APPARATUS FOR STREAMING POTENTIAL MEASUREMENTS ON GRANULAR FILTER MEDIA

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ABSTRACT: This paper is intended to provide the necessary information to construct and properly operate a simple streaming potential apparatus capable of measuring the zeta potential of granular media. Through an understanding of the principles of the technique, such a device can readily be used in the study of a variety of granular materials including unstable and dynamic surfaces, as shown for surface coatings and even biofilm growth. The simplified mathematical theory of the streaming potential is herein explained, as well as operational factors and the general reasons for nonreproducible measurements such as electrode maintenance, electrode polarization, nonzero rest potentials, and sample equilibration. This specific apparatus design is intended for use with granular materials and has intentionally been developed in a simplistic fashion to encourage wider usage of the technique. The overall precision of this instrument was ±10% based on a 95% confidence interval. In addition, the accuracy of the device was found to be very good based on comparisons with literature values.

INTRODUCTION

Zeta potential is a relevant parameter in the study of surface/surface interactions. The development and success of a stability theory for dispersions by Derjaguin and Landau (1941) and independently by Verwey and Overbeek (1948) (DLVO theory) has served to highlight the importance of zeta potentials in surface/surface interactions. The measurement of zeta potential, although well developed theoretically (Overbeek 1952; van der Put 1980), has historically been problematic. A few relatively complex streaming potential devices have been developed within the past several years in an attempt to reduce analysis time and enhance data acquisition (Fitzpatrick 1972; Fairhurst and Ribitsch 1991; Scales et al. 1992). For systems of membranes, capillaries, and flat plates where sample equilibration time can be quite short, these systems are fairly efficient. Granular systems, however, often suffer from complications and the need for longer equilibration times. The goal of the present technical note is to educate and inform the reader on how to build and operate a very simple streaming potential device to measure the zeta potential of granular media accurately and in a reproducible manner.

THEORETICAL BACKGROUND

Surface charge refers to the charge character of a surface due to its actual molecular composition. Zeta potential is a term used to describe the potential due to that charge at some finite distance away from the surface, at what is termed the plane of shear. At this plane, the potential is somewhat smaller in magnitude than the surface potential due to ion association of the surrounding solution (the electrical double layer). Under idealized conditions of dilute electrolyte concentration, the number of these associating ions shielding the surface charge are very few, and the zeta potential and surface potential are generally assumed to be identical (Hilmenz and Rajagopalan 1997). This allows for a relatively easy estimation of surface potential through the measurement of zeta potential with the streaming potential instrument. Unfortunately, when it comes time to evaluate the charge of a surface, much of the work presented in the literature tends to favor electrophoresis, an instrument used to measure electrophoretic mobility and calculate zeta potential of very small particles capable of undergoing Brownian motion. The act of grinding or crushing large particles for use in electrophoresis, particularly those in which the surface composition differs from the inner bulk material, as in the case of coatings and biofilm, will lead to incorrect conclusions of surface potential. In addition, modifications of experimental procedures to allow for micron sized particles capable of undergoing electrophoretic analysis are often impractical or industrially irrelevant, resulting in complicated working conditions and large pressure drops within filtration systems. It is for this reason that a particular emphasis should be placed on the proper design and usage of a streaming potential device for reproducible evaluation of the zeta potential on granular media.

The theory behind the streaming potential apparatus is rooted within irreversible thermodynamics and the corresponding flux balances. By allowing a charged solution to physically flow past a charged surface, a potential is created due to motion of the ions within the electrical double layer of the granular material. For systems near equilibrium, the fluxes are expected to be linearly dependent on specific driving forces. Ohm’s law, Darcy’s law, and Fourier’s law are well known examples of the linear relationship between conjugate forces and fluxes of a system. When these expressions are made to incorporate nonconjugate driving forces (i.e., forces usually assumed to be negligible), a set of equations is developed from which all electrokinetic phenomena can be described. In the case of the streaming potential, the incorporation of the non-conjugate terms within Ohm’s law results in an expression that can be used to describe the system (van der Put 1980)

\[ \frac{i}{A} = \frac{dE}{dx} + \frac{d}{dx} \ln C + \frac{dP}{dx} \]

where \( i = \) electrical current; \( A = \) area; \( L_n = \) phenomenological coefficients; \( E = \) electromotive potential; \( C = \) concentration of the electrolyte; \( P = \) pressure; and \( x = \) dependent length variable. The first phenomenological coefficient \( L_1 \) can be represented as \( 1/R \) or \( K \), the specific resistivity of the electrolyte, through the realization that (1) must reduce to \( V = IR \), voltage equaling the product of current and resistance for a simple electrical system. \( L_2 \) can then be shown to represent the electrokinetic effect, \( \xi e \mu /4\pi \), through the use of Onsager’s reaction relation and the linear expressions of the Darcy and Fourier laws (Overbeek 1952), where \( \xi = \) zeta potential; \( \mu = \) viscosity of the electrolyte solution; \( e = \) dielectric constant of...
the electrolyte; and ε₀ = dielectric constant of a vacuum. Further simplification of (1) can be made under the assumption that the concentration gradient of electrolytic species throughout the streaming potential’s sample bed remains a constant during operation so that the d ln C/dx term can be set to zero. Additional recognition that no electrical current is applied during the streaming potential operation (i = 0) allows for final simplification. The resulting equation relates voltage drop across the material within the sample cell as a linear function of pressure drop in what is known as the Smoluchowski equation in cgs units (Hiemenz and Rajagopalan 1997)

$$\xi = \frac{4\pi \mu K \Delta E}{\varepsilon_0 \Delta P}$$

(2)

where ΔE represents change in electromotive potential (voltage); and ΔP = corresponding change in pressure.

Streaming potential theory also stresses the use of pressure drops within the regime of laminar flow in order to avoid random voltage instabilities created by turbulence and eddy formation within the packed bed’s electrical double layer. This laminar restriction is widely found within the literature pertaining to this technique but has often been overlooked in application. The Reynolds equation (Bird et al. 1960) can be used to calculate a conservative value of the superficial velocity (V₀) for a granular system under laminar conditions

$$R = \frac{D_p V_0 \rho}{(1 - \varepsilon) \mu} < 1$$

(3)

where Dₚ = particle diameter; ρ = density of the liquid media (water); and ε = void fraction of the packing. The limiting superficial velocity for the system under investigation is, in turn, applied as a restriction to the Burk-Plummer equation (Bird et al. 1960)

$$\frac{\Delta P}{L} = \frac{150 \mu V_0 (1 - \varepsilon)^3}{D_p \varepsilon^4}$$

(4)

where L = length of the packed bed. This allows for an estimation of the upper pressure drop limit corresponding to the laminar flow regime. This pressure drop value should not be exceeded during streaming potential measurements. Any onset of turbulent behavior will result in a disturbance of the electrical double layer of the particles being analyzed and the possibility of unstable zeta readings from the streaming potential apparatus. For the granular media used within the present study (0.6–0.7 mm diameter), a maximum pressure drop of 7 cm of water was calculated as a conservative upper bound of the laminar fall regime.

STREAMING POTENTIAL DESIGN

The streaming potential apparatus was constructed from readily available materials [Fig. 1(a)]. The sample cell was created from a piece of clear polycarbonate pipe in order to allow for visual inspection and verification as to the absence of air pockets and overall packing uniformity between the electrodes. The inner diameter (ID) for this sample cell was chosen to be 1.9 cm (0.75 in.) to minimize possible wall effects for granular media with a diameter equal to or less than 1.5 mm (ID ≫ diameter of sand). The length component of the sample cell was another important design consideration necessary to ensure reproducible measurements for granular media. Smaller sample cells where the packed bed length was less than 20 cm (8 in.) produced erratic zeta potential readings for materials with particle diameters greater than 0.7 mm. This inconsistent behavior was attributed to pressure fluctuations within the granular sample bed during operation.

FIG. 1. Diagram of: (a) General Streaming Potential Layout; (b) Adjustably Threaded Silver/Silver Chloride Electrodes Used in Both Ends of Sample Cell

![Diagram](image)

The removable portion of the sample cell, Fig. 1(b), supported the electrode and allowed for some adjustment of the volume within the sample cell to ensure similar environments for both electrodes with no voidages or gas pockets within the granular media (Horn 1978). The electrodes themselves consisted of 99% pure 18 gauge silver wire and 40 mesh sized silver gauze (Newark Wire Cloth Co., Newark, N.J.). These components were spot welded together so that the silver wire could be extended perpendicular from the center of the circular mesh. The mesh portion of the resulting union was then anodized with 5 mA (Bio Rad, power pac model 300, Richmond, Calif.) in a 0.1 N hydrochloric acid solution with a copper cathode for 1 h in order to chloridize the silver (Janz 1961). The finished electrodes had a brown to grayish plum color and were allowed to age overnight in 10⁻⁴ M KCl solution. The electrodes were then sealed into the electrode supports as shown in Fig. 1(b). It has been strongly suggested that these electrodes be regenerated or replaced every three weeks to ensure proper performance. The semiharsh environment around the electrodes, particularly during sample loading, may wear down the coating. In the absence or degradation of the silver chloride, the electrodes will no longer process the generated voltage signal produced within the apparatus in a phenomenon commonly known as electrode polarization.

STREAMING POTENTIAL OPERATION

Before actual use of the streaming potential apparatus, the following three operational factors should be considered: (i) The evaluation procedure requires 60 mL of packed bed material; (ii) temperature must be consistently maintained or the temperature dependence of μ and ε must be accounted for in (2); and (iii) care must be taken if and when conductive materials such as unions, pumps, or pressure transducers are used in the construction of this device. The use of conductive ma-
terials will result in some degree of electrical interference and a dramatic decrease in the signal to background noise ratio. Ultrahigh impedance differential amplifiers and/or a Faraday cage can be used to reduce the noise problem if such alterations are desired (van der Put 1980).

The overall setup of this device required an electrometer (Keithley Instruments 610C, Cleveland, Ohio) to be connected to the silver chloride electrodes to measure voltage drop and a water manometer to monitor the pressure drop of the flowing electrolyte. The remaining tubing ports were used to purge the packed bed with CO₂ before analysis to lessen the risk of air pockets within the sample media and allow for the gravity feed of weak KCl electrolyte solution [Fig. 1(a)].

Preparation of the sample prior to analysis required the granular media to be systematically rinsed in a nylon mesh sieve tray with distilled water. This was done to remove loose particulate material from the granular surfaces that could result in dissimilar environments of the upstream and downstream electrodes during operation. After packing the media into the sample cell, 1–2 L of KCl solution were generally allowed to flow through the packed bed (1 L/h) to further rinse and equilibrate the sample. All experimental runs were performed with the use of 10⁻⁵ M KCl solution under laminar flow conditions. During the actual measurement procedure, the electrodes were used to monitor the electromotive force generated as the charged ions in the electrolyte solution passed the charged sample surface under investigation. These voltage measurements were performed as a function of the pressure drop across the sample bed. After recording a voltage and pressure reading, the electrolyte flow was stopped and the electrometer was allowed to return to its zero potential. The voltage measurement was then corrected to account for any deviation away from zero. This procedure was followed for multiple voltage and pressure drops in order to collect enough data to plot voltage versus pressure drop (Fig. 2). The slope from the measured voltage and pressure drop data along with solution conductivity were then used to calculate the corresponding zeta potential (ζ) via the Smoluchowski relation (2).

The plot of the resulting voltage/pressure drop line in general will not pass through the origin (Fig. 2 shows the intercept to be -0.64 mV). This “erratic rest potential” has been a common observation throughout the streaming potential literature (Fitzpatrick 1972; Ball and Fuerstenau 1973; Egland and Allen 1977; van der Put 1980). This absence of a nonzero intercept has many times been mistaken to indicate poor quality results. Several of the aforementioned authors have noted, however, that this time dependent deviation does not affect the slope of the voltage/pressure line used in the Smoluchowski equation and thus the calculated zeta potential. A thorough investigation by van der Put (1980) attributed these erratic rest potentials to salt rejection by the porous media sample. This, in turn, has resulted in the violation of the initial assumption that the d ln C/dz term could be set to zero in the simplification of (1). Adequate results, however, can be obtained through equilibration procedures as outlined earlier, and careful monitoring of the influent and effluent electrolyte conductivity and pH. In the case of biofilms or unstable coatings where solution contact time may be an issue, analysis procedures may begin as soon as the conductivity and pH values for the electrolyte solution entering and leaving the sample cell are the same. The streaming potential measurements under these less equilibrated conditions will, however, exhibit greater erratic rest potentials and complications due to the drifting of the voltage readings as measured with the electrometer.

**ACCURACY AND PRECISION**

To demonstrate the reliability of the previously detailed measurement technique, a comparative study was performed

![FIG. 2. Sample Data from Streaming Potential Analysis of Metal Hydroxide Coated Ottawa Sand after 62 d of Exposure to Wastewater Flow for pH 4.3 [Linear Regression Was Used to Determine Slope and Corresponding 95% Confidence Bend (Dashed Lines) Shown Here; Full pH Curve for This Biosystem Is Shown in Fig. 5](image)]

![FIG. 3. Comparison of Two Zeta Potential versus pH Curves for Granite System As Determined by Streaming Potential and Electrophoresis (Errors for Streaming Potential Curve Were Uncharacteristically Large in This Case due to Apparent Zeta Hysteresis Dependent on pH (Equilibration Effect); Electrophoresis Curve (Brookhaven Zetaplus Instrumentation) Is from Global Consulting Co. (Gainesville, Fl., Unpublished Data, No Errors Provided))](image)

**TABLE 1. Comparison of Experimentally Determined Zeta Potentials with Reported Literature Values**

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>Experimental zeta potential</th>
<th>Referenced zeta potential</th>
<th>Reference source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ottawa sand (sieved and rinsed)</td>
<td>5.5</td>
<td>-68 ± 3 mV</td>
<td>-65 mV</td>
<td>Electrophoresis*</td>
</tr>
<tr>
<td>Pure silica</td>
<td>5.6</td>
<td>-96 ± 3 mV</td>
<td>-94 mV</td>
<td>Goodwin et al. (1990)</td>
</tr>
<tr>
<td>Silica modified with quaternary amine</td>
<td>6.65</td>
<td>45 ± 3 mV</td>
<td>50 mV</td>
<td>(Suhara 1995)</td>
</tr>
<tr>
<td>groups</td>
<td></td>
<td>47 ± 3 mV</td>
<td>50 mV</td>
<td></td>
</tr>
<tr>
<td>Silica modified with quaternary amine</td>
<td>5.3</td>
<td>44 ± 4 mV</td>
<td>50 mV</td>
<td></td>
</tr>
<tr>
<td>groups</td>
<td>4.3</td>
<td>-140 ± 11 mV</td>
<td>-136 mV</td>
<td>(Fitzpatrick 1972)</td>
</tr>
<tr>
<td>Glass beads washed (chromic acid/acetone/distilled water)</td>
<td>5.5</td>
<td>pH 7.5</td>
<td>pH 7.5</td>
<td>(Adamson 1967)</td>
</tr>
<tr>
<td>Iron hydroxide PZC (point of zero charge)</td>
<td>—</td>
<td>pH 7.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Experimental zeta potentials were run on particles with roughly 0.7 mm diameter (20–30 mesh). Weak solutions of hydrochloric acid or potassium hydroxide were used to control pH for all studies. Error within all pH measurements was taken to be ±0.15.

*Zeta analysis was done on microtomed Ottawa sand with Brookhaven Zetaplus zeta potential analyzer, model v3.21 at University of Florida.
on a granite sample. Half of this sample was crushed into microparticles and used in an independent electrophoretic evaluation of the zeta potential (El-Shall 1997). Note that in this case, the interior and exterior of the granite samples were expected to be the same in composition. The other uncrushed portion of the granite sample (~0.7 mm diameter) was analyzed by streaming potential. The results are presented as Fig. 3 over a range of pH. The comparison indicated a relatively good match of the results obtained by the two techniques. Table 1 is included to compare additional zeta potentials measured by this streaming potential apparatus with literature values of various materials and coatings.

This apparatus was determined to provide reproducibility with an error generally on the order of ±10% of the measured zeta potential using a 95% confidence interval as based on the pressure voltage slope determined for each run (Fig. 2) and a 95% confidence interval on the conductivity measurement of the electrolyte solution used in the measurement. The standard deviation between replicates was determined to be on the order of 3%. Exceptions did exist due to equilibration phenomena and the ever-present possibility that particle fines, coatings, or microorganisms could break free from the granular substrate during measurement.

APPLICATIONS

The streaming potential technique has traditionally been used to estimate the surface potential of generally well-behaved surfaces. Two such surfaces have been evaluated and included (Fig. 4), showing the pH dependent charge character of two readily available granular materials. The observed differences in zeta potential between these two types of sand served to highlight the importance of analysis on even compositionally similar materials (Truesdail et al. 1998).

This technique can also be used to monitor granular surface coating stability and biofilm mediated charge effects. Fig. 5 demonstrates the usefulness of this device and technique to monitor these somewhat more complicated surfaces. In this particular case, a packed column of aluminum hydroxide coated Ottawa sand, prepared as described elsewhere (Lucaskis et al. 1997), was exposed to nonchlorinated municipal wastewater for several months under column flow-through conditions. The filtration column was periodically backwashed, and samples were taken and rinsed in a sieve tray to remove any nonreversibly adhered biomaterials. The streaming potential was then used to monitor the surface potential of the granular material as a function of nonchlorinated water exposure. The initial drop observed in the zeta character of the coated media between day 0 and day 15 was determined to be due to the loss of loosely adhered positively charged precipitated metal coating. The resulting surface after day 15 was then observed to undergo conditioning and biofilm growth. In this latter stage, day 62 and day 117, the zeta curves indicated a decrease in negative charge as the surface appeared to take on the charge character of the microbes in the biofilm. The zeta potentials of several individual microorganisms common to biofilm have been reported to range from ~10 mV to ~60 mV (Vitaya and Toda 1991; Nicholov et al. 1993; Achouak et al. 1994). A more in-depth analysis relating streaming potential results to stability and filtration performance for such systems has been published elsewhere (Chen et al. 1998; Truesdail et al. 1998). These results illustrate the usefulness of this technique to monitor not only the coating stability of the metal hydroxide used in the present study, but also how biofilm development affects the granular surface's zeta potential. This information can then be used to better understand the particle interaction forces at work within these types of systems.

CONCLUSIONS

The influence of surface charge in the study of particle interactions has been a major area of interest for several decades. The streaming potential device provides the research opportunity to better understand the potential interactions between granular media and various materials like precipitated coatings, bacteria, and biofilm. The streaming potential device should be recognized and utilized as a versatile and useful tool in the evaluation of charge character.

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The present technical note is dedicated to the memory of Dr. Gerald Westermann-Clark.

APPENDIX I. REFERENCES


APPENDIX II. NOTATION

The following symbols are used in this paper:

- $A$ = area;
- $C$ = concentration;
- $D_p$ = particle diameter;
- $E$ = electromotive potential;
- $e$ = void fraction;
- $i$ = electric current;
- $K$ = specific resistivity (1/ohm·m);
- $L$ = length of packed bed in streaming potential device;
- $L_n$ = phenomenological coefficients;
- $P$ = hydrostatic pressure;
- $R$ = resistance;
- $R_l$ = Reynolds number;
- $V$ = voltage;
- $V_0$ = superficial velocity;
- $x$ = dependent variable;
- $\varepsilon$ = dielectric constant (−water);
- $\varepsilon_a$ = dielectric current (vacuum);
- $\mu$ = viscosity (−water);
- $\zeta$ = zeta potential; and
- $\rho$ = density (water).