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The Impact of High Salinity and Seawater on Aggregate Structures in Clay Tailings flocculation

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ABSTRACT

The use of seawater, hypersaline or other low-quality water supplies in mineral processing operations has strong benefits in places like Chile and Australia, not just economically but in ensuring social license to operate. Despite this commercial application, the effect of dissolved salts on tailings flocculation is not yet fully understood. This partly stems from the operator-dependence that plagues normal cylinder testing and the tendency in some previous literature studies to make flocculant activity comparisons under a narrow range of conditions (single dosage, solids concentration and/or fixed mixing).

Six acrylamide/acrylate copolymers with the same anionicity (30%) but different molecular weights, were evaluated in the flocculation of standard kaolin slurries prepared in seawater or solutions containing selected cations at various concentrations. Settling rate-dosage response curves were collected for these polymers, combining continuous Couette flocculation with real-time aggregate sizing and off-line determination of individual aggregate settling rate vs. size, from which their densities could be derived. Shifts in the dosage response curves under different conditions reflected changes in both the aggregate size and density.

From the large body of flocculation data produced under tightly controlled conditions, new insights were gained on how salinity alters mixing requirements for aggregation, responses to molecular weight and aggregate structure. Some salt addition was beneficial in producing an initial low level of aggregation of fines that reduced the effective surface area of the suspension and subsequent flocculant dosage requirements. At high ionic strength, a reduction in flocculant bridging capacity due to chain coiling resulted in open, low density aggregate structures, which substantially increased the flocculant demand to achieve a target settling rate. The potential impact should be a much more robust basis for flocculant selection, which is currently very much trial-and-error.

INTRODUCTION

The influence of multivalent cations on the performance of anionic polyacrylamides (PAMs) is relevant not only to mineral processing industries using seawater but also those with brackish or hypersaline process streams. Multivalent cations can have a significant effect on thickener performance depending on how specific cations interact with the substrate surface and the flocculant molecule (Peng and Di, 1994; Witham *et al.*, 2012; Jeldres *et al.*, 2014). At high ionic strength, cations such as Ca^{2+} and Mg^{2+} can reduce particle-particle distances by compressing the electrical double layer, thereby promoting coagulation. This can make subsequent flocculant addition more effective. The conformation of anionic PAMs will be strongly affected by dissolved salts, with the shrinking of electrostatic fields around charged functionalities by counter-ions resulting in chain coiling. While such coiling would reduce the number of effective collisions that lead to bridging, the effect of liquor cations on aggregate structures (size and density) produced with flocculants of different molecular weights (MW) is not yet fully understood.

As part of a wider study on optimizing clay tailings treatment, continuous Couette flocculation under tightly-controlled mixing conditions has allowed the performance of six anionic PAMs, all possessing the same charge density but different MWs, to be investigated as a function of key process variables. Mudline settling rates measured after isolating a cylinder of flocculated solids provide the primary indication of the extent of aggregation, with evolution of aggregate size monitored by focussed beam reflectance measurement (FBRM). The FBRM results will be reported elsewhere; this work focuses on the determination of aggregate size-density relationships in salt solutions, for which over 7,200 individual free-settling aggregates were characterised by image analysis.

METHODOLOGY

Materials

Clay slurries

Kaolin clay (Prestige NY) supplied by Unimin, Australia, was used. Its mass composition was as follows: 46.1 % SiO_2, 36.5 % Al_2O_3, 0.9 % Fe_2O_3, 0.9 % CaO, 0.8 % TiO_2, 0.5 % MgO, 0.2 % K_2O, and 0.1 % Na_2O. The particle density was 2.68 g cm^{-3}, with a moisture content of 1.5 wt.% (from drying at 90 °C). Slurries were prepared in a 200 L baffled tank at solid concentrations of 40–80 g L^{-1} in the specified liquor, with stirring by an overhead stirrer equipped with triple three-pitched-blade impellers (each 12.8 cm long, 5 cm wide at the drive shaft, tapered to 3 cm at the tip). Conditioning of the slurries at a high stirring intensity (250 rpm, 5 days), followed by a lower intensity (100 rpm) for the duration of testing, ensured a stable, reproducible particle size.

Flocculants

Six anionic polyacrylamide-based (PAM) flocculants were used in this study. They span a distinct range of MWs but with a fixed 30% charge density, all synthesised by copolymerisation of acrylamide and acrylic acid. The intrinsic viscosity ([η]) of polymers, providing a relative indication of solution dimensions, was measured in phosphate buffered 1 M NaCl, as described by Costine *et al.*, (2018).

Stock solutions were prepared by adding absolute ethanol (2 g) to powdered flocculant (0.50 g) in a glass jar, which was gently shaken by hand for 0.5 min, and then let to stand for 2 min. DI water was added to give a 0.50% stock solution, with vigorous shaking for 2 min to properly disperse the powder, followed by gentle agitating on a tabletop shaker at 150 rpm for 16 h. Working solutions (0.005%) were prepared immediately prior to testing by diluting the stock solution with DI water.

Flocculant performance testing

The Shear Vessel system

The Shear Vessel accomplishes continuous flocculation under the controlled agitation conditions that occur in the annular gap (5 mm) between a stationary outer cylinder (acrylic, I.D. 110 mm) and a rotating inner cylinder (316 stainless steel, O.D. 100 mm), as shown in Figure 1a. Flocculant inlets (ports 1 to 4) are positioned on one side of the outer cylinder, allowing the reaction time under the applied agitation to be varied. The slurry inlet port is positioned on the side opposite from the flocculant ports. Slurry was pumped from the feed tank to the Shear Vessel using a peristaltic pump at a constant delivery rate of 300 mL min^{-1}. A detailed description of the Shear Vessel is given elsewhere (Farrow and Swift, 1996).

Flocculated slurry flows through a glass analysis column, which can be isolated for the determination of hindered settling rates, with continuous flow maintained using a diversion line. An FBRM probe was inserted below the column to monitor the aggregation state. A second peristaltic pump was used to control the underflow flow rate and was set to draw 95% of the total incoming flows. Flocculated slurry was sampled for floc density analysis at a point below the column and before the underflow pump.

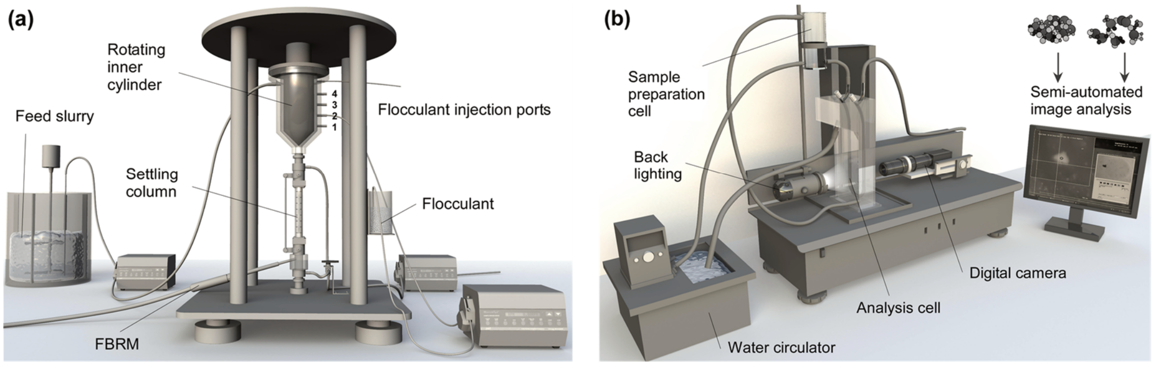

Figure 1 (a) The Shear Vessel for continuous flocculation, and (b) the Floc Density Analyser for determining settling rate vs. size from image analysis.

Aggregate density measurements

The floc density analyser (FDA) developed by Farrow and Warren (1989) was used to estimate the density of individual aggregates, based on their size and settling velocity. Figure 1b illustrates the FDA set-up used in this study. A small sample was diluted in the preparation cell with DI water to 0.1 wt% and pumped to a glass analysis cell, with the taps then closed to ensure convection-free settling. Since the aggregate suspension in the FDA analysis cell is extremely diluted, undisturbed free settling velocities and structures of hundreds of individual aggregates can be quantified by use of a digital camera, connected to image processing software. By assuming that the aggregate shape is roughly ellipsoidal, it is possible to calculate the diameter of a sphere of equivalent settling velocity (d_{st}) using the expression proposed by Happel and Brenner (1973), valid for vertical to horizontal diameter ratios between 0.1 and 20,

$$d_{st} = \left[0.8248 + 0.168\left(\frac{a}{b}\right) + 1.033 \times 10^{-2}\left(\frac{a}{b}\right)^2 - 1.264 \times 10^{-3}\left(\frac{a}{b}\right)^3 + 3.728 \times 10^{-5}\left(\frac{a}{b}\right)^4\right] b \quad (1)$$

If Stokes's Law is assumed, the density of an individual free settling aggregate (ρ_a) can be calculated as

$$\rho_a = \frac{18\mu}{g}\frac{U}{{d_{st}}^2} + \rho_l \qquad (2)$$

where U is terminal settling velocity of the aggregate of equivalent size (d_{st}); μ, ρ_l, and g are fluid viscosity, fluid density, and the gravity constant, respectively.

RESULTS AND DISCUSSION

Flocculant product comparisons at a single fixed dosage has been identified as a potential deficiency in some published literature and many testwork programs (Fawell *et al.*, 2015). To ensure that potentially subtle variations in performance were not missed, the preference was to collect full dosage response curves for each flocculant, covering dosages from the onset of aggregation through to (where possible) high settling rates (>30 m h^{-1}) well above what may be required in practice. Figure 2 shows how the MW response of anionic flocculants is affected by the ionic strength of the water.

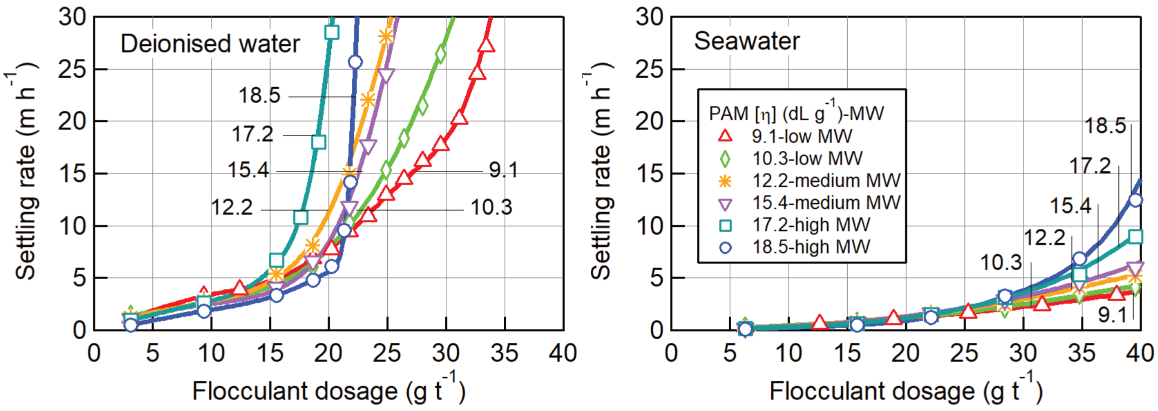

Figure 2 Settling rates of kaolin slurries (60 g L^{-1}) prepared in DI water or seawater as a function of PAM dosage and MW. Flocculant solution (0.005%) dosed at port 2 (residence time of 16.5 s); rotation rate 250 rpm.

High salinity within the clay slurry has a significant detrimental effect on flocculant performance, particularly the lower MWs (PAM[9.1], PAM[10.3], and PAM[12.2]), shifting their dosage curves to the right and limiting the settling rates at high dosage. The high MW flocculants (PAM[17.2] and PAM[18.5]) could better tolerate high salinity, however, the dosage requirements to give a moderate settling rate of 15 m h^{-1} are still double those in freshwater.

The flocculation response in seawater increases monotonically with PAM MW, with the effects of polymer chain extension and availability more apparent in freshwater. On the latter, as flocculant dosage is based on a weight of flocculant, the lowest MW, PAM[9.1], has about twice as many polymer chains available compared to PAM[18.5], hence its settling rate in the early stages of flocculation (<10 g t^{-1}) is essentially double that of PAM[18.5] in salt-free slurry. These conditions favour a more extended chain conformation due to repulsions of the carboxylate groups, with the lower MWs producing more bridging connections between particles, thus favouring fines capture and the formation of small slow-settling aggregates. Longer chains of higher MWs are then required to flocculate such aggregates into larger clustered structures, often giving a sharp response over a narrow dosage range.

Comprehensive settling-dosage data are not reported here for individual salts (NaCl, KCl, $CaCl_2$, $MgCl_2$), but Figure 3 summarises the typical MW response of anionic PAMs to increasing concentrations of mono- and divalent cations. It is useful to contrast the impact of calcium cations on the dosage response curves against slurries containing sodium cations to properly differentiate from general electrolyte effects. The dosages required to give 10 m h^{-1} as a function of flocculant MW (or solution dimensions) were derived by interpolation of the corresponding dosage curves.

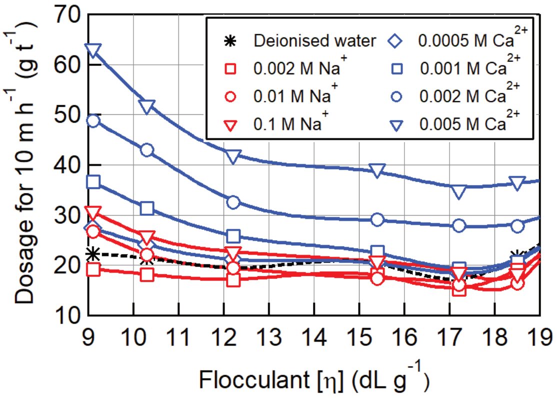

Figure 3 Effect of Na^+ and Ca^{2+} concentrations in kaolin slurry (60 g L^{-1}) on the dosages needed for a settling rate of 10 m h^{-1}. Flocculant solution (0.005%) dosed at port 2 (residence time of 16.5 s); rotation rate 250 rpm.

For low sodium concentrations (0.002–0.01 M), it was found that the dosage curves shifted slightly to the left (lower dosages) compared to DI water, with their shape remaining largely constant. This suggests that the main effect of Na^+ at low concentrations is on the exchangeable groups of the clay surface, favouring some degree of particle coagulation. At higher Na^+ concentration (0.1 M), a reduction in bridging capacity became apparent, but this effect was small and only affected the lower MWs. Comparison of the results for Na^+ and Ca^{2+} cations at a fixed ionic strength highlighted the detrimental effect of Ca^{2+} on the dosages required by lower MWs to meet a target settling rate. For example, whilst the dosage required by PAM[18.5] to give 10 m h^{-1} was almost the same in 0.002 M Na^+ and 0.001 M Ca^{2+} solutions, the dosage requirement for PAM[9.1] doubles in Ca^{2+} solution. The implication is that Ca^{2+} in the slurry caused a much stronger coil contraction compared to an equivalent amount of Na^+ cations. Consistent with this, static light scattering and viscosity measurements of sodium polyacrylate in dilute NaCl and $CaCl_2$ solutions have shown that chain coiling is more severe in the presence of calcium salt (Huber, 1993).

The dosage-response curves in Figure 2 will be influenced not only by changes in aggregate size, but also aggregate density. While direct measurement of density is not possible, determining microscopic properties of individual aggregates without removing them from their process liquor allows the measurement of size and settling velocity, from which density can be derived. Samples of flocculated slurry (10 g t^{-1}) were collected for PAM[9.1], PAM[12.2] and PAM[18.5] at a relatively low Shear Vessel rotation rate of 150 rpm and fixed residence time within the shear zone of 16.5 s. Figure 4 shows the aggregate size-density relationships observed in freshwater and seawater, comparing the standard fitted curves (the individual data points are not shown for clarity).

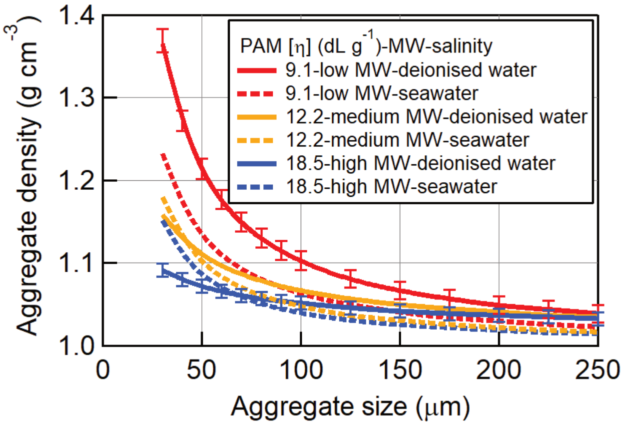

Figure 4 Density vs. size as measured by FDA for individual aggregates formed by three different anionic flocculants when dosed into kaolin slurry (50 g L^{-1}) prepared in DI water or seawater. Flocculant solution (0.005%) dosed at port 2 (residence time of 16.5 s); rotation rate 150 rpm.

Under salt-free conditions, the greater number of bridging connections produced by the lower MW flocculants resulted in denser, faster settling aggregates than equivalent sizes formed by higher MWs. The effective aggregate densities, which represents the ratio of the mass enclosed by the ellipsoid (particles and liquor) to the volume of the ellipsoid, were 1.103, 1.067 and 1.052 g cm^{-3}, respectively, for PAM[9.1], PAM[12.2] and PAM[18.5]. While the differences appear marginal, this corresponds to volumetric liquor/solid ratios for these aggregates of 15:1, 24:1 and 32:1, respectively. It is clear that flocculated structures produced by low MWs under mild mixing have substantially less intra-aggregate liquor than those formed by high MWs.

These effects are also apparent in seawater, though are less pronounced, with consistently lower-density structures formed from each flocculant in the presence of salt. Small aggregated structures (<50 μm) are an exception, particularly for the medium and high MWs, with surface charge modification via multivalent cations leading to denser coagulated micro-aggregates, as shown for unflocculated slurry in Figure 5.

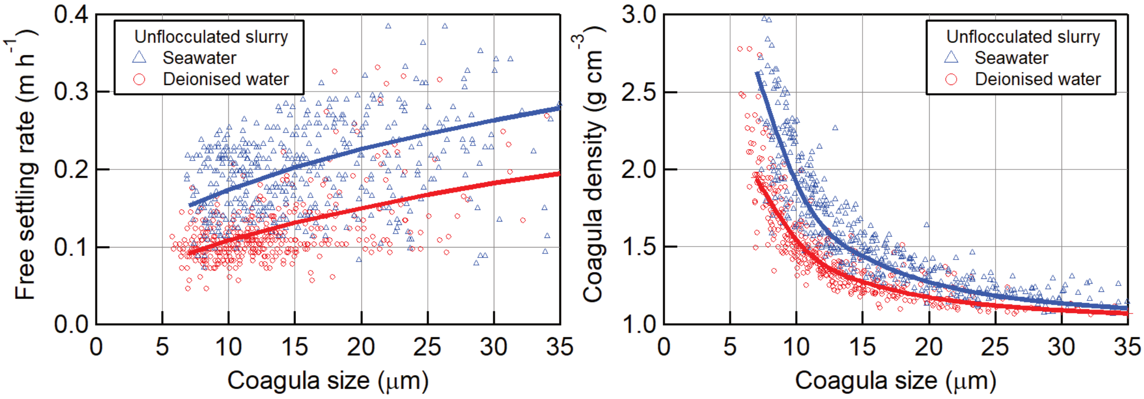

Figure 5 Free settling rate and density vs. size as measured by FDA for individual coagula formed in unflocculated kaolin slurry (50 g L^{-1}) prepared in DI water or seawater.

Similar FDA experiments for individual salts confirmed that this coagulation effect increases in the order $Ca^{2+} > Mg^{2+} > K^+ > Na^+$, though such weak structures are only likely to persist under low fluid shear. High concentrations of cations in the liquor clearly affects the clay surface (with cation adsorption possibly changing the sites available for flocculant adsorption), but the response to MW in Figures 2 and 3 suggests that it has a much stronger effect on flocculant conformation.

Figure 6 shows the effective densities of average 100 µm-aggregates formed by PAM[9.1], PAM[12.2] and PAM[18.5] after dosing into slurry prepared with increasing concentrations of Ca^{2+} or Na^+. That similar structures (densities) were observed above 0.001 M Ca^{2+} for all flocculants suggests that the superior performance of higher MWs in Figure 3 is mainly due to larger aggregate sizes accessible through the longer chains. Consistent with this, Arinaitwe and Pawlik (2013) have shown a strong affinity of Ca^{2+} at low concentrations (0.001 M) for anionic PAM, effectively reducing the intrinsic viscosity to a value indicating a physical limit of coiling. Some NaCl addition favoured aggregate densification with the higher MWs, but approaching seawater concentrations, more open, fractal structures were produced with these flocculants. While the overall response in seawater is dominated by multivalent cations (Figure 4), the internal aggregate structure as revealed through density determination, directly influences sedimentation, resistance to shear, and dewatering.

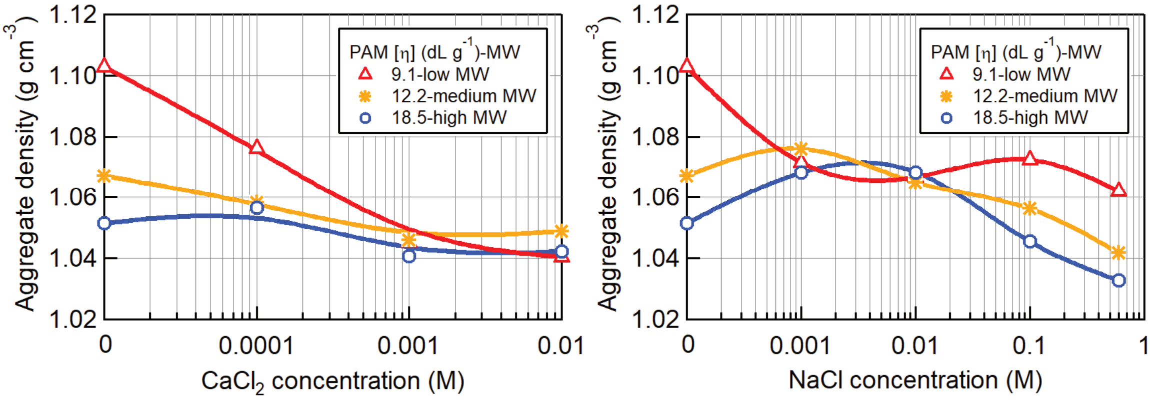

Figure 6 Density of average 100 µm-aggregates formed by three different anionic flocculants when dosed into kaolin slurry (50 g L^{-1}) prepared in Ca^{2+} or Na^+ solution. Flocculant solution (0.005%) dosed at port 2 (residence time of 16.5 s); rotation rate 150 rpm.

CONCLUSION

Continuous flocculation within the Shear Vessel provides controlled mixing conditions, with offline density measurements then allowing the impact of liquor salinity on flocculated structure properties to be determined. All flocculants studied were adversely affected by increasing concentrations of multivalent cations such as Ca^{2+}, with the effects of a reduced bridging capacity particularly apparent in the lower MWs – such results are also relevant to flotation/gold plants that practice lime addition. Aggregate structures >50 µm formed in seawater were less dense than those formed in freshwater under equivalent conditions (flocculant MW, mixing time and intensity), which could potentially impact achievable underflow densities in thickener operations.

In this study, we have shown how microscopic characterization of settling velocity and size for free-settling aggregates can be used to provide better quantification of the structures formed in saline liquors, offering insights on how novel polymer chemistries with high-salt tolerance can be optimized.

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