

THE EFFECT OF SODIUM, POTASSIUM AND CAESIUM ON GIBBSITE AGGLOMERATION IN BAYER SOLUTIONS

J. S. C. Loh^a, H. R. Watling^b and G. M. Parkinson^a

A. J. Parker Cooperative Research Centre for Hydrometallurgy,

^aSchool of Applied Chemistry, Curtin University of Technology, GPO Box U1987, Perth WA 6845, Australia.,

^bCSIRO Division of Minerals, PO Box 90, Bentley WA 6982, Australia.

ABSTRACT

The seeded precipitation of gibbsite from caustic aluminate solutions is accomplished by a combination of three crystallisation processes, secondary nucleation, agglomeration and growth. They usually occur together during precipitation: but the contribution of one can be promoted over the others by careful selection of precipitation conditions, so that the effects of variables on each part of the precipitation process can be studied.

In this study, the effects on gibbsite agglomeration of substituting potassium and caesium for sodium in synthetic Bayer liquors were investigated using Hydral 710 seed.

Precipitation data obtained as a function of time from sodium aluminate solutions, supplemented by particle size data and the examination of scanning electron micrographs of gibbsite samples, showed that agglomeration was a rapid process, accompanied by significant gibbsite deposition. It was confirmed that for the selected conditions, agglomeration was the dominant precipitation process. Similar data obtained under identical conditions for samples from potassium and caesium aluminate solutions revealed unexpectedly high levels of secondary nucleation.

The results are discussed in relation to the role of the cation in the precipitation process, and their implications for our understanding of supersaturation and crystallisation driving force.

KEY WORDS:

agglomeration, gibbsite crystallisation, alkali metals, secondary nucleation

THE EFFECT OF SODIUM, POTASSIUM AND CAESIUM ON GIBBSITE AGGLOMERATION IN BAYER SOLUTIONS

J. S. C. Loh, H. R. Watling and G. M. Parkinson

1.0 INTRODUCTION

The precipitation of gibbsite is the slowest step in the Bayer process with precipitator residence times of approximately 24 to 36 hours, depending on refinery operating conditions. Growth of individual gibbsite crystals under industrial conditions occurs at a rate in the order of microns per hour. Considerable research is therefore focused on increasing gibbsite precipitation productivity (growth rate and yield) without sacrificing quality (size, strength and purity). Fundamental to this is an understanding of the mechanisms of gibbsite precipitation.

Gibbsite precipitation involves three main processes, secondary nucleation, agglomeration and growth. They are defined as follows: secondary nucleation is the production of new particles in the presence of seed material and is accompanied by a large desupersaturation

of aluminium from solution, agglomeration is the aggregation and cementation by growth of small particles (Seyssiecq *et al.*, 1998) and growth is the ordered deposition by which crystal surfaces are smoothed. These occur simultaneously, but to different extents, depending upon the supersaturation of the liquor. The supersaturation with respect to alumina, defined as $b=A/A^*$ (Vessler and Boistelle, 1993), where A and A* are the initial and equilibrium alumina concentrations respectively, gives an estimate of the driving force for gibbsite precipitation.

Significant increases in gibbsite crystal sizes occur mainly as a result of agglomeration of either the smaller gibbsite particles used to seed the liquor or the secondary nuclei generated during precipitation. Agglomeration is an important process because poor crystal aggregation creates weaker agglomerates, which may subsequently result in an unacceptable fines content in the product alumina.

Agglomeration is very dependent upon precipitation conditions and is promoted by

- high supersaturation (Scott, 1963; Sakamoto *et al.*, 1976; Yamada, 1980; Sang *et al.*, 1989; Lopez *et al.*, 1992; Seyssiecq *et al.*, 1998)
- high temperature (Sakamoto *et al.*, 1976; Yamada, 1980; Seyssiecq *et al.*, 1998)
- narrow seed particle size distribution (Scott, 1963; Sakamoto *et al.*, 1976)
- low seed charge (Scott, 1963; Sakamoto *et al.*, 1976)
- the presence of low amounts of calcium (Brown, 1988)
- lower stirring rate (Misra and White, 1971; Ilievski *et al.*, 1994; Vessler and Boistelle, 1994a)

As part of an ongoing fundamental study of the mechanisms of gibbsite crystallisation we have investigated the effect of substituting potassium or caesium for sodium in the aluminate system. Initial experimental conditions of high supersaturation, small seed charge and narrow seed particle size distribution were chosen to promote agglomeration. The results of these experiments indicated the need for further comparisons at lower supersaturation, and caused us to reconsider the definition of supersaturation in relation to gibbsite agglomeration.

2.0 EXPERIMENTAL

Four sets of seeded experiments were carried out at 80°C in sodium, potassium and caesium aluminate solutions. Solution concentrations for these were (1) $b=1.8$, C200, A/C 0.65, (2) $b=1.5$, C200, A/C 0.55, (3) $b=1.3$, C200, A/C 0.48 and (4) $b=1.1$, C200, A/C 0.40. Aluminium concentrations are expressed as equivalent g/L Al₂O₃, and alkali hydroxide and total alkali concentrations are both expressed as equivalent g/L Na₂CO₃.

2.1 Liquor Preparation

The aluminate solutions were prepared by dissolving the appropriate hydroxide (NaOH - Rowe, >97%, KOH - Rowe, >85%, CsOH - Ajax, >99.5%, allowing for impurities) and C31 hydrate (Alcoa) in deionised water in a 1 L stainless steel beaker. The mixture was heated and stirred at atmospheric pressure. The appropriate carbonate was added to sodium and potassium aluminate solutions as no caesium hydroxide without significant carbonate contamination was readily available (a 4M CsOH solution had 26 g/L equivalent as Na₂CO₃). [Caesium hydroxide may be treated with barium hydroxide to remove the carbonate impurity. Trace amounts of barium remaining in solution might

alter gibbsite precipitation rates and crystal morphology.] The carbonate was first dissolved in 100 mL of hot deionised water and this solution then mixed with the hot aluminate solution. The liquor volume was made up to 500 mL in a volumetric flask and pressure filtered (0.45 mm pore size membrane).

2.2 Seed

Hydral 710 (Alcoa of Australia) was used as seed in these experiments. The material consists of blocky, hexagonal-shaped crystals. The average particle size ($D[v, 0.5]$) of Hydral is 1.55 μm (laser diffraction, Malvern Mastersizer) and the surface area was determined to be 8.9 m^2/g (5 point nitrogen BET following ASTM C1069 – '86). Powder XRD showed that the only phase present was gibbsite. The amount of Hydral 710 used in the experiments (0.29g) represented the equivalent surface area as for the seed loading of 100 g/L C31 hydrate (surface area 0.24 m^2/g). The seed loading of 100 g/L was chosen to simulate higher seed charges.

2.3 Precipitation Methods

Aliquots (50 mL) of the liquor were pipetted into 250 mL high density polyethylene bottles, sealed and equilibrated at 80°C in a temperature-controlled rolling bottle (end over end) water bath for 30 minutes. After this, warm seed (0.135g, 60°C) was added to the liquor and the bottle was replaced in the water bath for the required time.

The samples were vacuum filtered (0.45 mm pore size membrane) and the liquor analysed (Woods *et al.*, 1993). The solid samples were washed copiously with hot deionised water and dried overnight in an oven at 60°C. Particle size distributions and surface areas were determined using laser diffraction (Malvern Mastersizer) and 5 point nitrogen BET following ASTM C1069 – '86, respectively. Crystal morphologies were examined using scanning electron microscopy (SEM, Jeol 5800 LV, W hairpin filament, 20 kV accelerating voltage, 10 mm working distance, carbon and gold coatings).

3.0 RESULTS

We found no significant differences in equilibrium gibbsite solubilities in sodium, potassium and caesium hydroxide solutions, required for the calculation of b as defined by Veessler and Boistelle (1993), which were determined from above and below supersaturation (unpublished data, this laboratory).

The progression of agglomeration was monitored by examining the scanning electron micrographs (Figure 1A-D) and comparing changes in the surface areas and median particle size as a function of time (Figures 2A-B and 3A-D respectively).

The decreases in liquor aluminium concentrations as a function of time are an indication of the rates of gibbsite precipitation (Figure 4A-D). They vary relative to the initial supersaturation and cation. For $b > 1.5$, the rate of gibbsite deposition decreases, from equivalent caustic aluminate solutions, in the order of $\text{K} > \text{Cs} > \text{Na}$. Below $b < 1.5$, the gibbsite deposition rate decreased from equivalent caustic aluminate solutions, in the order of $\text{K} > \text{Na} > \text{Cs}$. (Please note the different time scale in Figures 2A, 3A and 4A. This is due to the shorter duration of the experiment.)

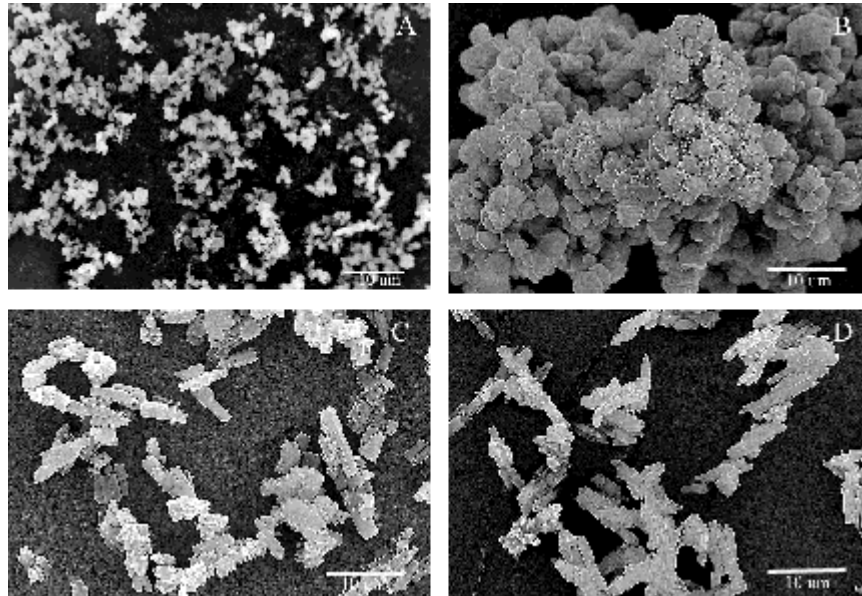


Figure 1

Scanning electron micrographs of A: Hydral seed and products from B: Sodium, C: Potassium, D: Caesium aluminate liquor at 24 hours ($b=1.5$)

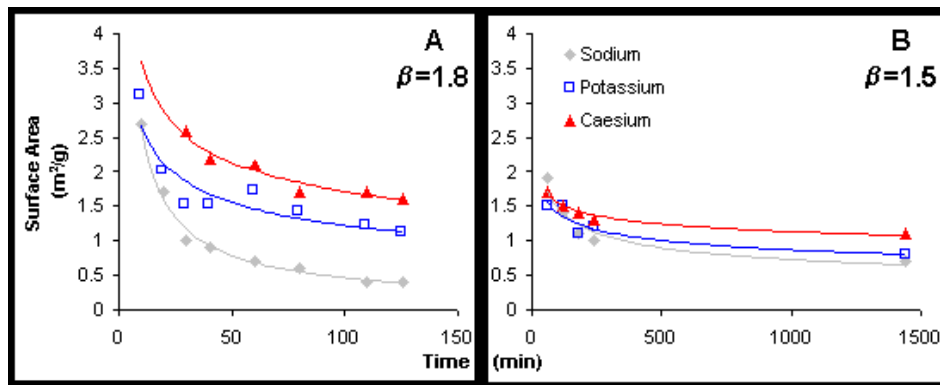


Figure 2

Surface area as a function of time and supersaturation ratio (b)

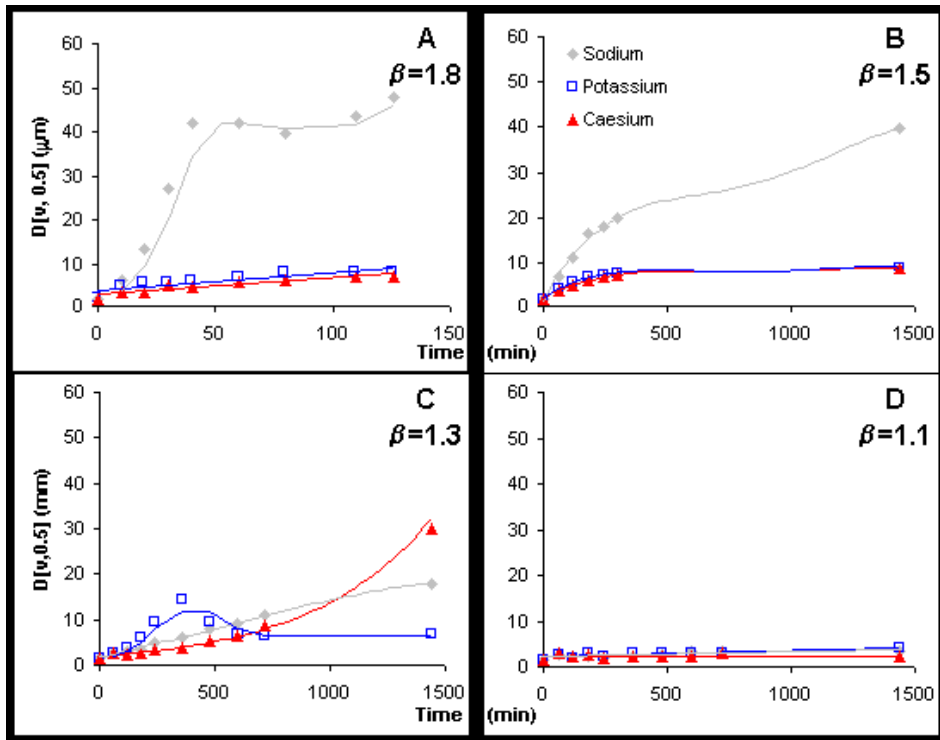


Figure 3

Median particle size as a function of time and supersaturation ratio (b)

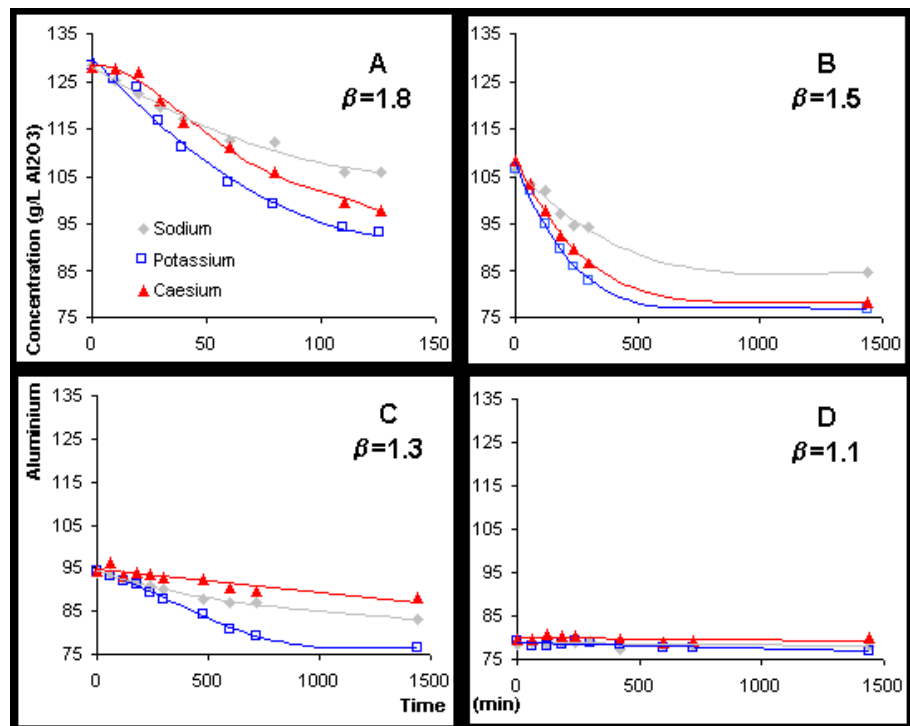


Figure 4

Decrease in liquor aluminium concentration as a function of time and supersaturation (b)

3.1 Agglomeration from Sodium Aluminate Liquor

In all experiments, there was no indication of an induction period prior to gibbsite deposition (Figure 4A-C). Indeed, agglomeration was rapid from the start. This is confirmed by the steady increase in the median particle size with time (Figure 3A-C). The absence of any secondary nuclei at any of the supersaturations studied and the decrease in the surface areas (Figure 2A-B) of the products indicate that agglomeration was the main precipitation process occurring. All crystals undergo agglomeration, as none of the original seed particles remain at the end of the experiment (Figure 1B).

The morphology of the aggregates is as expected: hexagonal-shaped crystals cemented into chunky "spheres". The effects of the shortened period under which the experimental conditions promote agglomeration (caused by decreasing the initial supersaturation) are reflected in the median particle size of the products (Figure 3A-D). There is a decrease in the median particle size of 44 nm between final samples taken from solutions with the initially highest and the lowest supersaturations.

3.2 Comparison with Potassium and Caesium Liquors

Very significant differences were observed when the agglomeration results from potassium and caesium liquors are compared to those from sodium aluminate liquors. There was a short (20 min) induction period in the caesium aluminate liquor at high supersaturation (Figure 4A) before any decrease in liquor aluminium concentration was observed. This, however, is not reflected in the particle size measurements. There was an increase in the median particle size from the onset of the experiment. The scanning electron micrographs indicated there was a small amount of agglomeration of the Hydral seed during this time. Halfon *et al.* (1976) previously observed the agglomeration of gibbsite seed during the induction period in sodium aluminate liquor.

The occurrence of secondary nucleation in potassium (at intermediate levels) and caesium (as the dominant process) aluminate liquors, which produced a large amount of fine particles, follow the large decrease in the liquor aluminium concentrations at high supersaturations (Figure 4A-B). Elongated hexagonal crystals, characteristic of gibbsite nucleated from potassium and caesium aluminate liquors (Lee *et al.*, 1996) were observed to be the dominant crystal shape with longer, narrower crystals forming from caesium liquors (Figure 1C-D). With time, these crystals grew and formed long chains, agglomerating predominantly on the prismatic faces of the crystals. The chains are typically between 5 and 10 crystal widths in thickness. No spherical aggregates were observed. Secondary nucleation and agglomeration occurred simultaneously, as shown by the increase in the median particle size (Figure 3A-C) and the decrease in surface area (Figure 2A-B). This indicates that lowering the supersaturation slightly did not significantly decrease secondary nucleation but it has had the effect of increasing the extent of gibbsite agglomeration in the solutions. Agglomeration in potassium and caesium liquors was incomplete, individual crystals being observed at the end of the experiments.

The experiment carried out at $b=1.3$ gave different results again. There does not seem to be a significant amount of secondary nucleation in this caesium aluminate liquor, although it still occurs in the potassium aluminate liquor. An SEM examination of the products sampled during an agglomeration run showed that particles produced in the potassium aluminate liquor grew and agglomerated into large 'spherical' aggregates (Figure 5A) of long crystals which, with time, broke up to give chains of elongated needles (Figure 1C). Agglomeration occurs in caesium aluminate liquor to a similar extent to that observed in

sodium aluminate liquor. Over time, growth occurs on the seed to form, after 24 hours, discrete 'spherical' aggregates of the characteristic needles, although these needles are shorter than those observed at the higher supersaturation (Figure 5B). Surprisingly, these aggregates are bigger than those formed in the corresponding sodium aluminate solution. These observations are consistent with the median particle sizes (Figure 3C). Agglomeration is almost complete and only a few individual seed particles remain.

Upon a further decrease in supersaturation to 1.1 no secondary nucleation and very little growth and agglomeration was observed in all three liquors (Figure 3D). This observation is consistent with findings by Veessler and Boistelle (1994) that, in sodium aluminate liquors, there is a critical relative supersaturation, at a given temperature, below which no growth takes place. At 80°C, in sodium aluminate liquors, they found the critical value to be $b_c=1.15$. Results from the present work suggest that this critical value may also apply to potassium and caesium aluminate liquors.

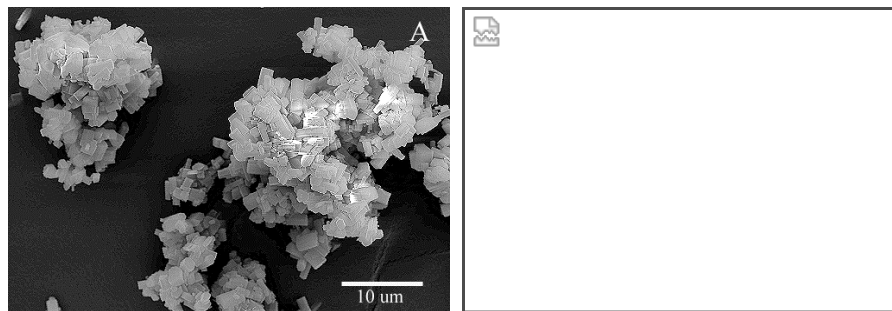


Figure 5

Scanning electron micrographs of product from A: potassium aluminate liquor at 6 hours and B: caesium aluminate liquor at 24 hours ($b=1.3$)

4.0 DISCUSSION

The initial experimental conditions designed to promote agglomeration were chosen on the basis of data from sodium aluminate solutions. These conditions produced rapid and complete agglomeration with no secondary nucleation.

The agglomeration of gibbsite in sodium aluminate solutions over the range of $1.3 \leq b \leq 1.8$ proceeded as expected. The results obtained from sodium aluminate liquors compare very well with observations by Misra and White (1971) that the seed particle size increased rapidly with no generation of fines from secondary nucleation. Particle size measurements and scanning electron micrographs indicated that the spherical agglomerates increased in size through growth of gibbsite, cementing the aggregate together. The present work contains the first published reports on the agglomeration of gibbsite from potassium and caesium aluminate liquors.

An unexpectedly high level of secondary nucleation was observed in potassium and caesium aluminate solutions under conditions ($b=1.8$) in which it is absent in sodium aluminate solutions. Traditionally, in sodium aluminate liquors, secondary nucleation is considered to occur at high supersaturation (b^3). In an attempt to decrease the amount of fines produced in potassium and caesium liquors, so that the agglomeration process could be isolated and hence reasonably compared in all liquors, the supersaturation of the solutions was lowered ($b=1.5$), all other conditions remaining the same. Decreasing the supersaturation had the effect of decreasing the extent of agglomeration in sodium aluminate liquor but increasing it in potassium and caesium aluminate liquors. Secondary nucleation was still present and elongated hexagonal crystals, characteristic of these

cations, were produced.

A further decrease of the supersaturation to $b^{1.3}$ gave more unexpected results. Whereas agglomeration in sodium aluminate liquor followed the expected trend and occurred to a lesser extent than at higher supersaturations, spherical aggregates were formed early in the potassium aluminate liquor which then broke up to give chains of elongated crystals. This indicated that the gibbsite deposition rate was not high enough for a long enough time period to securely cement the particles. On the basis of our experiments, we estimate that stable agglomeration in potassium aluminate liquor may be achieved at $b^{1.4}$. Seed agglomerated in caesium aluminate liquor to yield spherical aggregates of long needles after 24 hours. These aggregates were bigger than those formed in the equivalent sodium aluminate liquor.

The occurrence of different growth processes in sodium, potassium and caesium aluminate liquors at the same b indicates that the Veessler-Boistelle (1993) definition may not adequately describe the precipitation force for all caustic aluminate solutions. This definition only refers to the supersaturation of a solution with respect to aluminium (at a given temperature and caustic concentration). We have found that there are no significant differences in equilibrium gibbsite solubilities in all three caustic solutions over a range of temperatures (unpublished data, this laboratory). Thus on the basis of defining precipitation driving force as C/C^* , it should be the same for equivalent liquor concentrations regardless of the cation.

From the above, it is clear that other factors, such as water activities, ion pairing, cation adsorption on the gibbsite surface or crystal morphology, influence gibbsite precipitation. Vernon *et al.* (this conference) demonstrated that gibbsite growth rates for a given initial supersaturation decrease with increased ionic strength in sodium aluminate solutions and correlated this with decreased water activities in sodium hydroxide solutions. Although water activities have been reported for sodium aluminate solutions (Szabo *et al.*, 1975), no comparative data have been published for potassium and caesium aluminate solutions. Mashovets *et al.* (1965) found an inverse proportional relationship between water activities and the cation size for LiOH, NaOH and KOH solutions at the same concentrations. The order of magnitude and trend reported for the hydroxide solutions might be assumed to be similar to that for caustic aluminate solutions. However, our results show that the precipitation rates from potassium aluminate solutions are greater than those from corresponding sodium aluminate solutions for $1.3 \leq b \leq 1.8$. In addition, for $b \leq 1.5$, the gibbsite deposition rate from caesium aluminate solutions is greater than that for sodium aluminate solutions, while for $b \leq 1.3$, the rate is less than that for analogous sodium aluminate solutions. Thus, although water activity may play an important part in determining gibbsite precipitation rates, other factors must also contribute where potassium or caesium is substituted for sodium.

A related factor, which may affect the gibbsite precipitation rate in the different caustic aluminate solutions, is ion pair formation between the alkali cation and the aluminate ion. Sodium forms an appreciably stronger ion pair with aluminate ions than with hydroxyl ions (Sipos *et al.*, 1997). It is envisaged that the ion pairs between potassium and caesium cations with the aluminate ion would be less strong than that formed with sodium. The increase in size from sodium to caesium decreases the force of attraction of the protons with the outer electrons, due to the increase in number of electrons in the atom down a periodic group. This in turn decreases the effective charge of the larger cation. The strong ion pair of sodium aluminate would require more energy to dissociate, thus reducing the precipitation rate.

The strength of adsorption of the cation on the surfaces of the growing crystal is another factor that may affect the growth rate (as well as morphology). The growing crystal surfaces are present in a highly alkaline solution. Thus, it is likely that the exposed hydroxyl groups are deprotonated (pH of a Bayer liquor being >14, pK_a for the surface protons being in the range of 9 to 11). Adsorption of the cation onto the surface is enhanced by the negatively charged, deprotonated surface. Gibbsite consists of layers of aluminium hydroxide ($Al(OH)_3$) bound together by hydrogen bonds between hydroxyl groups of adjacent layers. If the cations are not removed from the surface, and the surface reprotonated, then there will be an insufficient number of sites available for hydrogen bonding and thus a new $Al(OH)_3$ layer will less likely to form. If adsorption is strong then it may require more energy to remove the cation and thus decreases the precipitation rate. The increase in the size of the cation from sodium to potassium to caesium and the associated hydration sphere increases the steric hindrance for adsorption onto the surface. This steric hindrance is reflected, not only in the amount of the cation incorporated into the gibbsite crystal, but also the calculated energy required to incorporate the cation into the crystal lattice (Lee *et al.*, 1996). Indeed, Eremin *et al.* (1980) suggested the substitution of sodium for hydrogen in gibbsite as a mechanism by which sodium is incorporated into the gibbsite lattice.

The question of the effect of the geometry of the crystals on the extent and rate of agglomeration also needs to be considered. Gibbsite grown in sodium aluminate is very blocky and hexagonal-shaped, while needles dominate the crystal morphology for potassium and caesium aluminate solutions. The morphology may be affected by the preferential adsorption of cations onto specific crystal faces and even the supersaturation (driving force) of the solution. The questions of whether the observed growth rate differences are due to differences in the solutions, the growing crystal surfaces or variations in growth on different crystal faces remain to be answered.

Future research into the effect of cations on gibbsite precipitation will include an investigation of the effect of the hydroxide solubility in water with the goal of establishing the liquor concentrations required for equivalent driving force and water activity regardless of cation. In this way, a better understanding of the relationship between supersaturation (b) and crystallisation driving force will be achieved. The effects of different crystal morphologies on precipitation rates and processes will also be investigated.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The initial experimental conditions designed to promote agglomeration were chosen on the basis of data from sodium aluminate solutions. The results obtained from sodium aluminate liquors over the range of $1.3 \leq b \leq 1.8$ proceeded as expected. The unexpected occurrence of secondary nucleation in corresponding potassium and caesium aluminate solutions is indicative of a higher crystallisation driving force. Through progressive reduction in the supersaturation of the solutions, the optimum experimental conditions for agglomeration for potassium and caesium were established (for K $b_{optimum} = 1.4$, Cs $b_{optimum} = 1.3$).

These results indicate that the relationship between aluminium supersaturation and crystallisation driving force must be reexamined. Factors, which may play an important part in a new description of gibbsite precipitation rates, include water activities, ion pairing, cation adsorption on the growing gibbsite crystal surface and crystal morphology.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Australian Government CRC Program and the sponsors of the AMIRA P380B Fundamentals of Precipitation project: Alcoa of Australia, Comalco, MERIWA, Nabalco, Queensland Alumina and Worsley Alumina. Helpful discussions with Dr. C. Vernon, CSIRO are also appreciated.

-

REFERENCES

Brown, N. (1988). Effect of calcium ions on agglomeration of Bayer aluminium trihydroxide. J. Crystal Growth, **92**, 26-32.

Eremin, N. I., Cherepanova, M. I., Makasakova, M. A. (1980). Statistical investigations into the nature of the inclusion of alkali in the structure of aluminium hydroxide. Sov. Non-Ferrous Metals Res., **8**, 263-266.

Halfon, A., Kaliaguine, S. (1976). Alumina trihydrate crystallisation Part 2. A model for agglomeration. Can. J. Chem. Eng., **54**, 168-172.

Ilievski, D., White, E. T. (1994). Agglomeration during precipitation: Agglomeration mechanism identification for Al(OH)₃ crystals in stirred caustic aluminate solutions. Chem. Eng. Sci., **49**, 3227-3239.

Lee, M-Y., Rohl, A. L., Gale, J. D., Parkinson, G. M., Lincoln, F. J. (1996). Influence of metal ion inclusion on the morphology of gibbsite. Chem. Eng. Res. Des., **74**(A7), 739-743.

López, J. E., Quintero, I. (1992). Evaluation of agglomeration stage conditions to control alumina and hydrate particle breakage. Light Metals, 199-202.

Mashovets, V. P., Krumgal'z, B. S., Dibrov, I. A., Matveeva, R. P. (1965). Vapour pressure of KOH solutions up to 400°C and activity of water in LiOH, NaOH and KOH solutions over a wide range of concentrations. J. Appl. Chem. USSR, **38**, 2294-2296.

Misra, C., White, E. T. (1971). Crystallisation of Bayer aluminium hydroxide. J. Crystal Growth, **8**, 172-178.

Sakamoto, K., Kanehara, M., Matsushita, K. (1976). Agglomeration of crystalline particles of gibbsite during precipitation in sodium aluminate solution. Light Metals, 149-162.

Sang, J. V., Gagnon, R. Y., Bernier, J. L., Paradis, E. (1989). Fines digestion and agglomeration at high ratio in Bayer precipitation. Light Metals, 33-39.

Scott, J. (1963). Effect of seed and temperature on the particle size of Bayer hydrate. Extractive Metallurgy of Aluminium, 203-218.

Seyssiecq, I., Veessler, S., Boistelle, R., Laméran, J. M. (1998). Agglomeration of Gibbsite Al(OH)₃ crystals in Bayer liquors. Influence of the process parameters. Chem. Eng. Sci., **53**(2), 2177-2185.

Sipos, P., Turonek, M., Fu, J. H., Watling, H., Duffield, J., May, P., Hefter, G. (1997). P380B AMIRA fundamentals of alumina precipitation, Nov 1995 – Feb 1997, Program 1: Speciation in Bayer liquors. Department of Chemistry, Division of Science, Murdoch University.

- Veesler, S., Boistelle, R. (1993). About supersaturation and growth rates of hydrargillite $\text{Al}(\text{OH})_3$ in alumina caustic solutions. J. Crystal Growth, **130**, 411-415.
- Veesler, S., Roure, S., Boistelle, R. (1994a). General concepts of hydrargillite $\text{Al}(\text{OH})_3$ agglomeration. J. Crystal Growth, **135**, 505-512.
- Veesler, S., Boistelle, R. (1994b). Growth kinetics of hydrargillite $\text{Al}(\text{OH})_3$ from caustic soda solutions. J. Crystal Growth, **142**, 177-183.
- Woods, G., Watling, H. and Smith, P. (1994). Analysis of Bayer type liquors by inflection point titrations. Confidential CSIRO Report No. IR/P-001, 13p.
- Yamada, K. (1980). Nucleation and agglomeration during crystallisation of aluminium trihydroxide in sodium aluminate solution. J. Japanese Inst. Light Metals, **32**(2), 720-726.