

## Zeta potential distributions in particle treatment processes

Jinkeun Kim, Jeffrey A. Nason and Desmond F. Lawler

### ABSTRACT

Most experimental studies of particle destabilization prior to flocculation and granular media filtration characterize the surface charge of particles using the observed average zeta potential. A more complete accounting of particle–particle and particle–collector interactions can be deduced from analyzing the complete distribution of particle zeta potentials. Zeta potential distributions (ZPDs) of silica particles under chemical conditions reflective of destabilization by pH control, ionic strength adjustment, alum destabilization, and polymer destabilization were investigated. Most of the ZPDs of silica particles were broad and skewed (i.e. not normally distributed). When particle surface charge is controlled by pH control, ionic strength adjustment, and alum destabilization, the variances of the ZPDs are comparable. However, when a high-charge-density polymer is utilized as the coagulant, under-dosed and optimally dosed systems result in ZPDs that are broad and over-dosed systems result in narrow distributions.

**Key words** | electrophoretic mobility, filtration, flocculation, particles, zeta potential

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### INTRODUCTION

Most particles acquire a surface electrical charge in water. For most particles in natural waters, the net surface charge is negative in the range of normal pH (e.g. 6–9), positive at low pH, and zero at some intermediate pH, known as the point of zero charge (PZC). The surface charge at normal pH arises from lattice imperfections, direct dissociation or ionization of surface groups, or preferential adsorption of ions (particularly natural organic matter) from solution (O'Melia 1988; Stumm & Morgan 1996). This surface charge attracts ions of opposite charge (counter-ions) from the solution and repels ions of the same charge (co-ions), leading to the formation of an electrical double layer (EDL) surrounding each particle. The result is that particles in water are usually stable; that is, they are unlikely to attach to each other or to other like-charged surfaces.

In engineered systems for particle removal, particles are often destabilized by adding various chemicals that change the surface charge. Both before and after such additions, different particles have different amounts of surface charge;

that is, suspensions likely exhibit a *distribution* of surface charges. Nevertheless, reports of surface charge in particle treatment processes usually report only the mean value. The objectives of this research were to investigate the distributions of particle charges in suspensions of silica particles under various chemical conditions reflective of different destabilization methods and to illustrate that the distribution, and not just the average charge, can impact particle behavior in treatment systems. For example, Tufenkji *et al.* (2003) noted several reasons why classical filtration theory, which predicts an exponential decay of the suspension particle concentration with distance into a filter column, might not hold true, and a distribution of surface charge characteristics is one such reason.

Chemical destabilization was accomplished in four separate ways in this research: changing the pH, changing the ionic strength, adding alum, and adding polymer. The focus in this paper is on particle destabilization and the effect on surface charge distributions, although a few results

from flocculation and granular media filtration experiments are shown; the work was performed as part of a larger study on the interactions of zeta potential distributions and particle behavior in granular media filters (Kim 2004).

The surface charge density on a particle is related to the potential at the surface ( $\zeta_0$ ) according to the Gouy–Chapman theory (Stumm & Morgan 1996). At low potential, the surface charge density is approximated as a linear function of the surface potential with the slope proportional to the inverse of the Debye length ( $1/\kappa$ ), a characteristic length of the diffuse layer that depends on ionic strength ( $I$ ) and temperature. The extent of particle destabilization achieved by coagulation prior to flocculation and granular media filtration can be assessed through measurements of the surface charge; minimization of surface charge leads to favorable conditions for attachment in such processes.

## EXPERIMENTAL METHODS

### Particles

Min-U-Sil 5 (U.S. Silica Company, Berkeley Springs, WV) particles were used throughout this research. These particles are white, natural crystalline silica powder with virtually all particles below  $5.0\ \mu\text{m}$  in diameter. Scanning electron microscopy (Jeol T330A, Jeol USA Inc., Peabody, MA) was performed and images (not shown) reveal that these particles are all quite angular; although the particles size varies, the general shape of all particles is (at least to the eye) quite similar.

In all experiments, supply water was chemically conditioned depending on the specific objective of the experiment. Distilled/deionized (Milli-Q system, Millipore Corp., Bedford, MA) water was used throughout. Min-U-Sil 5 was dispersed in this water to make the particle suspension. pH was adjusted using HCl and NaOH, and ionic strength was adjusted through the addition of KCl.

### Zeta potential

The surface charge characteristics of particles can be assessed with electrokinetic techniques, in which the

mobile part of the electrical double layer is sheared off by imposing a relative motion of the particles and surrounding solution. Electrophoresis is the most commonly used method for suspended particles (Elimelech *et al.* 1995, 2000; Hunter 2001) and was used throughout this research. The electrical potential at the shear plane, commonly referred to as the zeta potential ( $\zeta$ ), can be calculated from electrophoresis measurements. Kim & Yoon (2002) recently reviewed and extended the relationships between electrophoresis measurements and zeta potential for non-spherical particles.

Zeta potential distributions (ZPDs) were obtained from electrophoretic mobility measurements made with a Zetaphometer IV (CAD, France), a microscopic electrophoresis instrument equipped with an automatic tracking function made possible by digital image processing. This instrument tracks many particles in a single analysis, speeding sample analysis and eliminating operator subjectivity (the primary disadvantage of classic instruments that require human visual tracking). Stationary layers (where particles are not affected by water flow induced by electro-osmosis) occur in electrophoresis cells. All measurements were made at the stationary layer closer to the microscope. In the instrument employed, the cell is designed so that the stationary layer is vertical, with the benefit that sedimentation does not move particles into or out of the stationary layer. The number of tracked particles (i.e. electrophoretic mobility measurements) for each chemical condition was between 80 and 120 to ensure statistically significant distributions. Preliminary experiments, performed by taking measurements at various points across the cell (and not only at one of the stationary layers) indicated that the flow pattern in the cell, induced by electro-osmosis at the cell walls, was parabolic, as expected from theory.

Zeta potential can be approximated from measurements of the electrophoretic mobility,  $U$ , as shown in the various parts of Equation (1) (Oshima 1994; Hunter 2001):

$$\zeta = \frac{3U\mu}{2\varepsilon_w} \frac{1}{f(\kappa a)} \quad \text{for all values of } \kappa a \quad (1a)$$

$$\zeta = \frac{U\mu}{\varepsilon_w} \quad \text{when } \kappa a \gg 1 \quad (1b)$$

$$\zeta = \frac{3U\mu}{2\varepsilon_w} \quad \text{when } \kappa a \ll 1 \quad (1c)$$

where  $\mu$  is the viscosity,  $\varepsilon_w$  is the permittivity in water,  $a$  is the particle radius, and  $\kappa$  is the inverse of the Debye length.  $U$  has the same sign as the net charge on the particle surface and is negative if a particle moves toward the positively charged electrode in an applied field. In Equation (1a),  $f(\kappa a)$  is a correction function that varies between 1.0 and 1.5 depending on  $\kappa a$  values, as follows (Oshima 1994):

$$f(\kappa a) = 1 + \frac{1}{2(1 + 2.5/(\kappa a(1 + e^{-\kappa a})))^3} \quad (2)$$

Equation (1b), known as the Smoluchowski equation, was used throughout this research to calculate zeta potentials from electrophoretic mobility measurements because  $\kappa a$  was substantially greater than 1. The significance of Equation (1a) (in conjunction with Equation (2)) is that electrophoretic mobility and zeta potential are only weakly associated with particle size, and, when Equation (1b) or (1c) applies, they are independent of size. In this work, the particle sizes varied from below the limit of detection of the Coulter Counter (approximately  $0.7 \mu\text{m}$ ) to  $5 \mu\text{m}$ ; we estimate that particles smaller than approximately  $0.6 \mu\text{m}$  were unlikely to be seen in the electrophoresis apparatus. Over the diameter range from  $0.6$ – $5 \mu\text{m}$ , the calculated values of  $f(\kappa a)$  that occurred at low ionic strength were from 1.464 to 1.495, so at most a 2.5% error occurred from the assumption to use Equation (1b), at least on the basis of size.

According to Kim & Yoon (2002), particle shape can also influence electrophoretic mobility and the translation to zeta potential, although this influence is small at the high values of  $\kappa a$  found in this research. Based on a figure in their paper (extrapolated to higher  $\kappa a$  values) showing the difference in mobility of particles whose major axis is perpendicular vs. parallel to the electric field, it seems possible that the angularity of Min-U-Sil particles could cause a variation of as much as 6% in the measured electrophoretic mobility (and therefore calculated zeta potential). Such variations could account for a portion of the standard deviations in the ZPDs reported in this paper.

### Chemical conditions

For the destabilization by pH control, experiments were performed at a constant ionic strength ( $10^{-2} \text{M}$ ) and pH

values of 3.0, 4.0, and 5.0. The pH was controlled by adding HCl, and the ionic strength was bolstered as necessary by KCl. At these low pH values, no other buffering was provided. For the destabilization by changes in the ionic strength (which should not change the surface charge if the electrolyte is indifferent to the surface but compresses the double layer), the pH was held constant at pH 4, and the ionic strength was varied by adding different amounts of KCl. For both the pH variation and the ionic strength variation, the values were chosen based on prior knowledge of the expected behavior of silica suspensions.

The most popular destabilization method in conventional water treatment is using an inorganic coagulant, such as aluminum sulfate (alum) or ferric sulfate, that rapidly hydrolyzes to form several soluble species and, usually, insoluble precipitates. Amirtharajah & Mills (1982) noted that charge neutralization is the dominant destabilization mechanism in the pH range between 5.0 and 5.5 when alum is used as a coagulant at relatively low doses. In this pH range, the speciation among several alumino-hydroxyl complexes can include a relatively high concentration of positively charged polymers, although the formation of these polymers is somewhat limited in the presence of the sulfate that is supplied as part of the alum (Snodgrass *et al.* 1984; Bottero & Bersillon 1989; Van Benschoten & Edzwald 1990). Therefore, pH 5.2 was chosen to study alum destabilization. To supply alkalinity that was reasonably consistent with conditions in water treatment, Min-U-Sil 5 particles were dispersed in  $2 \times 10^{-3} \text{M}$   $\text{NaHCO}_3$  throughout the alum experiments.

The effect of alum dose on the zeta potential was studied using a standard jar-test in 11.5-cm square vessels: 1 min of rapid mixing (150 rpm, with the velocity gradient  $G$  estimated as  $230 \text{ s}^{-1}$  based on Cornwell & Bishop (1983)), 20 min of slow mixing (50 rpm,  $G = 47 \text{ s}^{-1}$ ), and 20 min of settling. Alum was added via digital pipet into the vortex formed by the paddle stirrer from a stock solution at 1 g/L of the purchased material,  $\text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$ , where  $14 < n < 18$ ; doses are reported in mg/L of this material. Turbidity and zeta potential measurements were performed on the supernatant suspension after settling, with the samples taken from a point approximately 5 cm below the water surface. This methodology might incorporate a slight bias toward relatively stable particles (since unstable

particles would flocculate and settle) but the low particle concentration (i.e. 20 mg/L) and short flocculation and settling times led to little settling, even in the most favorable conditions studied.

Several types of polymers are widely used in particle removal processes at water treatment plants, depending on the purpose of polymer addition (e.g. primary coagulant, coagulant aid, and filter aid). A cationic polymer with high charge density and relatively low molecular weight is often used as a primary coagulant because of its potential for charge neutralization, whereas nonionic, anionic, or low charge density cationic polymers with high molecular weight are usually used as a coagulant or filtration aid because of their bridging capabilities (Letterman *et al.* 1999). Since accomplishing destabilization by charge neutralization was desired in this research, high charge density cationic polymers such as poly-DADMAC and polyamine were considered as possible coagulants. On the basis of preliminary experiments, a polyamine (Superfloc C-572, Cytec Industries Inc., IN, dimethyl amine polymerized with epichlorohydrin) was chosen. Water chemistry (pH, alkalinity, and ionic strength) during the polymer destabilization experiments was the same as with alum destabilization. Jar tests, using the same procedures as for the alum experiments, were performed to find three polymer doses to make negative, near zero, and positive particle surface charges. Stock solutions were made by diluting the liquid product as obtained from the manufacturer on a volume basis, so doses are reported in ppm<sub>v</sub>.

### Filtration experiments

Granular media filtration experiments were performed in a down-flow column with an inner diameter of 3.8 cm and a short bed of only 10 cm to ensure that some particles did escape capture and were found in the effluent. Solid glass spheres (Potters Industries, Inc., NJ) in a size range of 0.5–0.6 mm were chosen for filter media. Separate gear pumps were provided for the water and the high-concentration suspension (i.e. 800 mg/L); after they were blended in-line, a syringe pump was used to inject the destabilizing chemical immediately prior to the filter influent, thereby ensuring that very little change of the size distribution would occur prior to the filter.

## RESULTS AND DISCUSSION

### pH control

To find the zeta potential of Min-U-Sil 5 as a function of pH at constant ionic strength ( $10^{-2}$  M), several measurements of zeta potential were taken. The mean zeta potentials, shown in Figure 1, were negative throughout the measured pH range between pH 2.0 and 9.0. The magnitude of these values was almost linearly related to the pH of the solution from pH 2.0 to pH 5.0 but it tailed off to reach a fairly constant value at higher pH. The standard deviations of the resulting distributions, indicated as error bars in Figure 1, ranged from 5 to 15 mV (generally around 10 mV). These results indicate that the point of zero charge of silica is just below pH 2.0 which is in good agreement with other studies (Parks 1965; Elimelech *et al.* 1995; Findlay *et al.* 1996).

The ZPDs of Min-U-Sil 5 at pH 3.0, 4.0, and 5.0 are shown in Figure 2; the corresponding mean zeta potentials ( $\pm$  one standard deviation) were  $-26.4 \pm 7.1$  mV,  $-38.7 \pm 9.2$  mV, and  $-54.7 \pm 9.3$  mV, respectively. The results in Figure 2 make it obvious that, even when all particles in a suspension have the same composition, the measured zeta potential (or electrophoretic mobility) can vary widely. The distribution of zeta potentials is not significantly influenced by the distribution of particle sizes; for all particles in these suspensions,  $\kappa a \gg 1$ , so that the relationship between electrophoretic mobility and zeta potential is nearly independent of particle size. Also, the broad distribution is not an experimental artifact brought

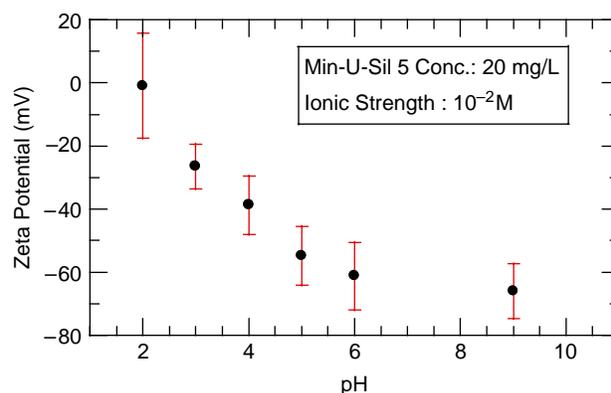
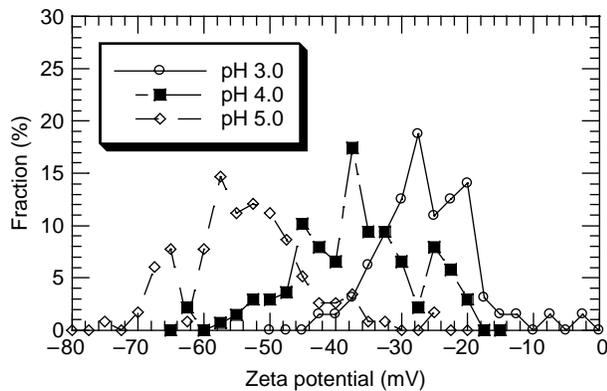


Figure 1 | Mean zeta potential of Min-U-Sil 5: effect of pH (error bars represent  $\pm$  one standard deviation).

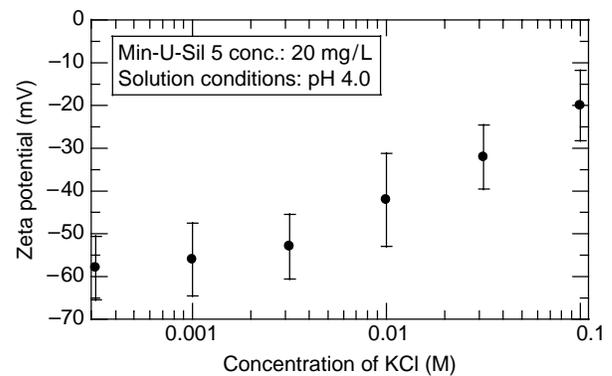


**Figure 2** | ZPDs of Min-U-Sil 5 at different pH values ( $I = 10^2$  M).

about by some particles being tracked that were not perfectly in the stationary layer of the electrophoresis cell; some distributions found in this research were much narrower as shown subsequently. The broad distribution of zeta potentials shown in **Figure 2** suggests that different particles are likely to behave quite differently in those engineered particle removal processes that rely on particle destabilization. As noted above, *Tufenkji et al. (2003)* demonstrated mathematically the effects of distributions of particle characteristics on granular media filtration.

### Ionic strength adjustment

The zeta potential of particles can also be changed by changing the ionic strength of a solution; an increase in ionic strength compresses the electric double layer, and thereby decreases the absolute value of zeta potential. The mean zeta potential of Min-U-Sil 5 at pH 4.0 under different ionic strengths, controlled by varying the concentration of KCl, is shown in **Figure 3**. Increasing ionic strength (from left to right in the figure) decreased the absolute value of zeta potential, but the standard deviations were similar. The fact that the values of  $\zeta$  are similar for the lowest few values of ionic strength is partially induced by the assumption that Equation (1b) was valid for all particles in this research. At the lowest ionic strength shown, the value of  $\kappa a$  for  $1\ \mu\text{m}$  particles is 23 which yields a value of  $\zeta$  that is approximately 10% higher (more negative) using the full Equation (1a) instead of Equation (1b). Larger particles would have a smaller correction. Also, at the low ionic strength, the rate of decrease in potential with distance is



**Figure 3** | Mean zeta potential of Min-U-Sil 5: effect of ionic strength (error bars represent  $\pm$  one standard deviation).

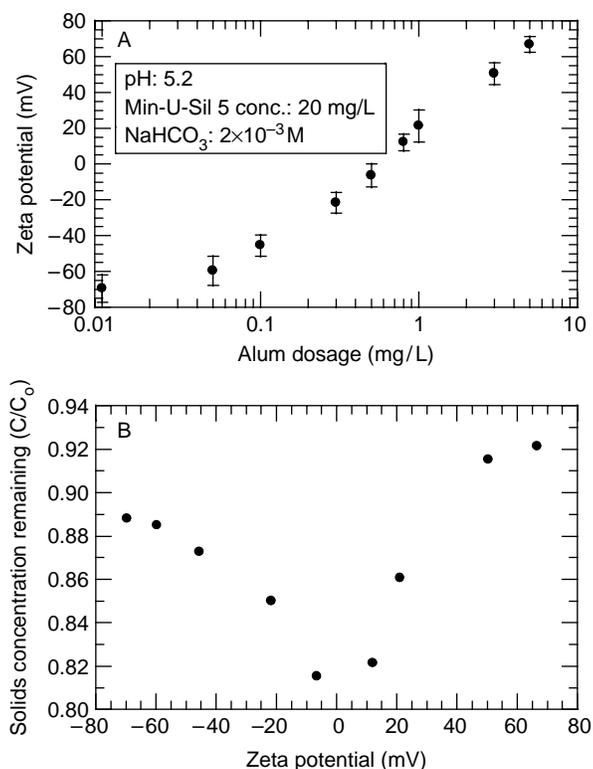
not only decreased in the diffuse layer (i.e.  $1/\kappa$  increases) but also between the particle surface and the shear plane (where electrophoretic mobility is measured); this fact mitigates the change of  $\zeta$  with ionic strength.

### Alum destabilization

The mean zeta potential of the Min-U-Sil 5 particles in 20 mg/L suspensions continuously increased (i.e. from negative to positive) with an increase of alum dose, as shown in **Figure 4(A)**. The zeta potential of Min-U-Sil 5 has a nearly linear relationship with the log of alum doses in the range  $-40 < \zeta < 50$  mV (corresponding to alum doses of 0.1 to 3 mg/L), but this relationship was weaker at lower alum dose. No systematic trend in the standard deviations is obvious.

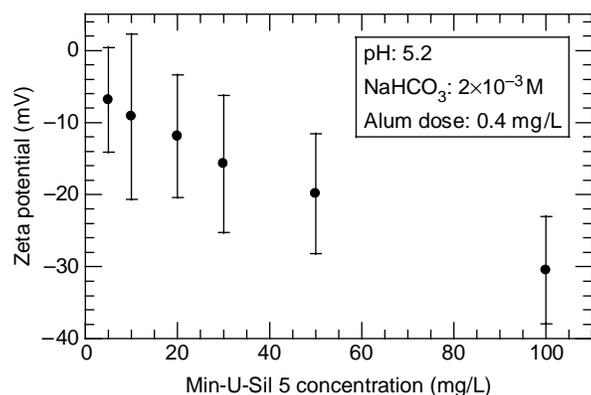
The solids concentration remaining ( $C/C_0$ ) versus alum doses in the jar-tests is shown in **Figure 4(B)**; solids concentrations were evaluated spectrophotometrically after development of a standard curve. As expected, the solids concentration removal was better when the mean zeta potential was near zero. With little electrostatic repulsion, the attractive van der Waals force was dominant at this point, leading to the best floc formation. Nevertheless, the low particle concentration and short flocculation and settling times meant that little removal was accomplished at any dose.

The amount of positive charge (i.e. coagulant) required for charge neutralization is proportional to the total surface area of particles in the suspension (*Letterman et al. 1999*). When alum is used to accomplish destabilization by charge



**Figure 4** | Effect of alum dose on mean zeta potential (A) and effect of zeta potential on jar test results (B) (error bars represent  $\pm$  one standard deviation).

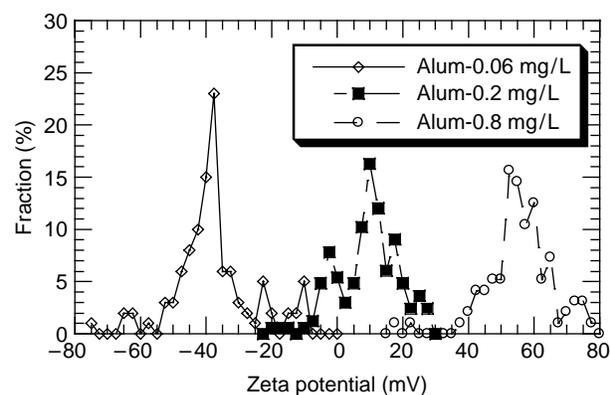
neutralization, the mean zeta potential of particles is a function of both alum dose and particle concentration. A plot of average  $\zeta$  versus Min-U-Sil concentration at a constant alum dose (Figure 5) reveals an increasingly negative zeta potential with increasing particle concentration. The relationship is not quite linear, but the ratio of



**Figure 5** | Effect of particle concentration on zeta potential with constant alum addition in jar tests.

alum dose to particle concentration was the principal determinant of the average zeta potential. The standard deviation of the ZPD was fairly constant ( $\approx 9$  mV) over the entire range of Min-U-Sil concentrations. These results reveal the difficulty in controlling the surface charge by chemical addition in a water treatment plant (or any engineered particle removal application) where the particle concentration varies over short time intervals, if the optimum dose is determined by the particle concentration rather than the NOM concentration.

Different alum doses resulted in different ZPDs. For Min-U-Sil suspensions at a solids concentration of 20 mg/L, an alum dose of 0.2 mg/L was considered the near optimum dose for the filtration experiments reported elsewhere (Kim 2004), while 0.06 mg/L was below-optimum dose, and 0.8 mg/L corresponded to above-optimum dose. The ZPDs of Min-U-Sil 5 at the three different alum doses in filtration experiments are shown in Figure 6. The mean zeta potentials ( $\pm$  one standard deviation) at alum doses of 0.06, 0.2, and 0.8 mg/L were  $-38.9 \pm 12.1$  mV,  $7.9 \pm 12.2$  mV, and  $54.3 \pm 9.9$  mV, respectively. The relationship between  $\zeta$  and alum dose is different in Figures 4(A) and 5 on the one hand and Figure 6 on the other because of differences in the mode of application of the alum. For the filtration experiments (shown in Figure 6), alum was added from 0.25 mg/mL concentration stock solutions in the influent line of a continuous flow system, whereas in the jar tests (Figures 4 and 5), the stock solution was at 1 mg/mL. The different stock solutions would have different speciation of the alumino-hydroxyl species (O'Melia 1978) and the



**Figure 6** | Zeta potential distributions of Min-U-Sil 5 at three different alum doses during filtration (pH 5.2 and 20 mg/L of MinU-Sil 5 dispersed in  $2 \times 10^{-3}$  M  $\text{NaHCO}_3$ ).

different modes of mixing between the two types of tests would also affect the relative rates of hydrolysis and particle adsorption (Klute & Amirtharajah 1991), so the differences in the two types of results are perhaps not surprising. Both methods of alum addition gave very repeatable results, so the differences cannot be ascribed to experimental error or variation; in addition, in some preliminary filtration experiments, the supply water contained the alum (but not the particles, which were added in-line immediately prior to the filter) and the ZPDs were essentially identical to the jar test results.

### Polymer destabilization

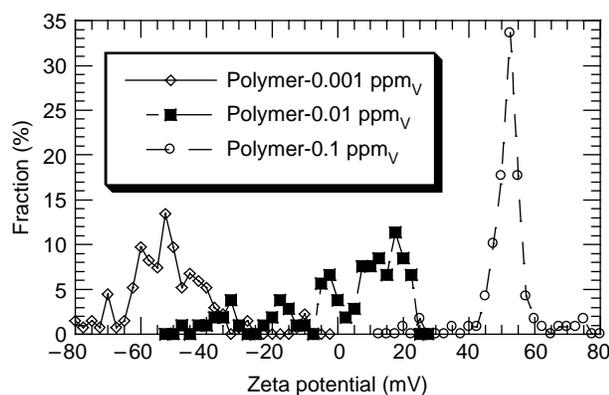
Based on jar-test results, three polymer doses were chosen: 0.001 ppm<sub>v</sub> (below-optimum dose), 0.01 ppm<sub>v</sub> (optimum dose), and 0.1 ppm<sub>v</sub> (above-optimum dose). The corresponding mean zeta potentials ( $\pm$  one standard deviation) were  $-53.3 \pm 13.1$  mV,  $1.0 \pm 18.1$  mV, and  $50.9 \pm 7.9$  mV. The ZPDs at the three different polymer doses in jar tests are shown in Figure 7. One distinct characteristic of these results is that the distribution at the above-optimum dose was quite narrow, as evidenced by the relatively small standard deviation, while the distribution at the optimum dose was wide. This result was not found during the pH, ionic strength, or alum addition experiments. The difference in the shape of the ZPDs under these different conditions is related to the polymer's high surface charge density; at low dose, adsorption was uneven, but at high dose, adsorption was quite uniform and the high charge density led to the

zeta potential being uniform. Also, the low doses might be more susceptible to variations in the amount of adsorption due to imperfect mixing because, at high doses, the number of sites available for adsorption would be much more limited; this limitation could mean that polymer molecules will bypass one particle that is already covered with many molecules for another that has more open sites.

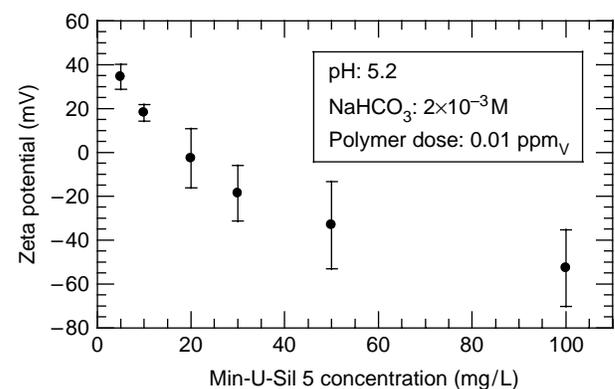
The broad distribution at the optimum dose could be advantageous in particle removal systems. Particles with opposite charges would be attracted to each other and form flocs even more easily than two neutral particles because the electrostatic attraction would influence the particle behavior at separation distances greater than those associated with van der Waals attraction.

These results are also consistent with, but extend, the ideas that underlie the patch model suggested by Gregory (1973). He noted that polymer adsorption would lead to positive patches on originally negative particles; i.e. that the high charge density of polymers would lead to uneven distribution of charge over individual particles. In the results reported here, some particles apparently adsorbed sufficient polymer to create a net positive charge while others adsorbed less polymer and were still negative overall.

Polymer destabilization experiments were performed with the solids concentration varying from 5 mg/L to 100 mg/L but the polymer dose constant at 0.01 ppm<sub>v</sub>. The mean zeta potentials and standard deviations are shown in Figure 8. As previously noted with respect to alum destabilization, the mean value of  $\zeta$  was determined primarily by the ratio of polymer dose to particle concentration.



**Figure 7** | Zeta potential distributions of Min-U-Sil 5 at three different polymer doses in jar tests (pH 5.2 and 20 mg/L of Min-U-Sil 5 dispersed in  $2 \times 10^{-3}$  M NaHCO<sub>3</sub>).



**Figure 8** | Mean zeta potential of Min-U-Sil 5 in jar tests as a function of solids concentration at a polymer dose of 0.01 ppm<sub>v</sub> (error bars represent  $\pm$  one standard deviation).

Again, the standard deviations reveal the narrowing of the ZPD at over-dosed conditions, i.e. at low particle concentrations that led to positive zeta potential. In comparison to alum, polymer changed the zeta potential of Min-U-Sil 5 more strongly as a function of solids concentration. With alum, the mean  $\zeta$  changed from  $-30$  mV to  $-6$  mV, i.e. a net change of 24 mV; with polymer, it changed from  $-54$  mV to 34 mV, i.e. a net change of 88 mV and charge reversal under the same conditions. The cause of these differences is unclear, though the complexation reactions of aluminum both in solution and on the particle surfaces could be an influence.

### Example ZPDs during filtration

The ZPDs of Min-U-Sil 5 particles during the early stage of filtration at pH 3.0 are shown in Figure 9(A); the results indicate that the ZPD of the effluent at 2 min was more negative than the influent and shifted to even more negative values by 6 min. This movement of the ZPD can be attributed to the fact that less negative (more destabilized) particles are selectively attached to the collectors, while particles with higher negative charges appear in the effluent at the beginning of filtration. These results are consistent with traditional expectations.

The ZPDs during later stages of filtration are presented in Figure 9(B). The mean values stayed nearly constant between 10 and 120 min, but showed a small tendency to rise to less negative values in comparison to the 6 min sample. Two factors apparently combine to influence the small decrease (absolute value) of the zeta potential during the later filtration stage. First, there was an influence of particle accumulation, i.e. ripening. The surface area of the collector

can be increased with the increase of solids accumulation, which leads to an improvement of transport efficiency. Second, there was a possibility of break-off of flocs from the filter media. Flocs that were once attached to the filter media but were broken off can be assumed to have less negative surface charge than particles in the suspension that were never caught (non-attachment particles). Therefore, detachment of flocs can decrease the mean zeta potential.

### Implications for filters

In granular media filtration, where the available surface area includes the particles in suspension and the media, the surface charge of particles entering the filter might change if adsorbed coagulants such as aluminum hydroxyl polymers desorb and subsequently attach to the media (Kim 2004). That is, the difference between the concentration of solid surface area available in the suspension prior to entering a granular media filter and in the filter itself could lead to changes in mean zeta potential of both the filter grains and the particles in suspension, and thereby affect the attachment efficiency of particles to filter grains or previously captured particles. This situation can arise immediately after backwashing when the surface charge condition of filter media is different from that of the influent particles. In this case, influent particles are destabilized but the filter media is not because some or all of the destabilizing materials that coated the media surface sloughed off during the backwash. During the course of a filter run, destabilizing polymers and destabilized particles coat the filter media, causing the surface charge of the media grains to shift towards those of the destabilized particles.

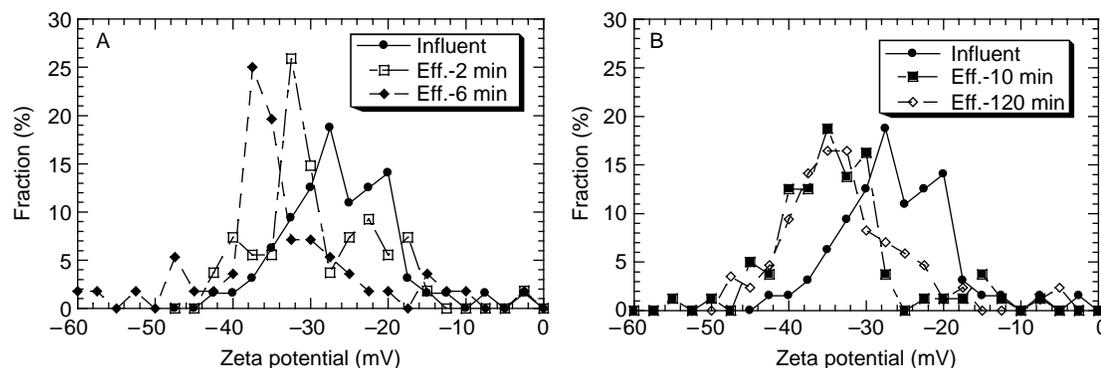


Figure 9 | ZPDs of Min-U-Sil 5 at pH 3.0 during the initial stage (A) and later stage (B) of filtration experiments.

Depending on solution chemistry and surface characteristics of both the suspended particles and the filter media, conditions may be favorable or unfavorable for filtration. Favorable conditions result from no repulsive interactions as suspended particles approach the surface of the filter media (O'Melia 1986), allowing the attractive van der Waals force to dominate; unfavorable conditions result when the repulsive EDL force dominates. The attachment efficiency factor,  $\alpha$  is defined as follows:

$$\alpha = \frac{\text{particle deposition at specified condition}}{\text{particle deposition under favorable conditions}} \quad (3)$$

Any of several transport models for deep bed filtration (Yao *et al.* 1971; Rajagopalan & Tien 1976; Tufenkji & Elimelech 2004) can be used to predict the rate of particle deposition under favorable conditions, i.e. the denominator in Equation (3). Experimental results can be used to find the particle deposition at a specified condition (the numerator in the equation). The ratio of the experimental to predicted results allows one to estimate the efficiency factor  $\alpha$ .

Several authors have developed correlations for  $\alpha$  based on the variables governing particle–collector interactions (Elimelech 1992; McDowell-Boyer 1992; Bai & Tien 1999). In these studies,  $\alpha$  was determined from laboratory scale filtration experiments at different operating conditions as indicated above. These results were then correlated with dimensionless parameters designed to account for the variety of factors governing particle–collector interactions. In all cases, the effects of the particle and collector surface potentials were included as mean zeta potentials. In essence, these authors have assumed that the zeta potential distributions of particles and collectors are narrow. Although this assumption might have been valid for the experimental systems employed (synthetic latex or polystyrene particles and glass-bead collectors), results from the present study illustrate that this is not the case for silica particles. It is highly probable that the ZPDs of naturally occurring particles are also broad; an example is shown in Figure 10, which illustrates the broad distribution of particle zeta potentials found in a natural water (Lake Austin, TX). The natural particles had a mean  $\zeta$  of  $-19 \pm 8$  mV; therefore, it seems that the Min-U-Sil 5 particles were a suitable surrogate in terms of the variability in zeta potential. In light of these findings, we agree with the

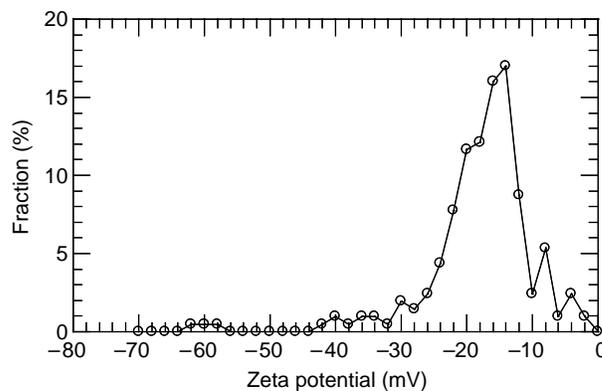


Figure 10 | Zeta potential distribution of natural particles from Lake Austin, TX.

suggestion of Tufenkji *et al.* (2003) that a more rigorous estimation of  $\alpha$  should account for the distribution of zeta potentials.

Song *et al.* (1994), investigating the kinetics of colloid deposition onto heterogeneously charged collectors, modeled the surface charge heterogeneity assuming that charged sites were normally distributed on the collector surface. The authors did not consider the distribution of particle surface potentials; however, a similar approach could be extended to such a case. If a ZPD were described mathematically (such as with a normal or log normal distribution), that distribution could then be substituted for the mean values in the correlations described above, resulting in a *distribution* of  $\alpha$  values to characterize a given system.

## CONCLUSION

Particles in suspension are characterized by a distribution of zeta potentials. Therefore, information is lost when the destabilization of particles is evaluated based on the mean value of  $\zeta$ , a common practice in research related to flocculation and granular media filtration. The ZPD of silica particles are broad when particle surface charge is controlled by pH control, ionic strength adjustment, and alum destabilization; the standard deviations of the ZPDs are comparable for these destabilization mechanisms. However, when polymer with a high charge density is utilized for destabilization, the standard deviation of the distribution is a function of coagulant dose. At under-dosed and optimal dosing conditions, the resulting ZPDs are

broad, but at over-dosed conditions, the particles are uniformly coated with the charged polymer and the resultant ZPDs are quite narrow. In some cases, the zeta potentials of silica particles are normally distributed, but in most cases the distributions are skewed. This research strongly suggests that the distribution of zeta potentials, and not just the mean values, should be considered in engineered particle removal processes.

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