THE IMPACT OF DESILICATION PRODUCT ON BAUXITE RESIDUE FLOCCULATION

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Abstract

The pre-desilication step within the Bayer Process seeks to transform reactive silica in bauxite into desilication product (DSP) prior to digestion, thereby reducing post-digestion precipitation and scaling. The precipitated DSP is removed with the other residue phases in the primary settling stage. While the proportion of DSP within the residue can be significant, there are surprisingly few open-literature studies that consider the impact of DSP on residue flocculation and settling. Such studies typically involve bauxites of a fixed composition, which limits the scope to vary residue properties while investigating flocculation mechanisms. In this study, DSP has been formed from the reaction of standard kaolin in synthetic Bayer liquor in the presence of iron oxides. Variation of the reaction conditions (temperature, duration, kaolin to iron oxide ratio) has produced a range of synthetic residue slurries that have been characterised in terms of their physical and flocculation properties. Effective comparison of the latter could only be achieved after detailed optimisation of test conditions, which included (i) slurry stability over time, (ii) solids concentration, (iii) temperature and concentration of the dosed flocculant, and (iv) flocculant make-up/shelf life. The detrimental impact of DSP is clearly reflected in lower settling rates, higher supernatant solids and poor consolidation over a range of solid densities and DSP contents of operational interest. Flocculant dosage response curves are also less steep and shifted towards higher demand. A number of flocculants are contrasted in terms of their suitability for high DSP residues, with the practical implications of their application discussed.
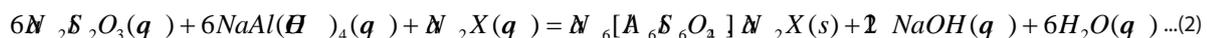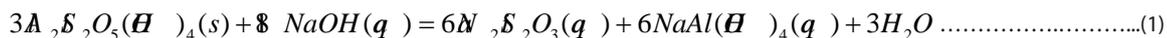

Notation and units

A is aluminium in the solution (expressed as g L^{-1} Al$_2$O$_3$), C is sodium hydroxide plus sodium aluminate (expressed as g L^{-1} Na$_2$CO$_3$) and S is C plus sodium carbonate (expressed as g L^{-1} Na$_2$CO$_3$).

1. Introduction

1.1 Pre-desilication

Processing of high silica bauxite through the Bayer Process consists of the following main steps: (i) comminution, (ii) predesilication, (iii) pressure dissolution/digestion of aluminium bearing phases, (iv) solid-liquid separation of liquor and residue, (v) precipitation and separation of aluminium trihydrate and (vi) calcination (thermal conversion) to product alumina (Smith 2009). In the pre-desilication stage, aluminosilicate clays, principally kaolin, dissolve and precipitate according to Equations 1 and 2 respectively (Smith 2009). By prioritising the precipitation of the so-called desilication product (DSP) in the beginning, the risk of excessive post-digestion precipitation and scaling can be significantly reduced (Oku and Yamada, 1971).

$$3Al_2Si_2O_5(OH)_4(s) + 18\ NaOH(aq) = 6Na_2Si_2O_3(aq) + 6NaAl(OH)_4(aq) + 3H_2O \dots\dots\dots\dots\dots(1)$$

$$6Na_2Si_2O_3(aq) + 6NaAl(OH)_4(aq) + Na_2X(aq) = Na_6[Al_6Si_6O_{24}]\cdot Na_2X(s) + 12\ NaOH(aq) + 6H_2O(aq)\ \dots(2)$$

$$X = SO_4^{2-}, O_3^{2-}, Cl^-, Al(OH)_4^-, OH^-$$

The pre-desilication process involves a sequence of dissolution and precipitation reactions, the kinetics and thermodynamics of which become the main issues. It has been claimed that the dissolution of kaolin is completed within 2 hours when the temperature is kept close to atmospheric boiling (Kotte 1981). However, the precipitation reaction is far more complex, as silica solubility is favoured by increasing temperature, caustic soda and alumina concentration, but tends to drop (precipitate) when it reaches 1-1.1 g L^{-1}. Higher temperature also helps the precipitation kinetic at a rate that is also influenced by the solution compositions (Lowe 2007), reflecting incorporation of anions in the following trend: SO$_4^{2-}$ >> CO$_3^{2-}$ ≥ Cl$^-$ > Al(OH)$_4^-$ > OH$^-$ (Whittington et al. 1998).

⬚Although there is little agreement in the literature as to what is initially precipitated, it is generally accepted that sodalite is the stable phase at approximately 150°C (Lowe 2007). Longer holding times and higher temperatures induce the transformation of sodalite to cancrinite (Gerson and Zheng 1997). Unless otherwise stated, sodalite is the primary synthetic DSP used in this work.

1.2 Bauxite residue flocculation

Achieving rapid solid-liquid separation between digestion and precipitation is critical, given the super-saturated state of the liquors. A large number of studies have sought to identify the causes of poor solid-liquid separation performance from bauxite residue flocculation. From these it is known that bauxites of differing origins are likely to produce residues that deliquor differently, reflecting variances in mineralogies and physicochemical properties, such as the proportions of goethite, reactive silica and rutile/anatase, particle size distribution (PSD), crystallinity, zeta potential and moisture content (e.g. Basu et al. 1983; Li and Rutherford 1996; Yamada et al. 1980).

Acrylamide/acrylate copolymers (PAA) were the first synthetic flocculants applied commercially to bauxite residue flocculation, and therefore much attention has been given to understanding how their properties (anionic content, molecular weight) influence flocculation under solution conditions specific to the Bayer process, such the presence of organic compounds and variable aluminate/caustic levels (Basu et al. 1983; Bublik et al.

1986; Jones 1998). Customisation of PAA flocculants to Bayer applications have included the incorporation of the salyclic acid functionality (Phillips 2004) and recently the development of rigid rod architecture (RRA) products thought to improve settling rate and underflow density (Eckart et al. 2010). By far the greatest commercial success has come from products with the hydroxamate (HX) functionality, which now dominate primary residue settling (Spitzer 1990). A number of publications have contrasted the performance of HX and PAA flocculants, as well as considering their co-dosing (Kahane and McRae 1996; Kirwan 2009a,b; Rousseaux et al. 2004).

At high pH, iron oxide particles are thought to have a negative surface charge (Sankey and Schwarz 1984). However, electrostatic physisorption of cations from highly ionic liquors shield the surface, reducing the "effective" potential to zero and generating sites for adsorption of highly anionic PAA as represented in Figure 1 (Basu et al. 1986; Bublik et al. 1986; Chen et al. 2003; Sankey and Schwarz 1984). In contrast, the HX functionality can chelate directly with an iron centre (Chen et al. 2003). Although its adsorption mechanism remains unclear, a polymeric flocculant with silane functionality has proven beneficial in capturing DSP (Dai et al. 2010, Davis et al. 2010).
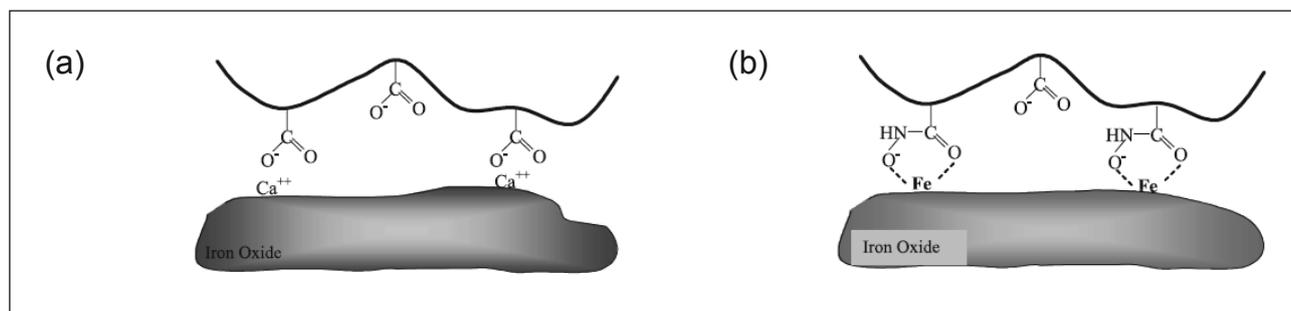

Figure 1. Interaction of iron oxide with (a) carboxylate and (b) hydroxamate functionalities (Chen et al., 2003).

1.3 The impact of DSP

While the proportion of DSP within the residue can be significant, few open-literature studies consider its impact on residue flocculation and settling in any detail. Such studies typically involve bauxites of a fixed composition, which limits the scope to vary residue properties while investigating flocculation mechanisms. Published findings relevant to DSP are limited to:

- the presence of DSP leads to lower settling rates and overflow clarities (Jones 1998; Rousseaux et al. 2004).
- flocculant selection influences overflow solids, with the expected trend: PAA > HX > silane functionality (Dai et al. 2010, Davis et al. 2010).
- a higher predesilication temperature results in higher settling rates (Peiwang et al. 1992).
- the silane functionality favours sedimentation and consolidation of residues containing DSP (Dai et al. 2010, Davis et al. 2010).

The present work seeks to achieve new insights into the impact of DSP upon the dewatering behaviour of bauxite residue. A well-characterised hematite (Fe_2O_3) is used as the model substrate, with which DSP is made in-situ under conditions that attempt to simulate the actual plant conditions. A comprehensive investigation of the flocculation behaviour both with and without DSP is being undertaken, utilising a range of techniques to characterise sedimentation, consolidation and aggregate structures. While this study is still at an early stage, a number of useful observations have already been made as to how different flocculants respond to the presence of DSP. This work has also highlighted how critical it is to carefully control flocculant make-up/dilution and the actual flocculation procedures to properly isolate the influence of selected factors.

2. Experimental

2.1 Solid characterisation and synthesis

Pure hematite (Aldrich) and kaolin (Imerys) were used in this work. DSP as sodalite, was made by reacting kaolin in synthetic Bayer liquor (A: 82 g L^{-1}, C: 233 g L^{-1}, S: 275 g L^{-1}, SO_4^{2-} = 20 g L^{-1}, Cl^- = 10 g L^{-1}, A/C = 0.35, C/S = 0.85) at 90°C for 24 hours before it was filtered, soaked overnight (in liquor of composition A = 81 g L^{-1}, C = 230 g L^{-1} and S = 232 g L^{-1}) and resuspended for the settling

test experiment The anions: carbonate (CO_3^{2-}), sulphate (SO_4^{2-}) and chloride (Cl^-) were present with the liquor to simulate real plant conditions.

Solids (hematite/kaolin/DSP) were characterised in terms of: (1) PSD by laser sizing, (2) quantitative chemical composition by X-Ray Fluorescence (XRF) and (3) qualitative mineralogical composition by X-Ray Diffraction (XRD). The consistency of the composition of DSP produced from six different batches is as follow: 34.4% SiO_2 (SD: 0.39), 30.9% Al_2O_3 (SD: 0.07), 0.41% Fe_2O_3 (SD: 0.01), 22.78% Na_2O (SD: 0.15), 4.60% SO_3 (SD: 0.03), 0.49% TiO_2 (SD: 0.01), 0.638% Cl (SD: 0.016) and 6.31% LOI (SD: 0.23). XRD confirmed that only sodalite was formed at the aforementioned conditions (90°C and 24 hours) both in the presence or absence of hematite.

2.2 Flocculants and flocculant solution make-up/dilution

Alclar 665 (Ciba Speciality Chemicals, now BASF) was used to represent PAA products; there are many similar products available, and there is no implication this was an optimised selection. HX emulsion flocculants (HX300 and HX600, from Cytec) were inverted (made water-continuous) as 1% solutions by addition to 20 g L^{-1} NaOH while being stirred; the PAA powder flocculant was made-up in deionised water to 0.5% solution (with the help of ethanol to initially wet the particles and prevent gel formation). HX 1% solutions were ready to be used immediately, while those prepared from powders were allowed to age under gentle agitation for at least 24 hours. From 0.5 and 1% solutions, flocculants are diluted as required prior to dosing, usually with a liquor equivalent to that of the slurry. However, dilution of HX 1% solutions with liquors containing high levels of aluminate and caustic led to lower settling rates and higher supernatant solids (Figure 3), suggesting some reaction of flocculant with aluminate. This represents another potential contribution to flocculant ageing and needs to be avoided in laboratory testing; 20 g L^{-1} NaOH was therefore the dilution liquor for both HX and PAA flocculants.

2.3 Cylinder batch settling test

To ensure a uniform particle distribution for the settling test, slurry was stirred in a water jacketed and baffled stainless steel beaker (diameter 12.5 cm, height 25 cm) fitted with a 8.9 cm diameter A310 impeller before it was transferred to several 250 mL graduated cylinders (diameter 3.5 cm, height 23.5 cm) which

were placed in an oil bath maintained at 95°C. Unless otherwise stated, the synthetic solution was composed of A = 81 g L^{-1}, C = 230 g L^{-1} and S = 232 g L^{-1}. Flocculant solutions were at 45°C when dosed; PAA was added as a single dose, while HX flocculants were added in two equal volumes (50:50 doses). The number of plunger strokes (a single stroke being considered as both down and up) after each dose was five. The plunger used throughout this study was a 3.5 cm diameter stainless steel plunger with six inner radial holes of 0.7 cm diameter. The settling rate was calculated from the linear plot of the mud-line height vs time. Supernatant solids were determined gravimetrically from 20 mL solution taken at the height of 18.1 cm, 1 minute after the last stroke (or immediately after the mud-line passes that point for relatively slow settling rates). Consolidation behaviour is quantified from the bed height measured after 30 min.

2.4 FBRM

Focused beam reflectance measurement (FBRM) has proven a robust in-situ method to contrast the real-time chord length distributions of mineral slurries (Heath et al. 2002; Owen et al. 2008), and has been applied to the flocculation of bauxite residue (Kirwan 2009a,b; Phillips 2004). The principle of FBRM has been previously described (Heath et al. 2002). A Lasentec M500 probe (Mettler Toledo) with C-electronics was used, the focal point set at 0 μm (the outer surface of the sapphire window); data collection was over 90 log channels between 1 to 1000 μm, the measurement duration 2 s, with distributions and statistics averaged over 5 measurements. The raw chord length data is intrinsically only length-weighted, offering sensitivity to fines, while applying a length square-weighting to the data provides an effective volume-weighted relationship, more representative of aggregate size.

Flocculation for FBRM studies was achieved in 400 mL tall-form beakers with the vertical probe positioned at an outer edge to also serve as a baffle (Heath et al. 2002), with the stirring rate maintained at 300 rpm. Prior to flocculation, slurries (2 wt%) were equilibrated at 70°C and stirred at 700 rpm for 1 hour.

3. Method optimisation

3.1 Reproducibility of hematite slurry

Preliminary tests into the ageing of standard hematite slurries were done in 2 M NaOH solutions at room temperature with HX flocculants. It was found that the settling rate declined as the pre-conditioning time increased, initially halving after only 1 h of conditioning before reaching a plateau from 4-48 h. This observation indicated that agglomeration exists within the hematite solids used to make the slurry. Therefore, another method of pre-treatment was developed to achieve more complete dispersion, with the steps summarised in the following sequence: (1) stir at 700 rpm and 70°C for 1 h, (2) stir at 300 rpm and 70°C for 1 h, (3) sonicate at 70°C for 10 min, (4) stir at 300 rpm and 70°C for 5 min, (5) transfer into 250 mL graduated cylinders, (6) heat in the oil bath to 95°C, (7) apply 5 plunger strokes to equilibrate prior to flocculant addition.

Settling rates measured after flocculation of slurries prepared by this method were independent of the slurry ageing time (Table 1), which validated the method for further used in this study. However, the supernatant solids showed a significant increasing trend with respect to flocculant aging time, most evident at times >75 minutes. It was therefore important to ensure completion of any series of batch settling experiment in less than 75 minutes from commencement of the first test.

Table 1. Reproducibility of hematite slurry settling data

Ageing time (min)	Settling rate (m h^{-1})	Supernatant solids (ppm)	Bed height (mL)
15	27.4	6	45
30	28.0	12	46
45	24.5	16	45
60	25.8	24	46
75	25.8	16	46
130	22.8	46	48

Table 2. Reproducibility of hematite and DSP mixture slurry settling data

Replicate	Settling rate (m h^{-1})	Supernatant solids (ppm)	Bed Height (mL)
1	14.5	190	44
2	18.4	190	43
3	15.6	150	44
4	16	160	44
Mean	16.1	173	44
SD	1.6	21	1

3.2 Reproducibility of hematite/DSP slurry

To prepare hematite/DSP mixtures, a slurry of hematite and kaolin were digested together (at 90°C for 24 hours), filtered, washed, re-pulped and then stored in synthetic sodium aluminate solution overnight. The detrimental effect of CO_3^{2-} and Si on the flocculation of hematite by PAA was previously reported by Jones (1998), and therefore filtration and washing of the solids were required to remove any remaining silicate and other anions (CO_3^{2-}, Cl^-, SO_4^-) from the digestion liquor (their individual impacts will be examined at a later stage). The reproducibility of this method is evident in Table 2. Although the results are not shown, soaking the hematite/DSP cake in the synthetic liquor overnight does not significantly change its dewatering properties and the variances with those tested immediately are found to be within experimental error (<10% for settling rate, supernatant clarity and bed height).

3.3 Temperature of dosed flocculants

At some Bayer plants, secondary dilution of flocculant solutions is undertaken with hot liquors; this not only increases the volume added, but the lower viscosity of the flocculant at temperature is also thought to help mixing through the slurry. In such cases the dilution is typically only achieved just seconds prior dosing into the slurry. Contrast this with a batch settling test performed at a high temperature (≥90°C), for which the flocculant solution is held at either, room temperature, 45 or 75°C prior to addition. No short-term ageing was observed for any of the flocculants when added as a room temperature solution to the hot slurry. Ageing was also minimal over a 45 minute period when flocculant solutions were held at 45°C (Figure 2). However, the hydroxamate flocculant HX 300 did display some loss in activity over time at 75°C. It is important to stress that this result is irrelevant to plant applications, but has implications for laboratory comparisons of flocculants, stressing the need to hold diluted flocculant solutions at a low-to-moderate temperature, or to only hold at higher temperatures for a very short time. This is not always done, and can lead to irreproducible results and invalid product comparisons.
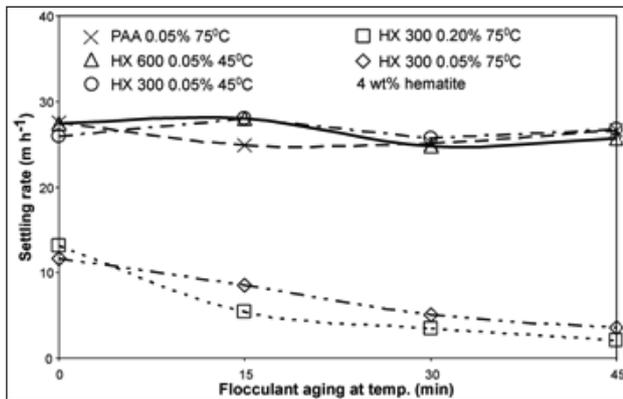
Figure 2. Effect of temperature of dosed flocculants on settling rates.
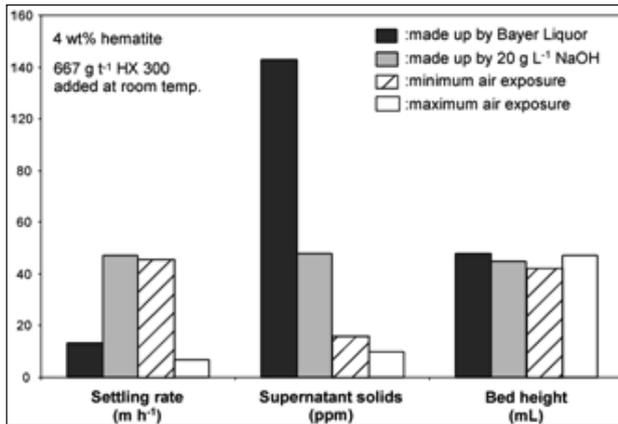

Figure 3. Effect of flocculant make-up on settling rates.

3.4 Concentration of dosed flocculants

The concentration of the flocculant solution as applied during flocculation can be one of the factors that affect settling properties, because the degree of mixing (and as a consequence, the effectiveness of flocculant distribution and adsorption) can also be different when the flocculants are added as dilute or concentrated solution at the same g t^{-1} dosage. To assess this, the settling data derived from two different concentrations of addition (0.05 and 0.20%) are compared and contrasted in Figure 2. Apparently, there was no difference since both concentrations resulted in the similar decreasing trend of settling rate when the flocculants were aged at 75°C.

3.5 Flocculant shelf life

It was proposed that contact with air may have led to an acceleration of the time-based loss of activity for 1% solutions of the HX flocculants. To test this, 300 mL of HX 300 1% solution was prepared, of which 200 mL was kept in a 200 mL jar, thereby ensuring a minimum presence of air. The remaining 100 mL portion was also stored in an equivalent jar, such that 50% of the volume is occupied by air. Settling tests done after 2 days showed a settling rate from the former to be at least six-fold higher than latter (46 vs. 6.7 m h^{-1}, see Figure 3). This problem was overcome by storing HX 1% solutions in several small bottles (50 mL) with a very limited head space, and no stock solution was retained for longer than 2 days.

4. The impact of DSP on settling properties

4.1 DSP content

Simulated digestions were conducted at hematite-to-kaolin ratios of 1:0, 10:1, 6:1, 5:1, 4:1 and 3:1, equating to DSP product contents of 0, 11, 18, 21, 25 and 31%, respectively. The settling rate responses to dosage for the different slurries at 4 wt% solids are presented in Figure 4. For both PAA and HX flocculants, increasing DSP content led to higher dosages required to achieve

similar settling rates to pure hematite. At fixed HX 300 and PAA dosages of 533 and 117 g t^{-1}, respectively, the settling rate dropped from 30 to ~5 m h^{-1} when the DSP content increased from 0 to 31% (Figure 5), while the corresponding supernatant solids increased almost twentyfold, from 20 to 400 ppm. While the performance of both flocculant deteriorated, the HX product gave an overall better resistance to the increase of DSP content. It is of interest that no significant adverse effect was seen in the case of consolidation behaviour when the HX flocculant was used, yet an increasing bed height (lower settled density) resulted at higher DSP content for PAA.
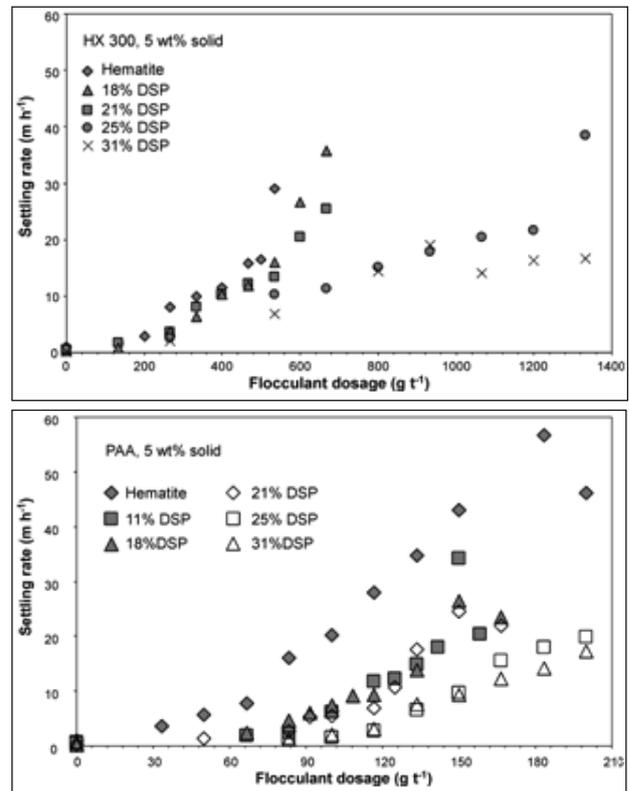

Figure 4. The effect of DSP content on the settling properties of hematite slurry.
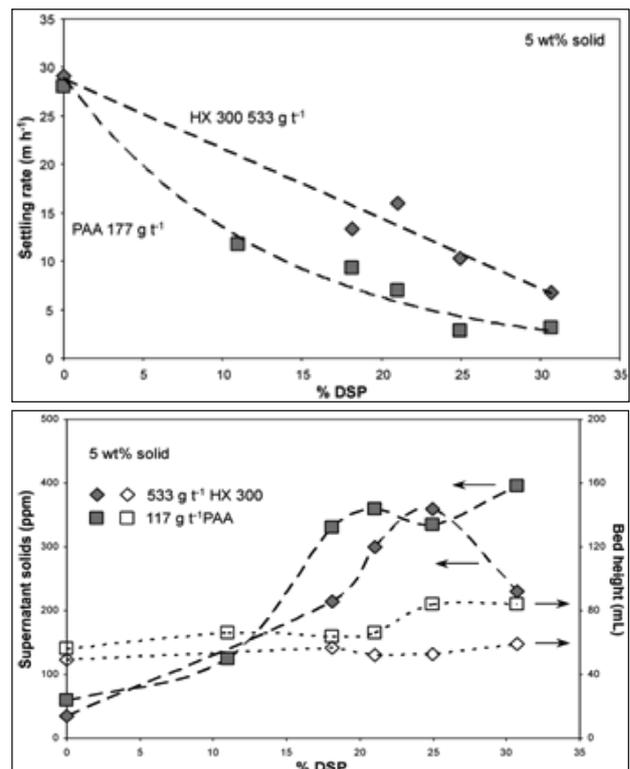

Figure 5. The effect of DSP content at a constant flocculant dosage.

In their study of DSP effects, Davis et al. (2010) added DSP to a bauxite residue sample from an operating refinery, observing settling rates and supernatant solids higher than obtained here for hematite/DSP mixtures. The very fine hematite (mostly 0.1-5 μm) used in this study largely explains the slower settling rates, and may contribute towards lower supernatant solids, given that a more definite mudline may help to "drag down" some unflocculated fines. However, the latter result could also be evidence of other solid phases that are not captured by the flocculant within the complex mineralogy of the bauxite residue solids.

PSDs of the starting hematite and discrete DSP that was made without the presence of hematite are given in Figure 6A, while those for the hematite/DSP mixtures are in Figure 6B. A higher proportion of 5-20 μm solids with increasing DSP content is apparent from the latter. While much of the hematite used is finer than the DSP as formed, it is the presence of this DSP that results in the decline in flocculant performance as seen in Figures 4 and 5.
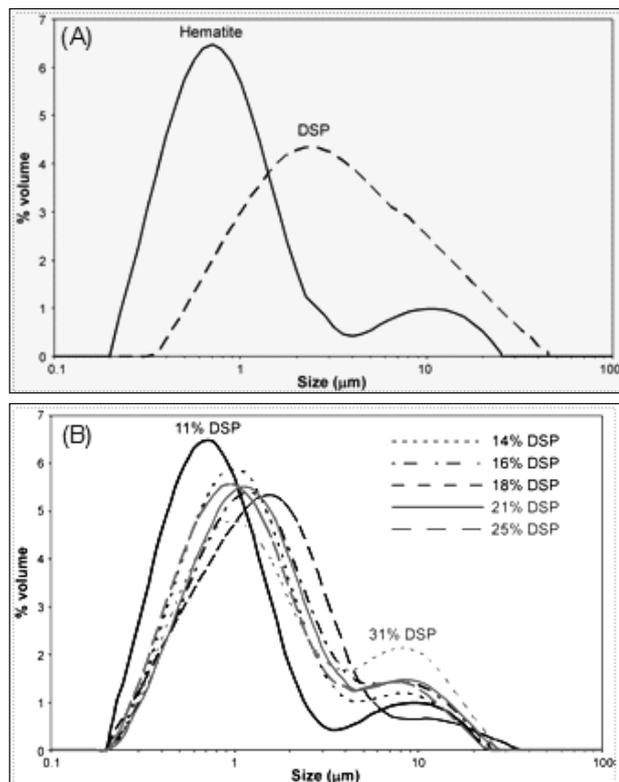

Figure 6. Measured PSD of (A) distinct hematite and DSP; (B) hematite/DSP mixtures.

4.2 Effect of solids concentration

A major flaw in many flocculation studies is to compare settling behaviour at only a single fixed solids concentration. Changes in particle size and aggregate structure both alter the flocculation response, and this can only be properly captured by quantifying flocculation at a range of solids concentrations.

The curves of settling rate vs HX 300 dosage for both hematite and hematite with 31% DSP show that higher flocculant dosages are required as the solids concentration increases (Figure 7A). For hematite alone the shift to higher dosages is significant, but the dosage curve remains quite steep; in contrast, the increase in total solids in the presence of DSP resulted in the dosage curves flattening out to the point that high settling rates could not be achieved. When these results are replotted as settling flux vs. wt % at a fixed flocculant dosage (333 g t⁻¹ HX 300), it can be seen that the response for hematite alone was much flatter, i.e. it did not decline greatly between 4 and 7 wt% (Figure 7B); in the presence of DSP, the settling flux was consistently much lower and was very sensitive to solids concentration.
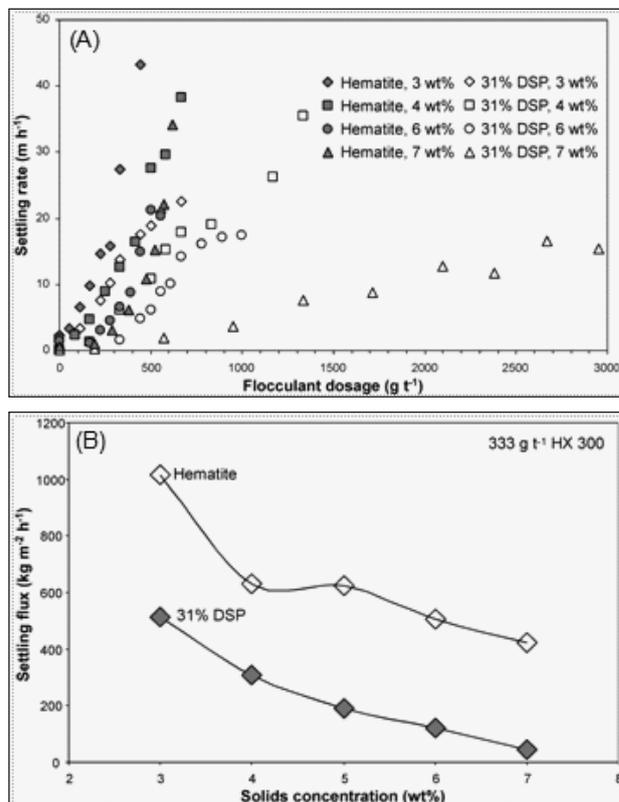

Figure 7. Plot of (A) settling rate vs. flocculant dosage, (B) settling flux vs. wt% solids (333 g t⁻¹ HX 300) for hematite and hematite/ DSP (31% DSP) slurries.

5. FBRM results

5.1 Effect of DSP content

The mean square-weighted chord length as a function of time for the split addition of HX 300 and the single addition of PAA to hematite/DSP mixtures is shown in Figure 8A and B, respectively. In both cases the decline in aggregate size with increasing DSP content is captured, as is the sensitivity of the aggregates to prolonged agitation.
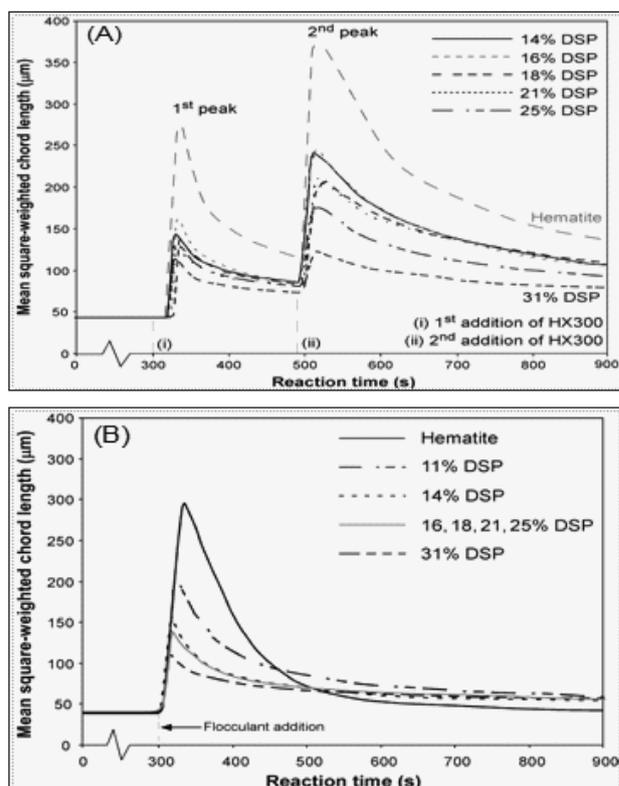

Figure 8. Plot of mean square-weighted chord length vs. reaction time of hematite/ DSP mixture (31%) flocculated by (A) HX 300 and (B) PAA.

The unweighted chord length distributions obtained with FBRM are sensitive to both the extent of flocculation and the efficiency of the process (i.e. the presence of fines). When measured at the peak following the 2nd addition of HX 300 (Figure 9A) show that increasing DSP content led to higher <40 μm counts, but this simply reflects smaller aggregates. The absence of bimodal character in these distributions suggests that while the extent of flocculation is limited, the majority of fine particles are still being captured, i.e. DSP is being flocculated.

Increasing DSP content also decreased the maximum aggregates size (as represented by the maximum mean square-weighted chord length) in a manner that was flocculant dependent (Figure 9B). For slurry flocculated by HX300, the maximum aggregate size decreased linearly with DSP content, whereas with polyacrylate the size dropped sharply when low (11%) DSP content was introduced, reached a plateau between 15 and 31% DSP. These trends are consistent with the settling rates responses for HX and PAA use shown in Figure 5.
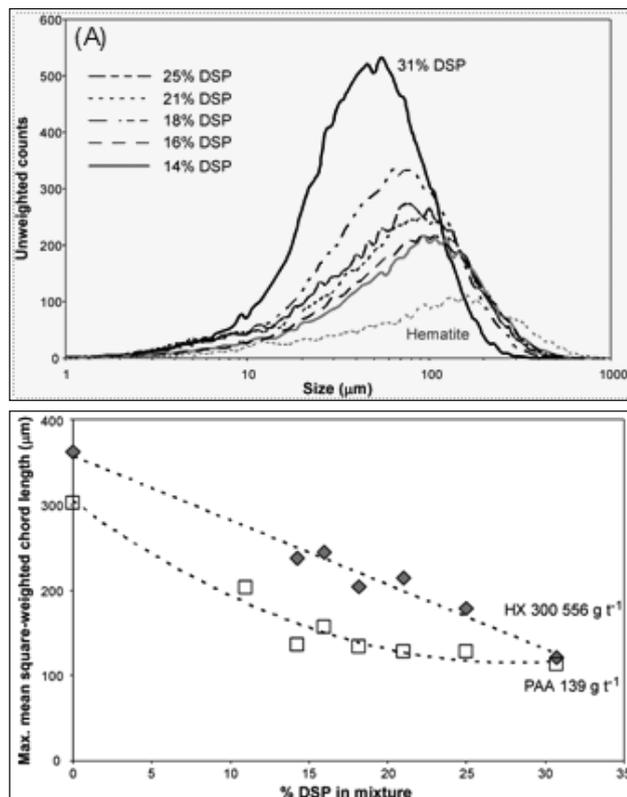

Figure 9. Effect of DSP content on the: (A) unweighted counts of hematite/DSP slurry flocculated by HX 300 at 2nd peak and (B) maximum mean square-weighted chord length of hematite slurry flocculated by HX 300 and PAA.

5.2 Effect of flocculant dosage

In contrast to pure hematite slurries, the 2nd stage addition of HX 300 to 31% DSP slurries did not in all cases generate aggregates larger than those produced following the 1st addition (Figure 10 A). The expected size enhancement from the 2nd addition was evident in the presence of DSP up to a combined dosage of 556 g t^{-1}, but beyond this dosage the maximum aggregate size from the 2nd addition never approached that initially achieved, despite representing a large additional dose. The impact on the maximum aggregate size is shown in Figure 10B, and may be consistent with the settling rate results in Figure 4, in which high DSP content led to a plateau in the flocculant dosage.

The seminal work by von Smoluchowski (1917) established that the rate of aggregate formation was proportional to the number of binary particle or aggregate collisions, with La Mer and Healy (1963) later modifying this to include a collision efficiency factor (E_{ij}), taking into account that not all collisions will result in (for flocculation) a bridging adhesion. All other variables being constant, the collision efficiency will be related to dosage through the fraction of surface coverage, and at high surface coverage, E_{ij} can begin to decline. In most mineral processing applications, surface coverage will be quite low, and aggregation increases with increasing dosage. The results in Figure 11 suggest that the presence of DSP interacting with the hematite surface may in effect deactivate the available sites for flocculant adsorption, thereby leading to a reduction in E_{ij}. This is an area of considerable interest in understanding the influence of DSP, and is being examined in more detail.

6. Conclusions

Previous investigations of bauxite residue flocculation are expanded upon through a systematic examination of how DSP impacts upon the flocculation process, preparing DSP in the presence of a model substrate (hematite). To achieve this, it has been necessary to carefully isolate contributions from the make-up and handling of flocculants and slurries that may otherwise complicate the observed flocculation performance. While still at an early stage, this study has shown that flocculated settling fluxes were consistently lower in the presence of DSP and very sensitive to solids concentration. Increasing DSP content within the hematite slurry gave poor dewatering properties; the severity of this effect was flocculant dependent, with HX flocculants responding better than simple PAA. FBRM examination of dosage effects on aggregate sizes during flocculation suggests a reduction in the effective surface area available to flocculants as a consequence of the introduction of DSP. The next step will be to extend these studies to the new generation flocculants containing a silane functionality believed to interact with DSP surfaces.

7. Acknowledgements

References

Basu, P 1983, Reactions of iron minerals in sodium aluminate solutions, in: Light Metals 1983, ed. EM. Adkins, TMS, Atlanta, pp. 190-196.

Bublik, E, Happs, C, Odor, G, Revesz, L & Sartowski, Z 1986, The use of synthetic polymer in alumina production, in: Proceedings of the 5th Yugoslav International Symposium on Aluminium, eds. A. Paulin & A. Smolej, Mostar, Univerza Edvarda Kardelja, pp. 505-517.

Chen, HT, Ravishankar, SA & Farinato, RS 2003, Rational polymer design for solid-liquid separations in mineral processing applications. *International Journal of Minerals Processing*, vol. 72, no. 1-4, pp. 75-86.

Dai, Q, Davis, MJ, & Zhang, R 2010, New flocculants for improved processing of high silica bauxites, *Travaux*, vol. 25, no. 39, pp. 200-204.

Davis, M, Dai, Q, Chen, HLT & Taylor, M 2010, New polymers for improved flocculation of high DSP-containing muds, in: Light Metals 2010, ed. JA. Johnson, TMS, Seattle, pp. 57-61.

Eckart, D, Kildea, J, Nicholson, D & Prinsloo, P 2010, Improved performance of red mud settlers at Worsley Alumina, in: Light Metals 2010, TMS, Seattle, pp. 107-112.

Gerson, AR & Zheng, K 1997, Bayer process plant scale: transformation of sodalite to cancrinite, *Journal of Crystal Growth*, vol. 171, no. 1-2, pp. 209-218.

Heath, AR, Fawell, PD, Bahri, PA & Swift, JD 2002, Estimating average particle size by Focused Beam Reflectance Measurement (FBRM), *Particle & Particle System Characterisation*, vol. 19, pp. 84-95.

Jones, F 1998, The mechanism of Bayer residue flocculation, Ph.D thesis, Curtin University of Technology.

Kahane, RB & McRae, C, 1996, Improved bauxite residue settler performance at Worsley Alumina, In: 4th International Alumina Quality Workshop, AQW, Darwin, pp.227-237.

Kirwan, LJ 2009a, Investigating bauxite residue flocculation by hydroxamate and polyacrylate flocculants utilising the focussed beam reflectance measurement probe, *International Journal of Minerals Processing*, vol. 90, no. 1-4, pp. 74-80.

Kirwan, LJ 2009b, A study of polyacrylate and hydroxamate co-dosing flocculation of stabilized bauxite residue material, *International Journal of Minerals Processing*, vol. 91, no. 1-2, pp. 28-33.

Kotte, JJ 1981, Bayer digestion and predigestion desilication reactor design, in: Light Metals 1981, ed. PG. Campbell, TMS, Chicago, pp. 46-81.

La Mer, WK & Healey TW 1963, Adsorption-flocculation reactions of macromolecules at the solid-liquid interface, *Reviews of Pure Applied Chemistry*, vol. 13, pp.112-133.

Li, LY & Rutherford, GK 1996, Effect of bauxite properties on the settling of red mud, *International Journal of Minerals Processing*, vol. 48, no. 3-4, pp. 169-182.

Lowe, JL 2007, DSP in the Bayer process: a fundamental study of its precipitation and role in impurity removal, PhD thesis, Curtin University of Technology.

Oku, T & Yamada, K 1971, The dissolution rate of quartz and the rate of desilication in the Bayer liquor, in: Light Metals 1971, ed. TG. Edgeworth, TMS, New York, pp. 31-45.

Owen, AT, Fawell, PD, Swift, JD, Labbett, DM, Benn, F & Farrow, JB 2008, Using turbulent pipe flow to study the factors affecting polymer-bridging flocculation of mineral systems, *International Journal of Mineral Processing*, vol. 97, no. 3-4, pp. 90-99.

Peiwang, L, Zhijian, L, Yucai, L, Hailong, C, Fengling, W & Hong, W 1994, The influence of the predesilication temperature of bauxite slurry on the sedimentation of red mud and the utilization of which in alumina production, in: Light Metals 1994, ed. U. Mannweiler, TMS, San Francisco, pp. 133-136.

Phillips EC 2004, Continued efforts on the development of salicylic acid containing red mud flocculants, in: Light Metals 2004, ed. AT. Tabereaux, TMS, North Carolina, pp. 21-26.

Rousseaux, J-M, Cristol, B & Torsiello, S 2004, Combination of hydroxamate and polyacrylamide based flocculants for settler performance improvement in ADG alumina refinery, in: Light Metals 2004, ed. AT. Tabereaux, TMS, 2004, North Carolina, pp. 15-20.

Sankey, SE & Schwarz, RJ 1984, The use of synthetic flocculant polymers in settling red muds derived from high goethite bauxite ores, in: Light Metals 1984, ed. JP. McGeer, TMS, Los Angeles, pp. 1653-1667.

Smith, P 2009, The processing of high silica bauxites - Review of existing and potential processes, *Hydrometallurgy*, vol. 98, no. 1-2, pp. 162-176.

von Smoluchowski, M 1917, Versuch einer mathematischen theorie der koagulationskinetik kolloider losungen. *Zeitschrift für physikalische Chemie,* vol. **92**, pp. 129–168.

Spitzer, DP, Rothenberg, AS, Heitner, Hl, Lewellyn ME, Laviolette LH, Foster T, & Avotins, PV 1991, Development of new Bayer process flocculants, in: Light Metals 1991, ed. E. Rooy. TMS, New Orleans, pp. 167-171.

Whittington, BI, Fletcher, BL & Talbot, C 1998, The effect of reaction conditions on the composition of desilication product (DSP) formed under simulated Bayer conditions, *Hydrometallurgy*, vol. 49, no. 1-2, pp 1-22.

Yamada, K, Harato, K & Shiozaki, Y 1980, Flocculation and sedimentation of red mud, in Light Metals 1980, ed. CJ. McMinn, TMS, Las Vegas, pp. 39-50.