e., from beakers 1 and 2) was decanted and the particles introduced from the top of the column. Potential difference was recorded as a function of time. This completed cycle 1 (Fig. 2). The column contents were then transferred to a beaker and conditioned for about 5 min. Particles were allowed to settle in the beaker and the column was re-filled with the supernatant. It was left in contact with the ele-

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alumina</th>
<th>Silica</th>
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<tr>
<td>Specific gravity</td>
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<td>2.65</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2040</td>
<td>1700</td>
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<tr>
<td>Chemical analysis (%)</td>
<td>Al2O3 &gt; 99.0</td>
<td>SiO2 &gt; 99.5</td>
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<tr>
<td>Na2O &lt; 0.4</td>
<td>TiO2 &lt; 0.1</td>
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</tr>
<tr>
<td>Fe2O3 &lt; 0.03</td>
<td>K2O &lt; 0.1</td>
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<tr>
<td>SiO2 &lt; 0.03</td>
<td>CaO &lt; 0.03</td>
<td></td>
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<tr>
<td>Fe2O3 &lt; 0.03</td>
<td>Al2O3 &lt; 0.01</td>
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</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silica (μm)</th>
<th>Alumina (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1</td>
<td>25−38</td>
<td>53−75</td>
</tr>
<tr>
<td>Set 2</td>
<td>53−75</td>
<td>25−38</td>
</tr>
</tbody>
</table>
trodes for 5 min while the suspension in the beaker was kept stirred. The background potential was measured and the suspension from the beaker was re-introduced to the column, initiating the start of cycle 2 (Fig. 2). The same procedure was repeated up to 6 times (or cycles; Fig. 2 illustrates the first three cycles). In this manner time was given to determine if particle surface properties changed due to inter-mineral contact.

In the last cycle, settling particles were collected from the bottom of the column at three incremental times for XRD and SEM analysis. The first collected fraction was designated as first fraction and so on.

5. Results

5.1. Single-mineral systems

Figs. 3 and 4 show example potential difference for background and suspension as a function of time for the alumina sample at a pH below (ca. pH 8) and above (ca. pH 9) the iso-electric point, respectively. For positively charged particles (Fig. 3), concentration of negative ions (counterions) is higher in the diffuse part of the double layer and the dipoles created by fluid drag are negative in the upper part and positive in the lower part of the column. That is why the potential difference is more negative in the suspension than for the background. The opposite is observed for negatively charged particles (Fig. 4). The $E_s$ was calculated using Eq. (2) and subsequently corrected by Eq. (4).

Fig. 5 shows an example of the variation of resistance for background and an alumina suspension. As alumina (and silica) particles are non-conducting, suspension resistance increases with increasing volume fraction of solid. The cycling pattern is due to the polarity reversal after each measurement. Using Eqs. (8) and (9), volume fraction of solid was calculated as a function of time from the resistance data (Fig. 6).

Zeta potential as a function of pH was calculated using Eq. (1) (with the corrected value of $E_s$) from three separate experiments. Results are shown in Figs. 7 and 8 for alumina and silica, respectively, with the standard deviation indicated by the error bar. The zeta potentials compared well with those measured by electrophoresis (Brookhaven ZetaPlus) and corresponded to the known trend for these two materials [24,25].

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Fig. 2. Experimental cycles (first three are shown here).

Fig. 3. Potential difference as a function of time for alumina suspension at ca. pH 8.

Fig. 4. Potential difference as a function of time for alumina suspension at ca. pH 9.

Fig. 5. Resistance as a function of time for alumina suspension at ca. pH 9.

Fig. 6. Volume fraction as a function of time for alumina suspension at ca. pH 9.

Fig. 7. Zeta potential as a function of pH for alumina suspension: (♦) zeta potential measured by sedimentation method and (□) zeta potential measured by electrophoresis.
5.2. Mixed-mineral systems

Thirty potential difference readings were taken on the suspension with 60 s pause after every ten readings, which itself took about 60 s. Background potentials were then subtracted to obtain the sedimentation potential. Fig. 9 shows the variation of sedimentation potential as a function of time (number of readings) for the two sample sets. For test set 1, Fig. 9a shows the sedimentation potential became more negative with time, corresponding to increasing concentration of the finer, slower settling silica; while Fig. 9b reveals the opposite trend as now (set 2) the slower settling mineral is alumina. From XRD analysis (Fig. 10) these trends were supported by the characteristic silica peak height ($2\theta \sim 26^\circ$) which increased with time for set 1 and decreased for set 2.

It was observed that the difference between the first and third fractions decreased with conditioning time (number of cycles). To track this behaviour the average of the ten readings of the third fraction, Avg(SP3), was subtracted from the average of the ten readings of first fraction, Avg(SP1). The decreasing trend is shown in Fig. 11. Heterocoagulation was a suspected cause of the decreasing trend. The possibility was investigated using SEM–EDAX micro-

Fig. 8. Zeta potential as a function of pH for silica suspension: (♦) zeta potential measured by sedimentation method and (□) zeta potential measured by electrophoresis.

Fig. 9. Sedimentation potential (SP) as a function of time for set 1 (A) and set 2 (B) in cycle 2. Note: The three groups of 10 readings are the three fractions collected.

Fig. 10. Silica peak height at $2\theta \sim 26^\circ$ as a function of fraction for set 1 (A) and set 2 (B).

Fig. 11. Difference between Avg(SP1) and Avg(SP3) as a function of experimental cycles for set 1 (A) and set 2 (B).

analysis. Little supporting evidence was found, for example Fig. 12 shows a non-aggregated sample with the two minerals clearly distinguished by the elemental analysis. We are left to consider the observation in Fig. 11 is due to cross-contamination of ions, released by the minerals.

6. Discussion

A method of using sedimentation potential to indicate surface charge that measures all the required parameters on-line has
been introduced. Background and suspension measurements were made close together in space and time in order that measurements refer to the suspension in the same state. The single mineral tests, conducted under conditions to apply the Smoluchowski model, showed zeta potential results comparable to electrophoresis; and the mixed mineral tests showed trends in sedimentation potential reflective of the minerals present.

The technique initially involved drawing suspension into the tube but that was later changed in favour of drawing supernatant to provide the background potential and resistance readings. By drawing supernatant in from the bottom, turbulence and entrainment of bubbles associated with pouring from the top were minimized. This speeded up initiation of signal collection.

Subsequent introduction of solids is a source of turbulence. By experimentation, a sufficient distance was provided between the delivery point and the first electrode to minimize the impact.

It was understood that the potential differences were likely to vary only over a few millivolts, which requires meters with high precision. The Keithley 2700 has a maximum voltage resolution of 0.1 μV, which is sufficient for present purposes. For resistance measurements, the necessary alternating current to avoid electrode polarization was applied using a flip switch. This successfully yielded a reliable trend in resistance as a function of time to provide the % solids (by volume) data required to calculate zeta potential. The calculated % solid values were in accord with the amount of solid added.

To limit interference between the potential, resistance and pH measurements, they were taken sequentially. On-line pH measurement proved helpful to check stability during a test.

The technique was explored to try to correlate sedimentation potential with the constituent minerals of a mixed system. In this, sedimentation potential was used rather than zeta potential as conditions no longer fitted the Smoluchowski model. For the intended purpose of characterizing samples of interest in mineral processing (e.g., ores) the sedimentation potential may be sufficient guide to surface charge. An analogy is using electrophoretic mobility rather than zeta potential in electrophoresis studies.

Figs. 7 and 8 confirm that at ca. pH 11 sedimentation potential of silica is more negative than the alumina. Sedimentation potential became more negative with time for set 1 (Fig. 9a), corresponding to the first fraction passing the electrodes being mostly alumina and later ones being progressively dominated by silica. Set 2 showed the opposite trend, as the fine fraction in this case is alumina.

Fractions collected from the bottom of the column were analyzed to correlate composition with the sedimentation potential data. The height of the XRD peak characteristic for silica was used for semi-quantitative analysis. Peak height as a function of fraction (Fig. 10) showed the dominance of silica in the third fraction of set 1 and first fraction of set 2.

A decreasing trend in sedimentation potential difference between fractions 1 and 3 with time (Fig. 11) suggested interaction between the minerals. SEM-EDAX microanalysis showed little sign of heterocoagulation (Fig. 12). Although it is appreciated that this analysis, by removing the sample from its environment, may introduce artefacts, the possibility of cross contamination by adsorption of dissolved ionic species is suggested, as reported by Healy et al. [26] for an alumina/silica system. Analysis using XPS and TOF-SIMS may clarify the matter.
7. Conclusion

The present work has proposed a fully integrated sedimentation potential method for study of surface charge. In-process measurement of all system variables and continuous measurement capability give the setup advantages over prior devices. The Matlab based system provided a fast and powerful tool for control, data acquisition and post processing. The approach was validated by single mineral tests which showed good agreement with zeta potential measured by electrophoresis and mixed mineral tests which showed sedimentation potential variation reflective of the minerals present. Results from the SiO2/Al2O3 mixed system show a possible use of this technique to characterize mineral processing systems.

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