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**ALUMINA AND BAUXITE**

## **Clarification**

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## SODALITE SOLIDS FORMATION AT THE SURFACE OF IRON OXIDE AND ITS IMPACT ON FLOCCULATION

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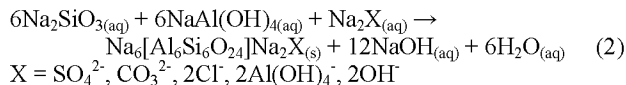
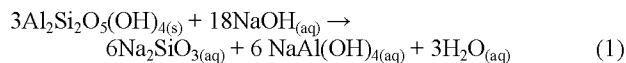
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### Abstract

Sodalite represents the main desilication product (DSP) phase formed from reactive silica during alkaline digestion of bauxite in the Bayer Process. Previous studies into DSP effects on bauxite residue flocculation have focused on flocculant selection or digestion optimisation, not answering a fundamental question: does DSP coat the residue and thereby change surface properties? This study sought to answer that question by contrasting the physicochemical properties of hematite slurries (as a model phase for residue) containing DSP where it was either made *in-situ* or added as a physical mixture. On the basis of differences found in dewatering behaviour, zeta potential, desilication rates and microscopy of the solids, it is proposed that DSP nuclei initially associate with the hematite surface and subsequently affect flocculant adsorption chemistry, resulting in different extents of flocculant adsorption and smaller aggregates. The practical implications for flocculation processes are discussed.

### Introduction

The Bayer Process is the dominant hydrometallurgical route for producing alumina, involving alkaline digestion of bauxite at elevated temperatures and pressure to form super-saturated aluminate liquors and a solid residue phase. A pre-desilication step, in which bauxite slurry is held at ~100°C (at atmospheric pressure) for 4-16 h, is involved when feeds contain a significant reactive silica fraction, typically as kaolin [1]. DSP forms through dissolution of the bauxite's reactive silica (Equation 1) and the precipitation of dissolved silica as aluminosilicate solids (Equation 2):



Pre-desilication of high silica bauxite mitigates the risk of post-digestion sodium aluminosilicate precipitation and scaling [2]. However, it creates a burden on the solid/liquid separation stage, with potential detrimental effects including increased flocculant demand, poor fines capture and a greater requirement for solids dilution prior to flocculation [3-5].

Results in previous studies were derived from substrates prepared by different methods, with DSP origin referred to as either "bauxite" or "synthetic". The former refers to DSP from the mineral's reactive silica, the latter to pre-addition of kaolin. The effect of DSP content was studied by mixing it with bauxite residue in all cases, except in the work by Senaputra et al. [5],

who used hematite as a model phase. Conventional polyacrylate (PAA) flocculants have been examined as well as hydroxamates (HX) and newer generation High-silica (High-Si) products (all from Cytec). Only Davis et al. [4] considered both *in-situ* and physically mixed DSP, but this was only for the evaluation of flocculant products, with no insights into the substrate surface properties sought.

To date, no detailed investigation has been undertaken to explain whether (i) DSP precipitates onto the major substrate surface, thereby changing the surface properties, or (ii) it precipitates as a distinct minor phase. From a flocculation perspective, it is important to answer this fundamental question, as it potentially affects how the industrial process may be optimised. Surface coverage by secondary nuclei may lead to less surface being available for flocculant adsorption, influencing aggregation kinetics and aggregate density. Precipitation as a separate phase increases the number of particles in the slurry, with aggregation then dependent on the activity of the new surfaces. Both processes can lead to a reduction in the optimum solids concentration for flocculation, but for very different reasons. The responses will also be very much dependent on the active flocculant functionalities and their potential to interact with the surfaces.

Various forms of iron oxide are reported to host the precipitation of different solid species in the sodium aluminate solution. Goethite, hematite and magnetite can act as seeds in Bayer liquor to promote  $\text{Al}(\text{OH})_3$  precipitation [6]. DSP (sodalite) can also deposit onto 316-stainless steel surfaces [7]. These facts suggest that iron oxide (either as a major residue phase or as a model substrate) might also exhibit the same seeding character for DSP.

Cylinder settling tests following flocculation are by far the most common method used to identify changes in particle properties in such studies and are also applied here. However, they need to be viewed with some caution. The reproducibility of settling rate measurements is hampered by a high standard error, which even in the best circumstances can be 8-12% [8]. Additional supporting evidence is therefore required, preferably by direct measurements on the solids and slurries. Hence, in the present work, the following measurements were performed on hematite/DSP mixtures prepared by different methods:

- Zeta potential as a function of pH to thereby derive isoelectric points (iep). Such measures are well known for their relevancy to the coagulation and flocculation phenomena. Zeta potentials for bauxite residue have been found to be sensitive to aggregation state, ionic strength and mineralogy [9], but DSP effects were not considered.
- Variation of the desilication (sodalite precipitation) rate. If the presence of hematite results in a higher precipitation rate, it can be implied that it promotes crystallization and DSP might partially or completely cover the hematite surface [6].

- SEM of the post-digested hematite surface. An SEM image will display the proliferation of DSP precipitates on the hematite surface if heterogeneous nucleation is the rate determining step [7].

The results are then discussed in terms of practical implications for the flocculation of bauxite residue slurries. In addition to the impact seen on the settling rate, information about aggregate size and the extent of flocculant adsorption influenced by the presence or absence of DSP is also obtained to seek a better understanding of the flocculation process at a fundamental level.

### Experimental

The experimental part of this study involves three major foci: (i) synthesizing various DSP and hematite slurries (through digestion), (ii) comparing slurry physicochemical properties (through settling tests, zeta potential analysis, desilication tests and SEM) and (iii) examining other possible impacts on flocculation (through flocculant adsorption and FBRM tests).

#### DSP Synthesis and Characterisation

Unless otherwise stated, for *in-situ* DSP formation in the presence of a model phase, hematite (Aldrich) and kaolin (Eckalite, Imerys Minerals) were digested at a ratio of 3:1 (produces ~ 31wt% DSP). Previous studies by our group confirm that sodalite is the only DSP phase detected by X-Ray Diffraction (XRD) when kaolin reacts with the so-called “digestion” liquor of the following composition: C = 230 g L<sup>-1</sup>, A/C = 0.35, C/S = 0.84, SO<sub>4</sub><sup>2-</sup> = 20 g L<sup>-1</sup>, Cl<sup>-</sup> = 10 g L<sup>-1</sup> at 90°C and 24 h [5]. For producing a physical mixture of model iron oxide and DSP, hematite was added after digestion.

Particle size distributions (PSD) were measured by a laser sizing method on sub-samples from suspended slurries. Surface area and pore structure analysis were determined using Brunauer, Emmet and Teller (BET) and Barrett Joyner Halenda (BJH) gas adsorption methods on dried samples. Solids dried at an elevated temperature (105°C) needed grinding; to avoid this, drying was performed at room temperature in a vacuum desiccator for a week before light grinding and re-drying to constant weight at 105°C.

#### Cylinder Batch Settling

To remove solution silica and ensure stability for settling tests, digested slurries were filtered (0.45 μm), washed (5 × 200 mL water), and the so-called “testwork” liquor added (C = 230 g L<sup>-1</sup>, A/C = 0.35, C/S = 0.99) prior to overnight equilibration. Settling experiments were also conducted with slurries immediately after digestion to confirm settling properties were not affected. To avoid slurry aging and achieve stable dispersion, they were pre-treated at a high stirring rate (700 rpm for 1 h and 300 rpm for 1 h at 70°C) and sonicated (10 min) immediately prior to settling tests all conducted at 95°C [5].

The flocculant used was Alclar 665 (100% anionic, BASF). Stock solutions (0.5 wt%) were prepared by wetting with ethanol (~2 mL) prior to dilution by water, with gentle agitation on a shaking table for 24 h to ensure dissolution. After dilution in 20 g L<sup>-1</sup> NaOH, the flocculant solution (at 45°C) was added as a single dose and the number of plunger strokes was five (a single stroke considered as both down and up). Settling rates were calculated from the linear portion of the plot of mud-line height vs. time.

Supernatant solids were determined gravimetrically on 20 mL samples taken from a given height one min after the last stroke (or immediately after the mud-line passed that point in slow settling cases). Consolidation behaviour was quantified from the bed height after 30 min.

#### Zeta Potential Determination

Zeta potential can be calculated by measuring the electrophoretic mobility and using the Henry equation (Equation 3):

$$z = \frac{3U_E \eta}{2 \epsilon f(ka)} \quad (3)$$

Where  $z$  is zeta potential,  $U_E$  is electrophoretic mobility,  $\eta$  is viscosity,  $\epsilon$  is dielectric constant, and  $f(ka)$  is Henry function. Such determinations were carried out on a Malvern Zetasizer ZS using Phase Analysis Light Scattering (PALS).

A low ionic strength (0.01 M NaCl) was chosen because electrophoretic mobility is difficult to measure at high ionic strength, a consequence of the large current required and its resultant distortion of particle movement [10]. The physical properties of pure water, such as dielectric constant and viscosity, can be used in the calculation results and do not introduce significant errors. Therefore, filtration and washing as done for settling tests was also required before the cake was re-suspended in 0.01 M NaCl (ambient temperature) and sub-sampled for the measurement. Since the iep of various hematite samples is reported to range from 5.5 to 9.3 [11], zeta potential determination was conducted on pure hematite, pure DSP and its mixtures at a pH range of 5-11 despite the fact that sodalite starts to dissolve at a pH less than 5.5 [12]. Accordingly, the measurements were done immediately (well within 10 min) after pH adjustment.

The challenge of utilising this method lies in distinguishing the hematite particles, which could be partly or completely covered by DSP nuclei and mimic the behaviour of DSP. A practical characteristic, seen in our previous study [5], is that hematite is typically 0.1-10 μm and synthetic DSP 0.3-40 μm, which helps somewhat. By filtering the re-suspended hematite and DSP slurry through a 0.2 μm membrane, hematite can be separated from DSP. For zeta potential determination, the hematite:kaolin ratio in the digestion was 10:1.

#### Desilication Experiment

Batch precipitation tests (“testwork” liquor, SiO<sub>2</sub> = 2 g L<sup>-1</sup>, precipitation time: 2.5-30 min) were conducted to test if hematite (45 g L<sup>-1</sup>) provides active sites to host DSP nuclei. Soluble silica from dissolved silicic acid (SiO<sub>2</sub>·xH<sub>2</sub>O) is preferable here as the source of silica, as unreacted kaolin may also act as seed. Preliminary tests showed that the unseeded desilication rate from soluble silica sources at 90°C is very slow; hence, the temperature was raised to 150°C by using a 250 mL stainless bomb connected to a thermocontroller and heated by a gas-fired flame. Afterwards, the pulp was centrifuged (10 min) and filtered (0.45 μm) to obtain clear solution for ICP determination of soluble silicon.

#### SEM Analysis

Visual evidence for deposition and/or growth of DSP on a hematite surface was sought from SEM. The flat surface ideally required was provided by polishing a natural hematite rock

mounted in high-temperature resistant resin on 400 and 1200 grit sand papers, respectively. Digesting this hematite slab in the presence of 40 g L<sup>-1</sup> kaolin was conducted for 24 h at 90°C in the “digestion” liquor to generate the post-desilication surface profile. After digestion, the slab was sonicated for 10 min in an ultrasonic bath to release physically attached DSP, its surface was rinsed and carbon coated prior to viewing on an Evo Zeiss SEM instrument. In addition, Energy Dispersive X-ray spectroscopy (EDX) was used to determine elemental composition, with the data collected at a working distance of 9.5 mm at a voltage of 15 or 20 kV.

### Adsorption Test

Flocculant adsorption tests sought to identify effective surface coverage for different substrates (hematite, DSP and its mixtures). Slurry filtration, washing and liquor replacement by “testwork” liquor was conducted, producing slurry at 5 wt% solid that was equilibrated overnight and suspended at 70°C. Flocculant (at ambient temperature) was injected to slurry then stirred at 300 rpm for 15 min to ensure optimum adsorption. For comparison to adsorption at a pH of 5 (ambient temperature, 0.2 M NaCl solution matrix) a 50% anionic powder flocculant (Magnaflow 919, BASF) was used.

Determination of residual flocculant was required to calculate the adsorption isotherm, and was achieved by the Hyamine turbidity method [13]. A sample of post-adsorption slurry was centrifuged for 30 min at 4500 rpm, then (to avoid autprecipitation) 10 mL of gluconate solution (concentration 400 g L<sup>-1</sup>) was mixed with 30 mL of supernatant. After equilibration, 20 mL was added to a vial containing 5 mL of Hyamine 1622 solution (4 g L<sup>-1</sup>). The measured turbidity (NTU) was converted to ppm following calibration with known flocculant-containing solutions. A filtration method, which utilises the relationship of efflux time vs. flocculant concentration in the liquor, must be used for the solution from pure DSP slurries since the blank (no flocculant) solution from the DSP slurry reacts with Hyamine and causes an unidentified precipitation (presumably from dissolved silicate).

### FBRM Study

FBRM experiments were comparable to those for adsorption tests, except the aggregate size data as a function of reaction time and shear was measured in 2 wt% slurries. A Lasentec M500 probe (Mettler Toledo) with C-electronics was used for *in-situ* data collection. Data collection was over 90 log channels from 1 to 1000 μm, with each measurement of 2 s duration then averaged over 5 measurements. The raw chord length data is intrinsically only length-weighted, offering sensitivity to fines, while applying a length square-weighting provides an effective volume-weighted relationship, more representative of aggregate size.

## Results and Discussion

### Settling Test

Figure 1 shows that settling rates of hematite and DSP slurry as a physical mixture were always higher than when DSP was made *in-situ*, regardless of pre-treatment. Although not shown here, it is also of interest that the PSD of the slurries were very similar to each other. Higher post-flocculation supernatant solids for the physically mixed slurry might indicate higher fines (particle numbers), a consequence of DSP precipitation as a separate phase

(Table I). These results demonstrate that there is a surface interaction between DSP and hematite during DSP formation.

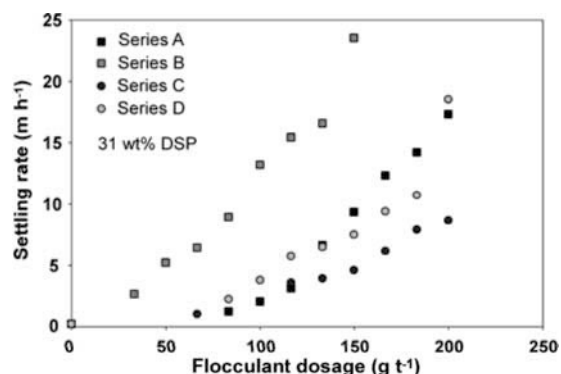


Figure 1. Settling rate vs. dosage for hematite and DSP slurries (Series refer to Table I)

Table I. Settling properties of hematite and DSP slurries

	Mixture	Washing Filtration	Settling Rate (m h <sup>-1</sup> )	Supernatant Solids (ppm)	Bed Height (mL)
A	In-situ	Yes	17.3	235	72
B	Physical	Yes	23.5	430	61
C	In-situ	No	8.6	340	84
D	Physical	No	18.5	380	81

The difference in settling rate was less pronounced in the absence of washing and filtration (series C and D) but a notable gap still remained at higher dosages (~200 g t<sup>-1</sup>). This may be due to the deleterious effect of remnant silica as reported by Jones [13], where dissolved silica is adsorbed onto hematite and decreases the settling rate proportionally. Liquor analysis proved there was ~120-130 ppm of SiO<sub>2</sub> in the unwashed slurry samples; Jones [13] attributed a substantial reduction in settling rate (~10 m h<sup>-1</sup>) to such levels of solution SiO<sub>2</sub>.

### Zeta Potential Determination

The zeta potential of *in-situ* prepared hematite/DSP slurry was very similar in magnitude to that of pure DSP (Figure 2), whereas that of the physical mixture of hematite and DSP is likely to be a combination between the values of the pure phases. This observation is also seen in the case of the iep, which increases in the order: hematite < physical mixture hematite/DSP (6.5-7) < *in-situ* prepared hematite/DSP (8) ≈ pure DSP (8).

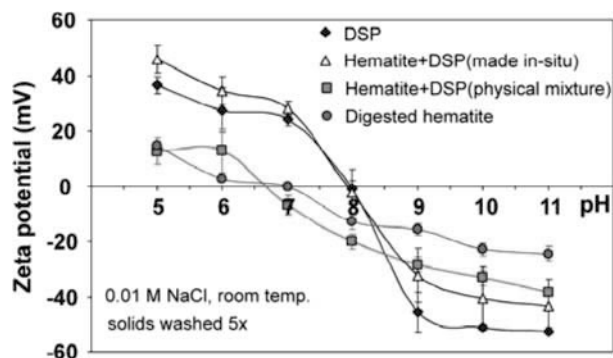


Figure 2. Zeta potential of hematite and other suspension samples

It can then be inferred that DSP, to some extent, coats the surface of hematite. Although the iep of the *in-situ* prepared hematite/DSP suspension is in the reported range (6.5-8.5), the iep of pure DSP suspension is surprisingly higher than most known values for silica or kaolin (summarised in Kosmulski and Rosenholm [11]), however details on this phenomenon are outside the scope of this study.

### Desilication Rate

At 150°C the desilication behaviour of both seeded and unseeded experiments from a dissolved silica source followed the classical precipitation characteristic, initially being relatively fast before slowing as approaching an equilibrium extent (Figure 3). At 2.5 min, a remarkable difference was seen, with the seeded experiment achieving 58% desilication compared to only 1% in the unseeded case (844 vs. 1990 ppm of SiO<sub>2</sub> in solution, respectively). However, this gap became smaller as both cases approached the equilibrium of ~75% desilication. Like the zeta potential results, the desilication experiment also indicates that hematite seeds were partly covered by DSP nuclei during precipitation.

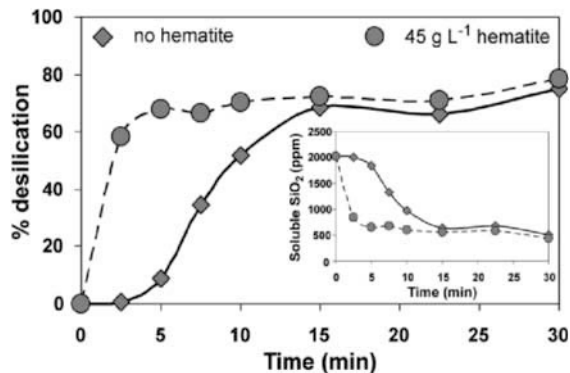


Figure 3. % desilication as a function of time

### SEM

SEM images of hematite surfaces before and after desilication are shown in Figure 4A and B, respectively. The appearance of nodules after desilication clearly reflects the deposition of DSP. Analysis by EDS failed to observe any localisation of silicon and aluminium content at those nodules; in fact both elements are evenly distributed in the area examined. This is not unexpected since adsorption (and subsequent desorption) of species containing these elements is evident even after repeated washing.

### FBRM study

In the FBRM study, a steady rise in aggregate size (represented by the maximum mean square-weighted chord length) as a result of higher flocculant dosages was seen in the case of hematite alone (Figure 5A); in contrast, a much weaker response to the higher flocculant dosages was seen for hematite with DSP made *in-situ* (Figure 5B). This observation is consistent with the results of the hematite with DSP made *in-situ* slurry flocculated by a hydroxamated-terpolymer [5]. Achieving a smaller aggregate size could be a physical factor responsible for the slower settling rates (Figure 1), but this can also be influenced by the aggregate density and its effect on the system's response to solids concentration; such aspects are the subject of further detailed studies.

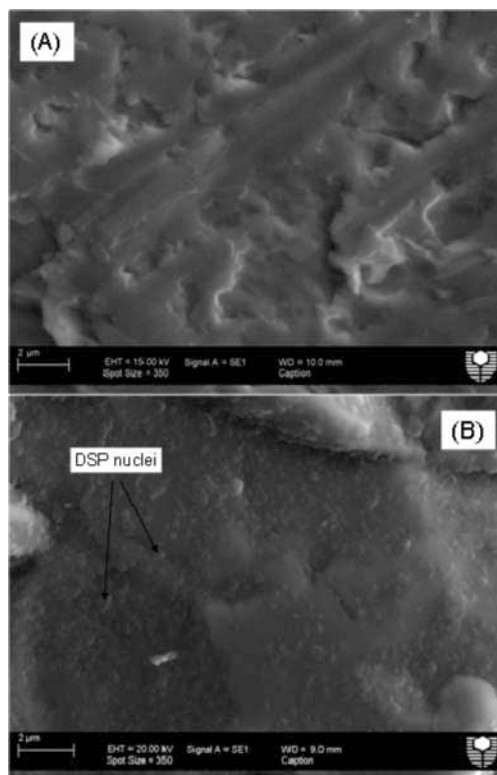


Figure 4. SEM of hematite surface: (A) before and (B) after desilication (magnification ×8500)

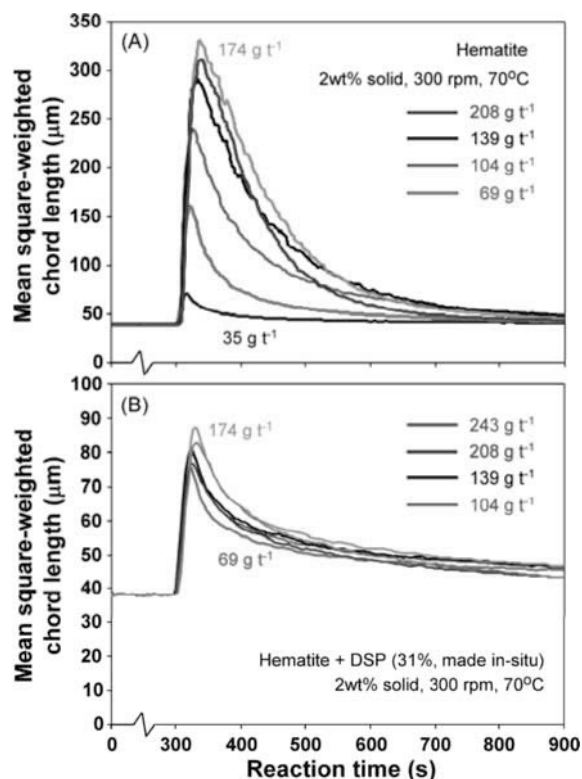


Figure 5. Mean square weighted chord length vs. reaction time for flocculation of: (A) hematite and (B) hematite and DSP slurry

### Adsorption of PAA onto the hematite and/or DSP

A complete understanding of polymer adsorption during flocculation is difficult to achieve due to the broad overlapping influences of factors such as the electrokinetics at the interface, mixing hydrodynamics and physicochemical solid properties. In practice, flocculation is also often achieved by split addition of a type or mixture of flocculants [14], with micro-aggregates formed from the initial dose reducing the available surface area and enhancing subsequent aggregation [15]. It is even more complex in a Bayer environment, as elevated temperature and high ionic strength can affect polymer chain conformation [13].

As proper quantification of flocculation kinetics requires larger scale experiments under controllable shear conditions, the initial focus has been to quantify the extent of maximum flocculant adsorption for the different solid phases and mixed phases. Such values are obtained at dosages many times higher than would ever be applied in practice, but serve as a useful guide to the surface sites available to the flocculant for adsorption and thereby may provide insights to collision efficiency effects on aggregation.

At a first glance, it was observed that adsorption onto hematite gave a higher surface excess ( $\mu\text{g m}^{-2}$ ) whilst DSP, either as a pure DSP or as 31 wt% DSP in the mixture with hematite, was responsible for a lower surface excess (Figure 6). However, it should be kept in mind that the calculation of surface excess takes into account the value of measured surface area, which is higher for DSP because of its porosity as a zeolite type mineral (Table II). To date, there is not enough evidence to support that porosity plays a role in flocculant adsorption, i.e. the flocculant's dimensions in solution may prevent access to surfaces within such pores.

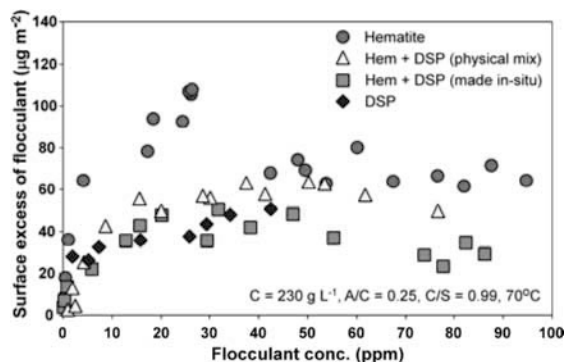


Figure 6. Flocculant adsorption in hematite and DSP slurries in  $\mu\text{g m}^{-2}$  vs. flocculant concentration (conditions: “testwork” liquor, 70°C, 300 rpm, Alclar 665)

Table II. Physical properties of hematite and DSP

Method	Value	Unit	Sample	
			Hem	DSP
BET	Surface area	$\text{m}^2 \text{g}^{-1}$	5.08	34.2
BJH	Ave. pore size	$10^{-9} \text{m}$	14.6	18.6
BJH	Ave. pore volume	$\text{cm}^3 \text{g}^{-1}$	0.02	0.16
Picnometry	Density	$\text{g cm}^{-3}$	4.98	2.48
Laser sizing	Average size ( $d_{(50)}$ )	$\mu\text{m}$	0.76	2.74
Calculation	Unit area per g	$\text{m}^2$	0.79	0.44

Note: area per g = (no of particle per g)  $\times$  (area per particle),  
no of particle per g =  $1 / (\text{mass per particle at average size})$

When the flocculant adsorption data is instead presented as per gram of solid substrate (Figure 7A), it can be seen that the extent of polyacrylate adsorption is higher when DSP is present in the system and it still gradually increases at a very high flocculant dosage (3000  $\text{g t}^{-1}$ ). How such adsorption data is best compared is still debatable, but what cannot be questioned is that flocculant does adsorb onto DSP, and certainly the presence of DSP with hematite does not greatly inhibit such adsorption.

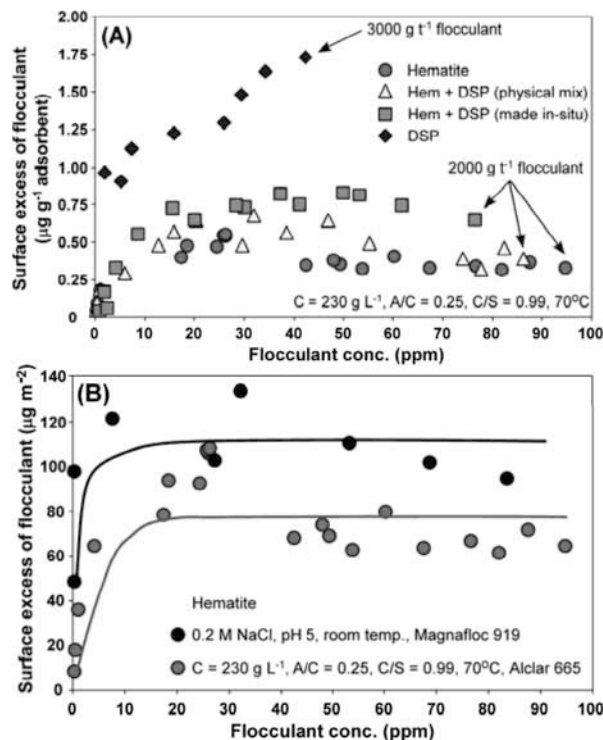


Figure 7. Flocculant adsorption of: (A) hematite and DSP slurries in  $\mu\text{g g}^{-1}$  vs. flocculant concentration and (B) hematite slurries in Bayer “testwork” liquor vs. 0.2 M NaCl at pH 5 (conditions: see Experimental – Adsorption Test)

It is important to also note that the fraction of the available surface area on a substrate may be affected by the solution conditions and the flocculant adsorption mechanism. This can be illustrated by comparing the adsorption of flocculants of comparable solution dimensions onto hematite under different solution conditions. At pH 5, flocculant adsorption reached a plateau of  $\sim 110 \mu\text{g m}^{-2}$ , while in synthetic Bayer liquor the corresponding plateau was only  $\sim 75 \mu\text{g m}^{-2}$  (Figure 7B). Applying the Fleer and Scheutjens model [16] that relates adsorption to flocculant molecular weight and radius of gyration [13], the estimated maximum hematite surface coverage by the adsorbed flocculant in synthetic Bayer liquor was  $\sim 22\%$ , yet a significantly higher coverage ( $\sim 31\%$ ) could be achieved in 0.2 M NaCl at pH 5. At the much lower dosages applied during flocculation, a reduced fraction of the surface that is available to the flocculant could lead to lower collision efficiencies during aggregation.

While the presence of DSP provides active sites for flocculant adsorption (Figure 7A), higher adsorption (from increasing flocculant dosage) does not result in either larger aggregate sizes (Figure 5) or higher sedimentation rates (Figure 1). The latter can perhaps in part be attributed to the lower density of the DSP phase relative to hematite (Table II), with lower settling rates than

expected from Stokes' Law. However, the poor aggregate growth response to increasing flocculant dosages for systems containing DSP has been not reported elsewhere and is harder to rationalize. Such a limitation in the aggregate size raises the possibility of aggregate strength issues that could reflect reduced bridging capacity for adsorbed flocculant, thus preventing the formation of larger aggregates. Further study to understand this behaviour may have a substantial impact for flocculant development and in optimising the operational parameters in the primary thickener.

### Conclusion and further work

The results from different experiments (settling test, zeta potential determination, desilication rates and SEM) all consistently suggest that DSP (sodalite) does initially form on the hematite surface. Settling rates for hematite slurries with DSP either formed in-situ or as a physical mixture are significantly different under the same flocculation conditions, and this could be because DSP nuclei are associated at the hematite surface (as observed in SEM images), thereby changing its surface chemistry. Further work in this particular area will be carried out to understand at what point sodalite starts forming on the hematite surface, the mineralogy of the initial phase and the degree of surface proliferation by DSP as a function of solution condition upon increasing reaction time.

In addition to the effect of DSP on decreasing the size of flocculated aggregates, it is also of interest that the adsorption of polyacrylate onto DSP is higher than onto hematite. Although high surface area and high porosity of DSP are major issues in rationalizing the adsorption data, further work is required to fully understand how the extent of flocculant adsorption, the fraction of surface site available for adsorption and the potential adsorbed conformation combine to influence the collision efficiency factor and subsequent aggregation processes.

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### Terminology

This work uses specific Bayer industry liquor properties terminology of which A is aluminium in the solution (expressed as  $\text{g L}^{-1} \text{Al}_2\text{O}_3$ ), C is sodium hydroxide plus sodium aluminate (expressed as  $\text{g L}^{-1} \text{Na}_2\text{CO}_3$ ) and S is C plus sodium carbonate (expressed as  $\text{g L}^{-1} \text{Na}_2\text{CO}_3$ ).

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