

## UNDERSTANDING GROWTH OF DSP IN THE PRESENCE OF INORGANIC IONS

Smith, P.<sup>b</sup>, Lowe, J.L.<sup>a</sup>, Rohl, A.L.<sup>a</sup>, Penniford, R.<sup>b</sup> and Parkinson, G.M.<sup>a</sup>

*AJ Parker Co-operative Research Centre for Hydrometallurgy*

<sup>a</sup> *Nanochemistry Research Institute, Curtin University of Technology, Bentley, Western Australia*

<sup>b</sup> *CSIRO Minerals, Waterford, Western Australia*

### Abstract

The effect of inorganic salt addition on the precipitation of desilication product (DSP) from kaolin-containing synthetic spent Bayer liquors at 95°C has been examined. Experiments were conducted to examine DSP formation in the presence of added sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium hydroxide (NaOH), sodium chloride (NaCl), potassium hydroxide (KOH) and potassium sulfate (K<sub>2</sub>SO<sub>4</sub>). The anions examined were found to influence the onset of precipitation, but did not influence the rate of precipitation, with the exception of hydroxide ions. Substitution of the sodium cation with potassium was found to delay onset of precipitation. The observed onset effects are thought likely to be related to the ability of individual ions to template the DSP, and/or to differences in the solubility of sodalites that contain different ions. It is proposed that the DSP precipitation rate is limited by the dissolution of kaolin. Dissolution was unaffected by the presence of anions except hydroxide, which elevated the dissolution rate, and also the DSP formation rate. Substitution of added NaOH in the liquor with KOH, resulted in a slowed rate of kaolin dissolution and DSP formation, suggesting that the sodium ions may be important for the elevation in the rates of these processes observed from the NaOH liquor. Sulfate was found to be the dominant inclusion in the DSP in competitive uptake experiments, and computer modelling results suggest that sulfatic DSP is thermodynamically more stable than DSP containing carbonate anions.

### 1. Introduction

Desilication product (DSP) is a sodium aluminosilicate by-product of the Bayer process, which typically has an initial sodalite-type structure under lower temperature processing conditions. DSP can incorporate ions from solution into its cage-like structure, and forms an important part of the strategy for removal of impurity anions such as carbonate, chloride and sulfate from the recycled Bayer liquor. The interplay of selected anions and DSP in synthetic Bayer liquors has been studied in one of our laboratories [1], with examination of competitive uptake of sulfate, carbonate, chloride and fluoride anions into DSP, building on early research by Seimiya [2]. This previous research found that sulfate was the dominant inclusion, and that sulfate concentration had more impact on uptake of carbonate and chloride than the concentrations of the latter two ions. It was concluded that fluoride did not incorporate to any significant extent. These experiments were used to develop models for impurity incorporation into DSP, some of which are currently in use within some Western Australian refineries.

The present study aims to achieve a fundamental understanding of the empirical models based on the earlier research, so that eventually impurity incorporation may be controlled rather than simply predicted. This work represents our present efforts towards ultimate development of a model to represent the non-equilibrium, dynamic process of DSP precipitation.

### 2. Experimental

All reagents used in this study were AR grade, with the exception of gibbsite (C-31 hydrate, Alcoa Arkansas, U.S.A.) and kaolin (English China clay "Eckalite" kaolin). Synthetic spent Bayer liquor concentrate was prepared by dissolving gibbsite (1844.90 g) and sodium hydroxide (3033.50 g) in deionised water, before filtering through a Supor 0.45 µm membrane and making up to mass (10 kg)

with deionised water. Experimental liquors were made up from the above liquor concentrate (1 kg) diluted with Milli-Q water (to 2 L) in a volumetric flask, to achieve a liquor A/C value of 0.300, C/S of 1.000 and TC of 200 g/kg. Salts for each experiment were pre-dissolved in the water used for dilution of the concentrated liquor. Salt concentrations were 0.50 M for the NaCl, NaOH and KOH liquors, and 0.25 M for the Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> liquors, in order to maintain a constant alkali level of 11.5 g/L sodium equivalent. Kinetic experiments were performed with single salt species, whilst the competitive uptake composition experiments were performed with mixtures of salts, each at the concentrations noted above.

Experiments were undertaken in a 2 L Parr Inconel reactor. The desired experimental liquor (1.8 L) was added to the reactor along with kaolin (18 g). The reactor was then sealed and pressurised to approximately 500 kPa with compressed high-purity nitrogen gas, before heating to 95°C with stirring. The experimental time was commenced once the reactor had reached 95°C. Samples were removed from the reactor through a valve at regular intervals, and filtered as previously described for the liquor concentrate. A sample of the filtrate was collected and cooled. The solids left on the filter were washed with deionised water until the washings were neutral to litmus, before being collected and dried overnight at 100°C. Both filtrate and solid samples were chemically analysed for sodium, aluminium, silicon, sulfur, chloride, potassium and inorganic carbon. The extent of DSP formation was determined by averaging the percentage of aluminium and silicon which were selectively leached from the solid samples with dilute sulfuric acid (0.05M). Composition of the DSP samples was determined from the analyses of the solid samples and the leached acid solutions.

Instrumental errors in acid leach results and solids analyses were estimated by a single point error calibration for each type of analysis. Errors were presented as a 95% confidence interval, estimated from 2 × standard deviation.

Errors in silicon analyses were determined using a multi-point calibration. Experimental errors were minimal compared with instrumental error.

### 3. Results and Discussion

#### 3.1 Effect of anions on DSP formation

Addition of individual sodium salts to the synthetic liquor resulted in alteration to the time before initial onset of DSP precipitation for some salts (Figure 1). Addition of  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$  and  $\text{NaOH}$  resulted in a reduced time for onset of precipitation, while addition of  $\text{Na}_2\text{CO}_3$  did not appear to influence the onset time. All liquors contained a low level (approximately 0.03 M) of sodium carbonate as an impurity however, so further experiments in a carbonate-free liquor are required to establish whether low levels of carbonate have any impact on DSP precipitation. The observed effects on the onset of precipitation are thought to be related to the relative abilities of particular anions to aid in templating the forming DSP, and may also be related to the solubility of the various sodalites formed.

X-ray diffraction patterns of the solids formed from experiments over extended time intervals, indicated the emergence of phases other than the sodalitic compounds initially formed. This suggests that the sodalitic compounds are not thermodynamically stable in equilibrium with the liquor at the experimental temperature. It was thus difficult to determine any effects due to differing solubilities of the sodalite compounds in the presence of the different ions. Computer modelling has been used to determine the thermodynamic stability of sodalite interactions with carbonate and sulfate anions however (see section 3.4), and this may provide some guide as to the respective solubilities of these anion-containing sodalites.

Addition of sodium hydroxide resulted in an increased rate of DSP precipitation. The rate of precipitation was not altered by addition of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$  or  $\text{NaCl}$  salts, although again any effects due to the presence of low levels of carbonate have yet to be established. Linear regression of DSP precipitation data for  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  salt addition over the 30-55 minute time interval (after removal of zero points) reveals slopes, and hence precipitation rates, within experimental error of one another. Slopes of DSP precipitation from liquors with added  $\text{Na}_2\text{CO}_3$  or no added salt were estimated by combining data from a longer experiment performed under identical conditions. Again, these slopes were within experimental error of the  $\text{Na}_2\text{SO}_4$  and

$\text{NaCl}$  liquor slopes. Errors in all of the slopes are large since the number of data points is small, and it should also be noted that the experimental flux and actual silicon supersaturation levels were not determined.

The observed effects on the rate of DSP precipitation may be correlated with the observed silicon solubility from kaolin in the various liquors. As may be seen in Figure 2, the liquors containing  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$  and no added salts show a similar kaolin dissolution rate over time. The liquor containing added  $\text{NaOH}$  has an elevated rate of kaolin dissolution, in agreement with the earlier findings of Roach and White [3]. This correlation of the ion effects on kaolin dissolution rate with their effects on the rate of DSP formation suggests that the dissolution of kaolin may in fact be the rate determining step in DSP formation.

Experiments using a soluble silica source are being undertaken in order to determine whether the added ions have any effect on the rate of precipitation when silica dissolution is not a step in the precipitation process.

#### 3.2 Effect of sodium and potassium cations on DSP formation

Replacement of added  $\text{NaOH}$  with  $\text{KOH}$  in the synthetic liquor delayed the onset of DSP precipitation (Figure 3). The delayed onset suggests that the added sodium ion (which represents approximately 13% of the total sodium in solution) may play some role in nucleation of the DSP or possibly result in a different silicon solubility in the liquor compared with potassium. A similar delay in onset of DSP formation was observed on substitution of  $\text{K}_2\text{SO}_4$  for added  $\text{Na}_2\text{SO}_4$ .

The substitution of  $\text{KOH}$  for  $\text{NaOH}$  also appeared to slow the rate of DSP formation, compared with the formation rate from the  $\text{NaOH}$  liquor. The slope of the regression line for the  $\text{KOH}$  liquor was estimated by incorporation of additional data as described previously. This estimated slope was within experimental error of all other liquors, except the added  $\text{NaOH}$  liquor, although again it should be noted that experimental errors were large. The liquor containing added  $\text{KOH}$  was observed to have a kaolin dissolution rate similar to the other liquors, which was lower than the dissolution rate measured from the  $\text{NaOH}$  liquor. The slowed rate of DSP precipitation and kaolin dissolution on substitution of added  $\text{KOH}$  for  $\text{NaOH}$  suggests that the sodium ion plays an important role in the increased rate of

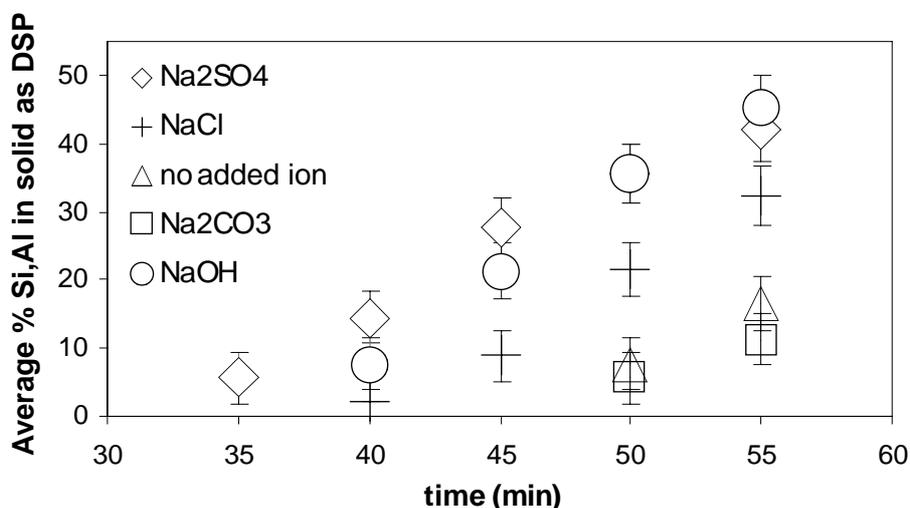


Figure 1 — Effects of individual salts on the formation of DSP from synthetic spent Bayer liquor at 95°C. Note points from the beginning of each run, with 0% average Si, Al as DSP, have been removed for the sake of clarity.

DSP formation/kaolin dissolution observed from the added NaOH liquor.

From these results, it appears that sodium cations are important to both the dissolution of kaolin/precipitation of DSP and also to DSP nucleation and/or silicon solubility in the liquor.

Variation in the onset of DSP precipitation with salt addition was in the order of 15 to 20 minutes for all of the salts examined.

### 3.3 Composition of formed DSP

Composition of the DSP formed was established from chemical analyses of sodium, aluminium, silicon, carbon and sulfur content. Errors associated with carbon levels were particularly large, due to the low concentrations and consequent lack of sensitivity of the analysis. The structure of the DSP was assumed to be a sodalitic structure over the short experimental period. X-ray diffraction patterns suggest that this was a reasonable assumption, however presence of additional phases in small amounts was difficult to rule out.

Proposed inclusion of aluminate ( $\text{Al}(\text{OH})_4^-$ ) ions in the DSP precipitate was calculated by assuming that excess aluminium over that required for a 1:1 silicon to aluminium ratio in the DSP framework was present within the sodalite cages as the aluminate ion. In some cases, the excess

aluminium was clearly higher than could be accounted for by aluminate inclusions. This excess is the subject of a separate study. Hydroxide inclusions were not factored into the compositional data, as there was no practical method of measuring hydroxide levels, and excess sodium levels (over framework and inclusion charge balance requirements) could not provide a guide as they were potentially lost with hydroxide during the washing step.

DSP samples from liquors containing added sulfate and carbonate were found to have roughly 98% and 88% respectively of sodalite cages occupied after 90 minutes at 95°C, with approximately 2/3 of cages occupied by sulfate and 1/2 of cages occupied by carbonate in the respective structures. Note that complete occupancy here allows for one empty and one occupied cage assigned for each divalent anion to be described as nominally full. The remaining cages in these sodalites were calculated to be filled with aluminate ions. DSP samples from the chloride liquor produced over the same timeframe were found to have approximately 80% of cages occupied, with chloride occupying approximately 1/6 of the cages, and aluminate occupying the remaining cages. Occupancy of sodalites precipitated from the no added ion and hydroxide containing liquors was difficult to assess, however approximately 48% of cages were calculated to be filled with aluminate ions.

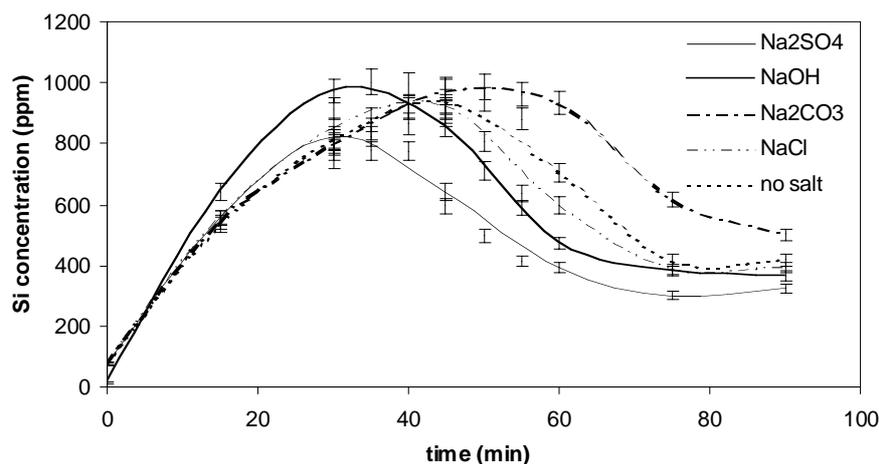


Figure 2 — Desilication in synthetic spent Bayer liquor at 95°C with added kaolin and inorganic salts. NaOH liquor in bold face. Note that curves are illustrative only and do not signify a fitted function.

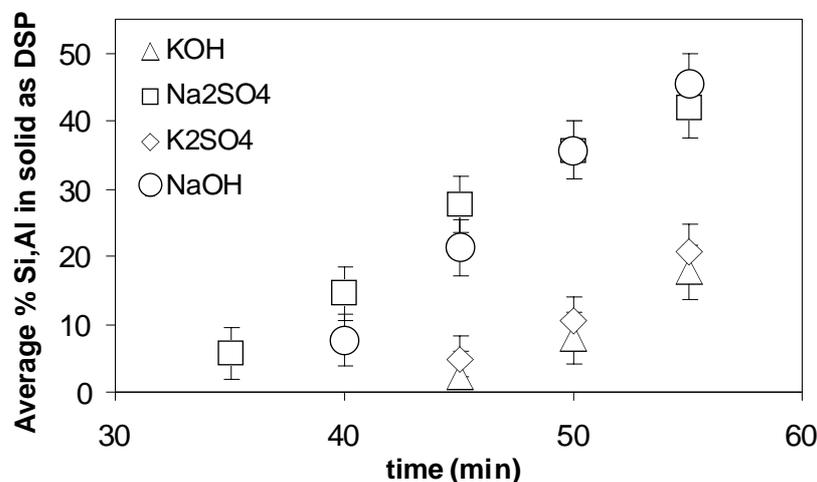


Figure 3 — DSP formation from synthetic spent Bayer liquor containing kaolin and inorganic salts at 95 °C — effect of replacing added NaOH with KOH. Note points from the beginning of each run, with 0% average Si, Al as DSP, have been removed for the sake of clarity.

Competitive uptake experiments, performed in the presence of all the salts examined in this study, indicated that sulfate ions were incorporated into the DSP structure at a much higher level than for other impurities. Sulfate was also reported as the dominant inclusion [1] in the earlier study. DSP produced from an additional competitive uptake experiment with added chloride and carbonate ions present had fully occupied cages, filled with chloride 1/4, carbonate 3/8 and aluminate 3/8 of all cages.

The dominant inclusion of sulfate ions into the DSP may be explained in part by the observed effect of this ion on the onset of DSP precipitation (section 3.1). The predominance of inclusion of carbonate ions over chloride ions in competitive uptake experiments, suggests that any effect on the onset of DSP precipitation due to the presence of carbonate ions may be observable at a low concentration, since we did not record any effects in our kinetic experiments above those obtained with a base level impurity of carbonate. The predominance of carbonate may also be related to an increased solubility of the carbonate-containing DSP. It should be noted that the competitive uptake of these ions may be different in experiments where kaolin dissolution is not the rate-limiting step, due to the potential effect of the ions on the rate of DSP precipitation.

### 3.4 Modelling of DSP interaction with sodium salts

Interactions of carbonate and sulfate anions with the DSP framework were modelled using empirical force-field potentials, developed from literature potentials [4, 5, 6, 7]. The developed potentials were tested variously on experimental data for chloride sodalite, silica sodalite, corundum,  $\alpha$ -quartz and sodium chloride to ensure that minimised structures were consistent with experimental data. The minimised carbonate sodalite structure gave a average unit cell dimension of 8.921 Å, which is within 2% of the experimental value of 9.084 Å, and represents good accuracy for an interatomic potential calculation. Comparison of the minimised sulfatic sodalite with experimental data was not possible, since the reported experimental structure contained water and potassium impurities, which are not present in our model.

Structures were minimised in the GULP program [8] with solvation energies determined using the COSMO algorithm [9] within GULP. The binding energy (BE) for the ion to the DSP framework is determined by

$$BE = (E_1) - (E_2 + E_3 + E_4 + E_5 + E_6)$$

where the energies within the system are represented as follows:  $E_1$  is the energy of the zeolite cage containing the anions,  $E_2$  the empty zeolite cage,  $E_3$  the isolated anions,  $E_4$  the sodium ions required to charge-balance the anions,  $E_5$  the solvation energy of the anions in water, and  $E_6$  the solvation energy of the charge-balance sodium ions in water. Calculations were performed both with and without solvation, and the results are shown in Table 1.

These results suggest that the sulfate anion is more stable than carbonate within the sodalite structure, although

the solvation energies were calculated in water rather than in Bayer liquor which is a high dielectric solution. Methods of simulating solvation in a medium closer to the experimental system are being examined. The difference in the binding energies in the absence of solvation is indicative of the importance of the solvation as an energetic step in the binding process.

The greater thermodynamic stability of sulfate anions binding in the sodalite structure suggests that observed experimental effects are likely to be due at least in part to differences in "equilibrium" solubility of sulfate-containing sodalite compared with carbonate-containing sodalite.

Table 1 — Binding energies of sulfate and carbonate anions within the DSP framework

	binding energy (kJ mol <sup>-1</sup> )	binding energy with solvation (kJ mol <sup>-1</sup> )
sulfate	-2153	-390
carbonate	-2275	-367

## 4. Conclusions

The DSP formation rate appears to be limited by the dissolution of kaolin, which is unaffected by the presence of added carbonate, chloride and sulfate anions. Hydroxide ions give an increased kaolin dissolution rate, and this appears to be responsible for the more rapid rate of DSP formation observed from liquor containing excess NaOH. The presence of various anions, however, affects the onset of DSP precipitation, which may be due to differences in the templating ability of different anions and/or differences in solubility of the anion-containing sodalites in the various liquors. Replacement of the added sodium cations with potassium also affected the onset of precipitation, indicating as for the anions, that the cation may affect templating of the DSP and solubility of sodalite in the liquor. The replacement of sodium cations in the hydroxide liquor was also found to reduce the rate of kaolin dissolution/DSP precipitation, indicating that the sodium cations play a role in these processes. Competitive uptake experiments have determined that sulfate is the dominant anionic inclusion. Computer modelling results provide some explanation for this, indicating that sulfate has greater thermodynamic stability in the sodalite structure than carbonate.

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