

THE INFLUENCE OF CRYSTAL GROWTH MODIFYING REAGENTS ON SECONDARY NUCLEATION OF BAYER ALUMINIUM HYDROXIDE

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Abstract

The kinetics of isothermal crystallisation of gibbsite from synthetic Bayer liquors was studied in the presence of a growth modifying chemical reagent at various temperatures, spanning the range found in typical crystallisation circuits. The de-supersaturation kinetic data were fitted with empirical power law models, wherein the secondary nucleation rate constant and activation energy were computed.

The studies presented here, in the absence of any chemical additive were consistent with those reported in the literature for synthetic aluminate liquors. It was found that in the presence of the chemical additive the crystallisation process could be markedly influenced. Compared to the undosed control liquors, the treated liquors yielded a marked reduction in the number of new fine particles produced, yet with an increase in total surface area. This finding was supported by the treated liquors exhibiting an increased rate constant, increased secondary nucleation rate as well as an increase in activation energy. SEM evidence indicated a more porous particle, with large amounts of secondary nuclei remaining on the surface for the treated samples.

1 Introduction

The Bayer process for the production of alumina (Al_2O_3) from bauxite involves a perennial gibbsite precipitation step, relating to an inherently slow crystal growth from supersaturated sodium aluminate solutions (pregnant Bayer liquors). Three major crystallisation mechanisms, nucleation, growth and agglomeration of crystals are in action for producing gibbsite as the preferred phase. The yield of gibbsite is largely determined by nucleation and growth of particles, while agglomeration is responsible for producing a coarse crystal of commercial interest.

The rate of crystal growth is dependent on two factors, the rate of diffusion of the particle to the surface of the seed crystal and secondly the rate of chemical inclusion of that particle onto the surface. Under industrial Bayer plant conditions the growth process is not mass transfer limited and thus the rate is dominated by the chemical inclusion of the particle onto the surface. This rate can be influenced by many factors such as seed surface area, temperature, caustic concentration and liquor characteristics (Misra, 1970). Factors that influence liquor characteristics would include the level of dissolved organic material, including substances which adsorb onto the surface of the crystal and change the surface energy. These substances can decrease the rate of crystallisation and even change the morphology of the crystal itself.

Optimisation of the Bayer plant precipitation parameters is the most important part of the entire industrial process. However optimum conditions for maximum yields do not always coincide with the optimum product size specifications, demanded by the smelters. The relationship between these operating parameters and gibbsite yield has been detailed in a number of publications over many years (Misra, 1970; Misra and White, 1971; Kanehara, 1971; Anjier et al, 1985; White et al 1988). A number of Bayer plants around the world employ a commercially available product which allows them to operate under optimum conditions and remain within the product size specification range. Industry has termed these surface active additives, Crystal Growth Modifiers (CGM). These additives were introduced over 10 years ago (Roe et al, 1988) and have gained general acceptance as additional control tools within the crystallisation section of the Bayer process. However, although there has been a number of recent publications postulating their mechanism of action, (Xie et al, 2001, 2002 and 2003) there still exists a degree of uncertainty as to the impact of these programs and their influence under various agglomeration and secondary nucleation strategies practiced within the industry.

This study examines the impact of a commercially available Nalco CGM on a system designed for secondary nucleating conditions, in order to answer the questions posed by industry. This represents part of the continued developments within Nalco on precipitation additives. The effect of a CGM on the new crystal formation, crystallisation kinetic parameters and morphology under constant supersaturation conditions in isothermal experiments was investigated.

2 Experimental

2.1 Chemicals used and solution preparation

Pure synthetic, supersaturated sodium aluminate solutions were used in this investigation. They were prepared from analytical grade and high purity grade reagents: aluminium trihydroxide, $\text{Al}(\text{OH})_3$, (C31 grade, 0.01% SiO_2 , 0.004% Fe_2O_3 , 0.15% Ba_2O ; ALCOA, Arkansas USA); sodium hydroxide, NaOH, (99.0% pure, 0.01% Si, Merck, Australia); Milli-Q water (surface tension $72.8 \mu\text{Nm}^{-1}$ at 20°C , specific conductivity $<0.5 \mu\text{scm}^{-1}$ and $\text{pH} = 5.6$).

The synthetic liquors used in the crystallisation measurements were prepared in a 2.5 dm^3 well sealed stainless steel crystallizer immersed in an oil bath at 150°C . A known mass of NaOH was dissolved in 1.3 dm^3 of Milli-Q water in the crystallizer with an agitation rate of 250 rpm. This was followed by slow addition of a known mass of the aluminium trihydroxide. After complete dissolution of 3–4 hours, the solution was transferred to a 2.0 dm^3 volumetric flask and made up to the mark with Milli-Q water.

The crystal growth modifier used in this study was the commercially available Nalco product, 7837.

2.2 Seed preparation and characterization

Broken seed fragments, formed via secondary nucleation, provide the main source of new crystals in the Bayer process (Loh et al, 1988; Hind et al, 1999). In this type of secondary nucleation process, fluid shearing action, crystal-crystal and crystal-vessel wall/impeller blade collisions are dominantly responsible for removing nuclei from the growing seed crystal surfaces into solution. It has been stated that particles $>20 \mu\text{m}$ in diameter are less likely to agglomerate as they do not have sufficient surface energy to do so (Misra, 1970). Therefore in order to focus on the effect of the CGM additive on secondary nucleation alone, especially in the early stages of crystallisation it was necessary

to use a large screened seed, high supersaturation, low seed charge and enough agitation to allow the seed to remain in the bulk solution, without settling.

Uniform coarse, gibbsite seed crystals were prepared from high purity $\text{Al}(\text{OH})_3$ (C31) by wet screening using both 55 and 90 μm sieves to give crystals in the size range 30–105 μm . These crystals were then treated with ultra-sonication, followed by decantation to remove the fine particles (<10 μm). The resulting product (washed and dried at room temperature in a desiccator) consisted of agglomerated, pseudo hexagonal-shaped crystals, in the size range 30–100 μm with reasonably smooth surfaces (Figure 1) and a corresponding BET surface area of 0.1445 m^2g^{-1} .

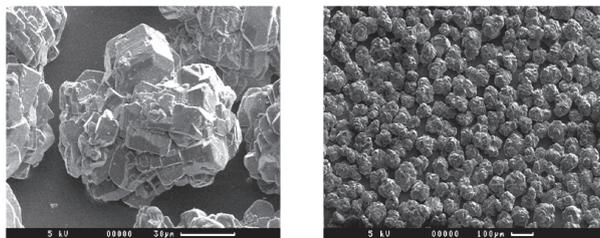


Figure 1: SEM photomicrographs of gibbsite seed crystals at high (left) and low (right) magnifications.

2.3 Batch crystallizer and nucleation experiment

A baffled, well sealed, 2.5 dm^3 , 316 stainless steel vessel was used for the isothermal (60, 65 and 75°C) batch crystallisation experiments. A central, 4 blade, 45° – pitch turbine impeller driven by a 70W, multi-speed motor provided a constant agitation speed at 400 rpm as well as fully developed axial flow, moderate shear and a high degree of suspension uniformity within the crystallizer. A thermocouple sensor and a conductivity probe were fitted through the lid of the crystallizer. The entire vessel was submerged in a 15 dm^3 , thermostatically-controlled oil bath, maintaining a constant temperature to within $\pm 0.05^\circ\text{C}$.

For each nucleation experiment, a fresh 2 dm^3 sodium aluminate solution was prepared and then placed in the crystallizer. As soon as the experimental temperature was reached, pre-heated seeds (at a loading of 50 gdm^{-3}) were added and the conductivity measurements commenced. Aliquots of duplicate 30 cm^3 samples were taken at specific time intervals. These were filtered through a 0.2 μm membrane, the filtrate was analysed by ICP for the Al(III) concentration. One of the filtered solids was washed with Milli-Q water and suspended in water in a tube for particle size determination using a Malvern instrument. The remaining sample was washed and dried in a desiccator for mass determination, SEM and BET surface area analysis. Experiments were run for 24 hours, however this work will focus on the first 4 hours of crystallisation.

For a nucleation experiment with the CGM additive present, the additive was added in the crystallizer as soon as the experimental temperature was reached and allowed to mix for 10 minutes prior to seed addition and the start of measurements. The dosage of the additive was 20 mg of CGM/ m^2 of seed surface. For both the control and dosed experiments, each aliquot removed at specific time intervals, was analysed for the Al(III) concentration, slurry crystal content, crystal surface area, particle size distribution of seed and initial and final crystallisation product crystals.

2.4 Models for the kinetic study

Quantification of the crystallisation kinetics data produced from the crystallisation experiments was performed using the semi-empirical power law model for secondary nucleation and growth of gibbsite as shown below:

$$-\frac{1}{S} \frac{d\sigma}{dt} = k(\sigma)^n$$

where σ is the Al(III) relative supersaturation which defined as $(C - C_e)/C_e$, where C and C_e are the instantaneous Al(III) concentration and Al(III) equilibrium solubility, respectively; S is the total particle surface area; k is the

nucleation rate constant and n is the reaction order. To quantify the influence of temperature and estimate the activation energy from the rate constant k , the Arrhenius expression was used.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

where k_0 is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.

3 Results and Discussion

3.1 New crystals formation

To investigate the influence of the additive on secondary nucleation, the isothermal batch crystallisation experiments were carried out over 24 hours. The tests were conducted under constant conditions of $\text{NaOH} = 4 \text{ M}$, initial $\sigma_{\text{Al}} = 1.5$, seed surface area = 7.23 m^2dm^{-3} and dosage of the additive = 20 mg CGM/m^2 of seed surface at temperatures of 60, 65 and 70°C.

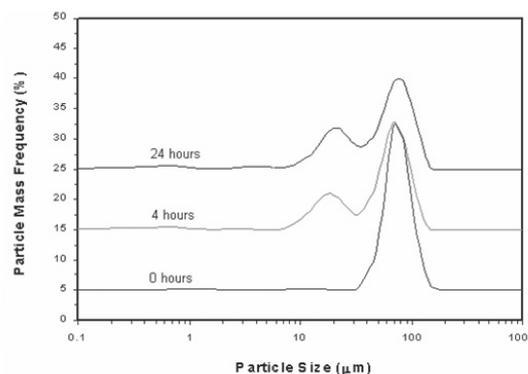


Figure 2: Gibbsite crystal size distributions as a function of time for seeded crystallisation from the untreated control sodium aluminate solution at 65°C over a time period.

Figures 2 and 3 exhibit a reasonably tight particle size distribution, with particles in the 30–105 μm size range, for the starting seed crystal at time 0 hours. In contrast, product crystals had a bimodal particle size distribution as indicated by the samples obtained from aliquots of the control experiment taken at 4 and 24 hours crystallisation at 65°C (Figure 2). Figure 2 indicates the presence of new crystals in the 0.1–30 μm size range, produced as a result of secondary nucleation.

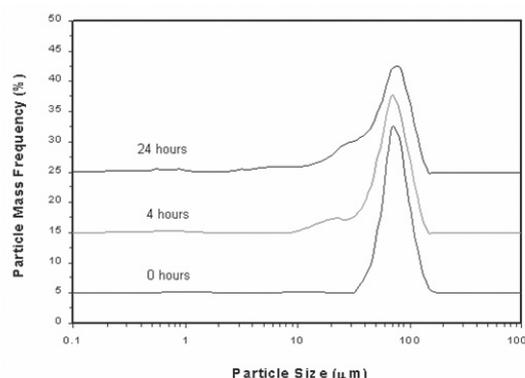


Figure 3: Gibbsite crystal size distributions as a function of time for seeded crystallisation from a CGM treated sodium aluminate solution at 65°C over a time period.

A much different observation was made for the corresponding CGM treated solution. At identical time intervals the number of secondary nuclei was drastically reduced in the presence of the additive as indi-

cated in Figure 3. The nuclei only appear as a small shoulder on the particle size distribution of the parent seed crystals as time progresses. This observation is summarised in Table 1, which indicates the particle number-size analysis for the generation of new fine particles (secondary nuclei) in the size range of 0.1–30 µm during all of crystallisation tests over the first hour. There is a marked difference between the control and treated samples for the 60 and 65°C runs, however no discernable difference could be detected over the first hour for the higher 70°C temperature run.

Table 1: Number of new particles generated for all crystallisation experiments under constant conditions over the first hour of crystallisation.

T (°C)	New Particles < 30 µm (10 ¹⁰ h ⁻¹ per 25 mL)	
	Control	With CGM
60	3.1	1.1
65	10.1	3.7
70	17.5	18.4

3.2 Effect of additive on the induction period and crystallisation

The induction times for the appearance of secondary nuclei were measured by conductivity and are given in Table 2. At a constant initial σ = 1.5 and seed charge of 7.23 m²dm⁻³ the induction time was found to decrease with increasing temperature for both the control and treated experiments. However, the induction time was significantly shorter in the control experiment than in the treated solutions at 60 and 65°C. At 70°C there was no detectable difference in the induction time measurement for the two scenarios. This observation would imply that the CGM additive was affecting solution speciation and/or crystal surface processes during the secondary nucleation. It is plausible that the CGM additive initially deactivated the seed surface to a high extent resulting in a lengthened time for generating sufficient active sites for fast growth. The negative effect of additive on the processes was negated at the higher temperature.

Table 2: Induction times for both control and CGM treated crystallisation tests as a function of temperature.

Temp (°C)	Induction time (mins) for control	Induction time (mins) for CGM treated
60	6	12
65	2	4
70	0	0

Although the additive involvement lengthened the induction times for secondary nucleation, decreases in Al(III) concentrations with time were significantly greater in CGM treated solutions than in the control solutions at similar temperatures. These results are indicated in Figure 4, where the Al(III) relative supersaturation is plotted over the time period for each experiment. This figure exhibits the strong additive addition and temperature dependence of this system. The apparent de-supersaturation rates increased considerably with increasing temperature and were higher in treated liquors than that observed for the control solutions under similar conditions of initial σ, seed surface area and temperature.

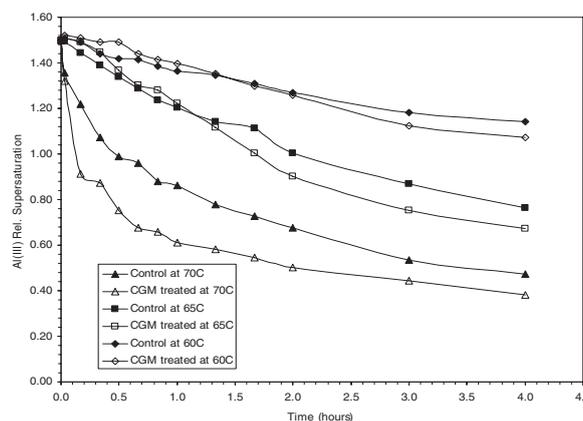


Figure 4: The variation of Al(III) relative supersaturation as a function of temperature for seeded, control and CGM treated crystallisation tests over time.

The net, total crystal surface area with time, as shown in Figure 5 appears to contradict the size data presented in Figures 2 and 3 and the number of new particles generated given in Table 1. The surface area markedly increased initially due to the large number of secondary nuclei formed within the first 4 hours of crystallisation, however the total surface area was much higher for the solids obtained from the treated solutions than the control. The control tests displayed a lower total surface area than that of CGM treated tests at the same temperature, which would tend to indicate the possible impact of agglomeration during the crystallisation. However, it is proposed that initially a larger number of secondary nuclei formed in the treated solutions and these nuclei immediately were either adsorbed back on the seed surface or rapidly agglomerated with each other to form aggregates with a high porosity. This resulted in a low number and a high net surface area of the crystals.

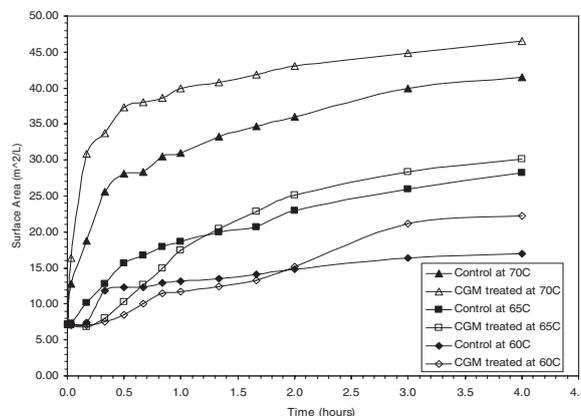


Figure 5: The variation of total available surface area for the crystallising slurry as a function of temperature for seeded, control and CGM treated tests over time.

SEM analysis strongly supported the above observations. The images of the product crystals revealed the existence of significant differences in the development and growth of the new surface layer and microstructures at the seed crystal surfaces, between the control and CGM treated tests. After 0.33 hours of crystallisation at 60°C, the seed surface became very rough and the presence of massive, microscopic protrusions was apparent at the seed crystal surfaces. The random formation of protrusions as a result of crystal growth appears to be consistent with a 2-dimensional surface nucleation – crystal growth mechanism (Pearson, 1955; Hind et al, 1999). Large numbers of discrete particles of 0.2 µm in size were visibly attached to the parent seed in both the control and CGM treated solutions (Figure 6A and 6A’). Figure 6B, a control test taken after 0.33 hours at 70°C, exhibits a trace amount of fine particles adhered and grew to the parent seed surface. It is possible

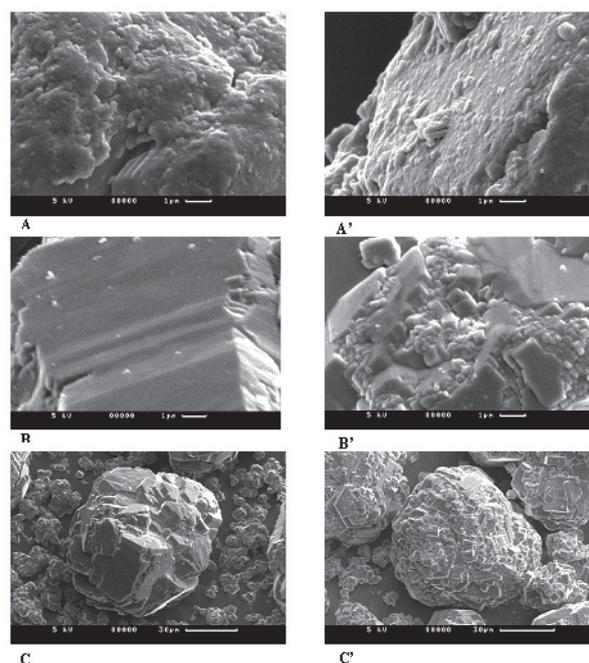


Figure 6: SEM photomicrographs of seed crystals during crystallisation at 0.33 h at 60°C (A and A'); 0.33 h at 70°C (B and B') and 24 h at 65°C (C and C') for control (A–C) and CGM treated tests (A'–C').

that the other secondary nuclei formed after this time were dislodged from the surface to bulk solution due to attrition from the parent crystal by mechanical contact or liquid shearing actions. In contrast, a large number of fine particles strongly adhered on the seed surface as aggregates and individual particles with a size range of 0.2–20 μm for the corresponding CGM treated test, given in Figure 6B'.

Figures 6C and 6C' were obtained for seed crystals after 24 hours of crystallisation at 65°C for the control and CGM treated test respectively. Figure 6C reveals that for the control, an insignificant number of fine particles generated by the secondary nucleation mechanism adhered onto the seed crystal surfaces during the experiment. Instead, these particles predominantly agglomerated into aggregates as soon as they were removed from the parent seed surface. These aggregates are evident in the figure, with sizes of up to ~30 μm. In the presence of CGM (Figure 6C') a large portion of the fine particles adhered and grew on the seed surface, whilst the remaining fraction formed aggregates in the bulk solution. This is clear evidence for the observation of the higher net surface area and correlates well with the lower number of new crystals in the treated systems compared with the control.

The conclusion from this evidence is that the involvement of the CGM additive in the seeded gibbsite crystallisation for all temperatures not only enhanced the parent seed growth mechanism, through accelerated secondary nucleation, with less attrition and hence particle surface roughening but also enhanced the secondary nuclei agglomeration behaviour.

3.3 Effect of additive on kinetics of secondary nucleation

As the growth rate of gibbsite is relatively slow when compared with other inorganic crystals (Misra et al, 1971; Halfon et al, 1976; Loh, 1988; King, 1973) it is feasible to assume the initial kinetics to be dominated by secondary nucleation at high σ (> 1.15). Therefore, the birth rate of 3-dimensional nuclei, reflected in a dramatic crystal population increase, is considered to far exceed the rate of growth (2-dimensional nucleation process) of both parent seed crystals and the nuclei (Halfon et al, 1976).

The crystallisation kinetics data produced from the seeded crystallisation at a high initial $\sigma = 1.5$ for which secondary nucleation occurred were analysed and duly quantified using a semi-empirical power law model (Equation 1). Typically, relative Al(III) flux changes with time, are a true measure of the precipitation kinetics, these were found to be

more significant for the CGM treated liquors than the control experiments over the first 4 hours. Plots of $\ln(-1/S)(d\sigma/dt)$ versus $\ln\sigma$ for both the control and CGM treated solutions over 4 hours at each of the specific temperatures were linear. From the slopes of these plots, the secondary nucleation dominated-reaction order (n) was reproducibly found to be equal to 4. The results are summarised in Table 3. The same value was reported for secondary nucleation of gibbsite from sodium aluminate solution under comparable conditions (Nesterov and Teslya, 1989; Li et al 2000).

Activation energies for gibbsite secondary nucleation for the control and CGM additive tests were estimated from Arrhenius plots (Equation 2 and Figure 7), the values are summarised in Table 3. E_a values of 162 ± 30 and 239 ± 40 kJmol⁻¹ for secondary nucleation were calculated for the control and additive tests, respectively. These values are higher than the 132 ± 15 kJmol⁻¹ reported for secondary nucleation from synthetic sodium aluminate solutions under similar conditions to the control (Li et al, 2000), but are much closer to the value of 160 kJmol⁻¹, reported in an earlier work (Nesterov and Teslya, 1989). The presence of the CGM additive in the crystallisation markedly increased the activation energy for gibbsite secondary nucleation. This result suggests that more temperature-induced, chemical perturbations occurred in the CGM treated solutions. It is proposed that the additive is not only involved in the clustering of aluminate ions in supersaturated

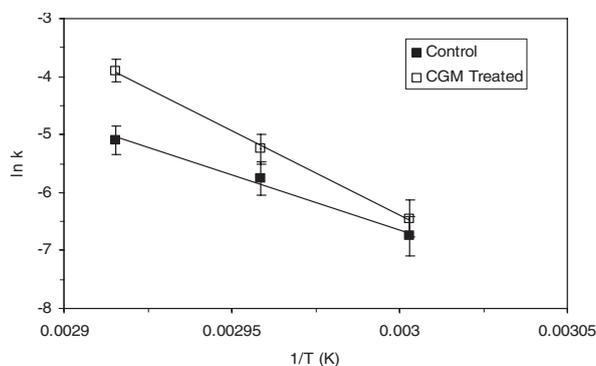


Figure 7: Arrhenius plots using the fourth order rate constants for secondary nucleation of standard and additive tests.

sodium aluminate solution but also the interactions between the clusters and surfaces of seed crystal, which are responsible for the development of microscopic growth units.

The pre-exponential factor of k_0 was found to be much higher for the CGM treated gibbsite secondary nucleation than for the control tests. It is therefore obvious that the successful collision frequency between the nuclei forming, Al(III) containing species was enhanced by the presence of additive.

Table 3: Kinetic parameters for seeded gibbsite secondary nucleation for the control and CGM treated experiments at 60, 65 and 70°C (NaOH = 4M, initial = 1.5, seed surface area = 7.23 m²dm⁻³ and dosage of the additive = 20 mg CGM/m² seed surface.).

Terms	T (°C)	Control	CGM Treated
k_0 (m ² h ⁻¹)	60, 65, 70	3.81×10^{22}	4.50×10^{34}
Reaction Order (n)	60	4.2 ± 0.2	4.1 ± 0.2
	65	3.9 ± 0.2	4.0 ± 0.2
	70	4.0 ± 0.2	4.1 ± 0.2
Ea (kJmol ⁻¹)		162 ± 30	239 ± 40

4.3 Effect of additive on gibbsite morphology and aggregation

SEM photomicrographs of gibbsite crystals obtained from the isothermal batch crystallisation experiments for the control are given in Figure 8 and for the CGM treated liquor in Figure 9. The product crystals formed from the control tests revealed that significant, random agglomeration occurred between the secondary nuclei. The primary crystals were pseudo-hexagonal plates (Figure 8A) which agglomerated and grew to secondary crystals with a size range of 10–30 µm (Figure 8B). Very few, if any secondary nuclei were found to attach and grow on the parent seed surface (Figure 8B). In general for the control solutions it was found that as the isothermal batch temperature was increased the aggregation of the small nuclei, broken off the parent seed surface, increased.

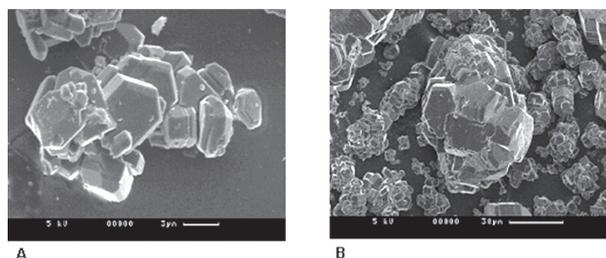


Figure 8: SEM photomicrographs of crystal products obtained from seeded crystallisation in the control solutions. Primary crystals (A) and parent seed crystal with secondary nuclei (B).

With the CGM present in the solutions, the secondary nuclei that formed either remained on the parent seed surface or if broken off, agglomerated as aggregates immediately. The degree to which the nuclei remained on the parent seed surface increased with increasing isothermal batch temperature. The primary crystals predominately exhibited pseudo-hexagonal plates in shape in the aggregates, however some were of irregular edges (Figure 9A). There was also elongated hexagonal shaped crystals produced (Figure 9B). The parent seed

surfaces were partly or fully covered by fine particles (Figure 9C). These particles exhibited stick or needle-like morphology along with the pseudo-hexagonal plates growing on the surface of seeds. The size of these primary crystals were in the range of 0.5–10 µm, implying quick attachment as soon as the nuclei formed. It is postulated that the CGM modified seed surfaces possessed a high surface energy interacting with the nuclei strongly with little or no repulsive energy barrier. In Figure 9B it is observed that the sticks grow out of the surface and are therefore most likely broken off by particle collisions to form new fine particles. However, as soon as these particles were dislodged into the bulk solution, they immediately either adhered onto the surface of other larger crystals or rapidly agglomerated with smaller crystals, due to the high surface energies.

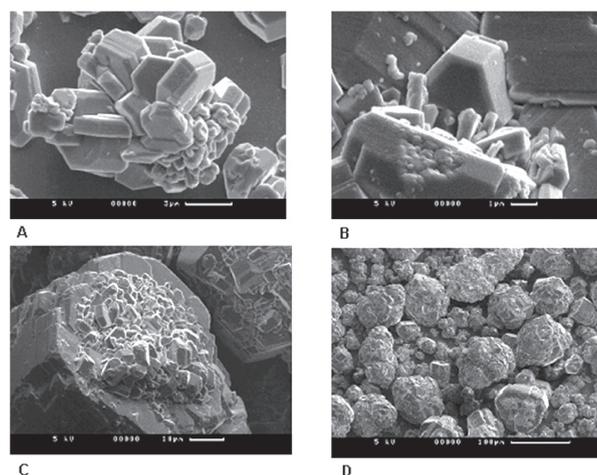


Figure 9: SEM photomicrographs of crystal products obtained from seeded crystallisation in additive induced solutions. Primary crystals (A-B), parent seed crystals (C-D).

4 Conclusion

Evidence has been presented here which would indicate that the CGM additive would aid in the control of the generation of secondary nuclei in the precipitation of sodium aluminate liquors. The additive appears to do this for all temperatures by increasing the successful collision frequency of not only Al(III) containing species but also small fractured gibbsite particles. The parent seed growth mechanism was enhanced through accelerated secondary nucleation, more specifically, particle surface roughening and also enhanced secondary nuclei agglomeration behaviour.

In a process where the chemical inclusion of the particle onto the surface of the seed is the rate limiting step and where particles are colliding and continually breaking off parent seed crystals, the addition of CGM may just allow the particle sufficient time to chemically bond with the seed surface and be incorporated into the structure. This phenomena would, ironically, also be beneficial to the agglomeration process. Two gibbsite particles will agglomerate if they have sufficient surface energy to do so and also have sufficient time to allow cementation to take place (Misra, 1970). Therefore to conclude that this specific CGM additive only controls secondary nucleation would be incorrect, it would also act as an agglomeration aid under specific conditions.

References

- Anjier, J and Roberson, H, 1985, "Precipitation Technology", Light Metals, pp 367–375.
 Halfon, A and Kaliaguine, S, 1976, "Alumina Trihydrate Crystallisation, Part 1 Secondary Nucleation and Growth Rate Kinetics", Canadian J. Chem. Eng., 54, pp 160–167.
 Halfon, A and Kaliaguine, S, 1976, "Alumina Trihydrate Crystallisation, Part 2 A Model of Agglomeration", Canadian J. Chem. Eng., 54, 168–172.
 Hind, A R, Bhargava S K and Grocott, S C, 1999, "The Surface Chemistry of Bayer Process Solids: A Review", Colloids and Surfaces, 146, pp 359–374.
 Kanehara, M, 1971, "Formulation of Alumina Hydrate Precipitation Rate in Bayer Process for Plant Design and Operation", Light Metals, pp 87–105.
 King, W R, 1973, "Some Studies in Alumina Trihydrate Precipitation Kinetics", Light Metals, 2, pp 551–563.

- Li, J, Prestidge, C A and Addai-Mensah, J**, 2000, "Secondary Nucleation of Gibbsite Crystals from Synthetic Bayer Liquors: Effect of Alkali Metal Ions", *Journal of Crystal Growth*, 219, pp 451–464.
- Loh, P I W, Ang H M and Kirke, E A**, 1988, "Secondary Nucleation of Alumina Trihydrate in a Batch Crystallizer", *Australia's Bicentennial International Conference for the Process Industries*, Sydney, pp 304–309.
- Misra, C**, 1970, "The Precipitation of Bayer Aluminium Trihydroxide", Ph.D. Dissertation, University of Queensland.
- Misra, C. and White, E T**, 1971, "Kinetics of Crystallisation of Aluminium Trihydroxide from Seeded Caustic Aluminate Solutions." *American Institute of Engineers Symposium Series* 438, 67(110), pp 53–65.
- Nesterov, A V and Teslya, V G**, 1989, "Mathematical Model for Crystallisation of Aluminium Hydroxide from Aluminate Solutions", *Zhurnal Prikladnoi Khimii*, 62, pp 1999–2004.
- Pearson, T G**, 1955, "The Chemical Background of the Aluminium Industry", Royal Institute of Chemistry, London, pp 22–23.
- Roe, W J, Owen, D O and Jankowski, J A**, 1988, "Crystal Growth Modification: Practical and Theoretical Considerations for the Bayer Process", *First International Alumina Quality Workshop*, Gladstone (Australia).
- White, E T and Bateman S H**, 1988, "Effect of Caustic Concentration on the Growth Rate of $\text{Al}(\text{OH})_3$ Particles." *Light Metals*, pp 157–162.
- Xie, Y, Bi, S, Wu, J and Li, G**, 2001, "Study on the Application and Mechanism of Cationic Surfactant on the Precipitation of Sodium Aluminate Liquor", *Light Metals*, pp 135–137.
- Xie, Y, Zhao, Q and Bi, S**, 2002, "Research on the Application and Mechanism of Crystal Growth Modifier on the Precipitation Process in Sodium Aluminate Liquors. *Light Metals*, pp 157–160.
- Xie, Y, Zhao, Q, Bi, S, Feng, C and Yihong, Y**, 2003, "Research on the Mechanism and Optimum Adding Method of Additives in Seed Precipitation", *Light Metals*, pp 87–91.