

MECHANISTIC INVESTIGATIONS OF GIBBSITE GROWTH

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Abstract

Despite decades of research into hydrate growth in the Bayer process, there is no consensus on how the mechanism operates or what form of equation best describes growth kinetics. Indeed, there are half a dozen equations in popular use and many others in the open literature. All seem to work within limits. Knowledge of the growth mechanism is a powerful tool, not just to arrive at a better equation to describe growth rate, but in order to understand the whole precipitation process including soda incorporation, crystal morphology, effects of liquor composition and the effects of organics and process additives.

The present paper reviews the fundamental studies undertaken by the Parker Centre and other institutions, especially in the AMIRA P380 series of projects. It brings together sometimes apparently contradictory conclusions from various authors to propose a mechanism for hydrate growth that is consistent with laboratory and refinery observations. There is little doubt that the rate determining step is surface controlled. It appears that the liquor composition has a significant role in moderating the surface chemistry, and therefore moderates the mechanism. Additionally, it appears that the mechanism changes according to process conditions and this may help to explain why the mechanism has been so difficult to elucidate.

1. Introduction

1.1 Background

The literature contains a large number of studies on the precipitation kinetics of gibbsite in aluminate liquors and many attempts to model the growth, agglomeration and nucleation. Many of the publications have focussed on empirical relationships which, while useful for describing precipitation under a narrow range of conditions, do not attempt to explain the fundamental mechanisms of crystal growth. Work in the past few years (e.g. at the AJ Parker Cooperative Research Centre [1–18] and the Ian Wark Research Institute [19–25]) has attempted to explore the fundamental aspects. Physical growth mechanism is now better understood, and speciation has been shown [2–8] to be less complicated than predicted in some publications in line with (although an improvement on) the predictions of Moolenaar *et al.* [26] Even the exotic tool of *ab initio* quantum mechanical molecular modelling [18] has been used in speciation prediction and agrees well with experimental findings for the most populous species.

Recent improvements in fundamental knowledge have allowed improved fitting of precipitation rate data, but this improvement has highlighted other problems. Ilievski [27] notes that driving force in gibbsite precipitation may be expressed in a number of ways, but none of these are satisfactory. It has become obvious that total aluminium concentration may not be the most important factor, especially if the aluminium is present as a number of different species and if not all of these species are involved directly in crystal growth. Further, other non-aluminium species in solution may also play a role in the precipitation reaction. The reactions commonly quoted as the precipitation process, such as:



are thought to be gross over-simplifications. Many representations of the rate law for gibbsite precipitation commonly use driving force relationships based on a simple difference between the concentration of aluminium in the

liquor and equilibrium aluminium concentration (e.g. some of King's [28] equations);

$$-d\text{Al}/dt = k_s \text{SA} (\text{Al} - \text{Al}_{\text{eq}})^2 \quad (2)$$

or a combination of the simple difference and a function of caustic concentration (e.g. King's and White & Bateman's [29] equations);

$$-d\text{Al}/dt = k_r \text{SA} \left(\frac{\text{Al} - \text{Al}_{\text{eq}}}{\text{FC}} \right)^2 \quad (3)$$

and;

$$-d\text{Al}/dt = k_s \text{SA} \frac{(\text{Al} - \text{Al}_{\text{eq}})^2}{\sqrt{\text{C}}} \quad (4)$$

(where Al represents a measure of aluminium concentration in the liquor, FC is the "free caustic" in liquor and C is the "total caustic"). Alternatively, there are some expressions derived from crystal growth theory, e.g. Veessler & Boistelle [30] published the following linear growth rate expression:

$$R_{\text{G}} = k_{\text{G}} e^{-\frac{\Delta G_{\text{c}}}{RT}} \beta^2 \quad (5)$$

and e.g. Cornell *et al.* [31]

$$-d\text{Al}/dt = k_{\text{G}} \text{SA} (\ln \beta)^3 \quad (6)$$

where

$$\sigma = \frac{\text{Al}}{\text{Al} - \text{Al}_{\text{eq}}} \quad \text{and} \quad \beta = \frac{\text{Al}}{\text{Al}_{\text{eq}}} \quad (7)$$

Veessler and Boistelle [32] further refined Equation (5), replacing equilibrium alumina concentration with "critical supersaturation", attributing this to a poisoning factor (possibly Fe ions):

$$R_{\text{G}} = k_{\text{G}} e^{-\frac{\Delta G_{\text{c}}}{RT}} (\beta - \beta_{\text{c}})^2 \quad (8)$$

where β_{c} is the critical supersaturation. There are many relationships published in the literature, each fitting the published data set. There have been few attempts to match

crystal growth mechanism with speciation considerations to produce a viable precipitation rate law due to lack of knowledge about the mechanism and the difficulties encountered in distinguishing between quality of fit for different equations. Indeed, almost any published rate law will adequately fit any data set if the parameters are allowed to vary even slightly.

1.2 Crystal growth observations

Lee [10, 12] plotted linear growth rates of single crystals of gibbsite in pure sodium aluminate solutions against supersaturation. She came to the conclusion that there are two growth mechanisms occurring within the normal range of supersaturations encountered in a Bayer refinery. Below A/C of 0.50 at 70°C, the growth mechanism appeared to follow the classical Burton Carrera Frank (BCF) "spiral" rate law (practically identical to Eq. (5) above) whereas above this supersaturation, a birth and spread type mechanism as described by:

$$-dA/dt = k_p SA e^{\beta \Delta \mu} \beta^{-1/2} \quad (9)$$

starts to dominate. Subsequent near-atomic resolution AFM observations of a growing gibbsite surface by Freij [14, 33] agreed with Lee's work and clearly showed that high supersaturations cause a birth and spread type growth, whereas more moderate conditions give smooth step spreading growth, best described mathematically by the BCF equations. Work by Vernon *et al.* [8, 16] confirms the applicability of the spiral rate law to precipitation kinetics in a bulk experiment (measuring growth rate from desuper-saturation, rather than linear growth of particles) but only at low supersaturation. The supersaturation at which Lee found a second mechanism beginning to dominate is not very high by refinery standards (C200, A/C 0.5, 70°C, $\beta \approx 1.6$), indicating that two rate laws may be necessary to describe growth in the entire supersaturation range encountered in a Bayer refinery.

Studies of gibbsite precipitation are hampered by changes in the precipitation mechanism over a small range of supersaturation. β (as defined in Eq. 7) can only be varied from about 1.3 (the "critical" supersaturations of Veessler and Boistelle) to about 1.6 (from Lee's observations) before mechanistic changes occur. As the supersaturation increases into this zone [34], secondary nucleation becomes a feature of precipitation in a stirred tank and measurements must take into account an evolving surface area. A study of gibbsite growth mechanism is therefore all but impossible using traditional bulk stirred tank techniques. It is little wonder then that the mechanism has proven to be so elusive and that so many equations describing gibbsite precipitation coexist in the literature.

In summary, gibbsite growth is described physically by a spiral (square law) mechanism at low supersaturation and increasingly by a birth and spread (fractal law) mechanism as the supersaturation increases. Appropriate forms of equations have been suggested. As interesting as these observations are, there are still a great number of factors not explained, such as the roles of surface chemistry, surface integration and solution speciation on the rate-determining step.

1.3 Solution speciation

Some surprisingly complicated Bayer liquor speciation has been published. Many of these are dependent on minimization of models that allow fits to a large number of possible species [35, 36] or species calculated by empirical (qualitative) molecular modelling [24, 25]. Some of the speciation schemes are attractive in describing the gibbsite

growth mechanism but none of these speciation schemes have been experimentally substantiated. The most rigorous and comprehensive experimental work [2–6, 8] suggests that a sodium aluminate solution is exclusively composed of $Al(OH)_4^-$ and OH^- ions and their sodium ion pairs, free Na^+ , a lesser concentration of an aluminate dimer (possibly $(OH)_3AlO_2Al(OH)_3 \cdot xH_2O$) and a very small concentration of $Al(OH)_6^{3-}$. *Ab initio* quantum mechanical studies also suggest [18] that a dimer is formed: $(OH)_3Al(OH)_2Al(OH)_3 \cdot 2H_2O$. This is not inconsistent with the experimental determination, as the two species cannot be distinguished by experimental methods. Further *ab initio* quantum mechanical work has suggested a minor concentration of an $Al_6(OH)_x^{y-}$ species but this is not yet certain. In the face of apparently simple speciation it is possible to compare the concentration of each species with easily measured growth rates. Unfortunately there are no simple relationships between gibbsite growth rate and species concentration other than those already empirically known; that is, growth rate correlates reasonably well with the concentrations of any selected Al containing species. Semi-empirical computational predictions initially seem an attractive proposition as they describe a wealth of minor species existing in Bayer liquors and suggest elaborate reaction mechanisms for gibbsite growth [25]. Alas, the equilibria suggested and the inherent very low concentrations predict gibbsite growth to be many orders of magnitude slower than is observed, and require significant liquor ageing before precipitation can occur.

In the absence of experimental evidence to the contrary, it should be assumed that speciation in Bayer liquors is quite simple and that gibbsite growth occurs through addition of aluminate (or a species in equilibrium with it) to the surface. Without a definite link between speciation and growth rate, surface integration appears to be the key to understanding the mechanism.

1.4 Surface chemistry and surface integration

Surface chemistry in highly concentrated highly caustic liquors is difficult to study. Classical surface chemistry concepts tend to break down completely at ionic strengths in excess of 0.01 to 0.1 mol L⁻¹. Gibbsite particles in Bayer liquor have been suggested [8, 19, 22, 37–39] to exhibit special properties that are inconsistent with the DLVO theory. Promising work has been conducted on probing the gibbsite surface with atomic force microscopy [38] and it would appear that the surface develops an organised layer many times thicker than predicted by theory. One author [25] has attributed the layer to a polymeric "fuzzy interface". However it appears there is only one other publication that proposes such a model in crystal growth, for silica formation [40]. One of the key requirements of this application of fuzzy interfaces is the presence of a *polymeric aluminate phase* on the gibbsite surface. The main hint at the existence of this lies in semi-empirical computational prediction of speciation, which has not been supported by physical measurements. It is not necessary however to invoke a polymeric fuzzy interface model to explain any of the physical observations of the gibbsite surface.

Water activity in aluminate liquors has been shown to be higher than expected [41] and there is some evidence [42] that this is due to the formation of water deficient ion pairs [2, 8], and significantly there is an indication from rigorous molecular dynamics [43, 44] that relatively large clusters of aluminate ions form, stabilised by sodium ions. Vernon *et al.* [8] have shown in preliminary measurements that the gibbsite surface appears to behave anomalously at high pH and at high sodium ion concentrations, indicating strong adsorption of sodium ions. The simpler explanation

therefore may be that gibbsite behaves as a charged plate and a layer of *ion clusters* develops. Such an approach agrees with observed X-ray diffraction spectroscopy of aluminate solutions (Radnai *et al.* [6] describe an 0.33 nm to 0.39 nm feature in Bayer liquors, which does not appear to grow), cryovitrification-TEM observations (Gerson *et al.* [20] noted the appearance of approximately 10 nm higher density features in Bayer liquors) and preliminary Small Angle Neutron Scattering investigations (unpublished observations by Vernon *et al.* suggest solution and surface features of the order of 0.5 to 10 nm).

1.5 The present work

The evidence to date suggests that surface integration is a slow step in gibbsite precipitation and that the surface is likely to have some special properties, one of these being a strongly adsorbed layer. The experimental work described in this paper explores the effects of different variables on precipitation and the likely relationship with the surface integration step, drawing on the wealth of fundamental information recently in the literature.

2. Experimental

2.1 General procedures

Diverse experiments were conducted over a period of time and hence the following description is fairly general. Experiments were performed using a variety of standard white-side laboratory equipment, including thermostatted bottle tumbling baths, stirred crystallizers with conductivity monitoring etc. Synthetic liquor makeup used Alcoa C31 hydrate and AR grade chemicals. All contacted surfaces were either stainless steel, PEEK, HDPE or PTFE. Liquor titration was by the Worsley Gran plot method customised within the CSIRO laboratory.

Precipitation was conducted using low charges (40 g L⁻¹) of C31 seed which had been wet sieved with deionised water to remove virtually all of the -45 µm and +106 µm particles.

2.2 Experimental observations

2.2.1 Effect of ions on precipitation

The effects of adding various salts to synthetic bayer liquors was investigated. Start supersaturation was maintained in each case with reference to the solubility equation published by Rosenberg and Healy [46] and in the case of salts not included in the equation, solubility measurements were made to modify the equation appropriately.

2.2.2 Apparent solubility as a function of caustic concentration

Simple extrapolation of precipitation desupersaturation curves often suggests a higher equilibrium solubility value than is measured using conventional methods (e.g. Rosenberg and Healy [46]) and we have referred to this phenomenon here as *apparent solubility*. It is possibly of a similar origin to the “critical supersaturation” observed by Veessler and Boistelle [32]. Figure 2 shows an example of the phenomenon.

A number of precipitation curves were fitted allowing the solubility value to float as a variable in curve fitting. Figure 3 shows the effect of varying caustic levels on the gap. As total caustic increases, the gap between projected and measured equilibrium widens. This is true for both sodium and potassium hydroxide liquors although there may be some difference between the effects of the cations (the effect does not start until higher concentrations in potassium hydroxide). Following the effects of cations seen in Figure 1 it might be expected that there would be a similar effect of Na⁺ on the apparent solubility, but this was not found to be the case — the predominant effect appears to be that of total caustic, not ionic strength or Na⁺ concentration.

2.2.3 Effects on morphology and sodium incorporation

It is well known that replacing the sodium ion with potassium ions alters the growth morphology of gibbsite from blocky to needle-like. We have long supposed that the change in morphology was connected with the relative

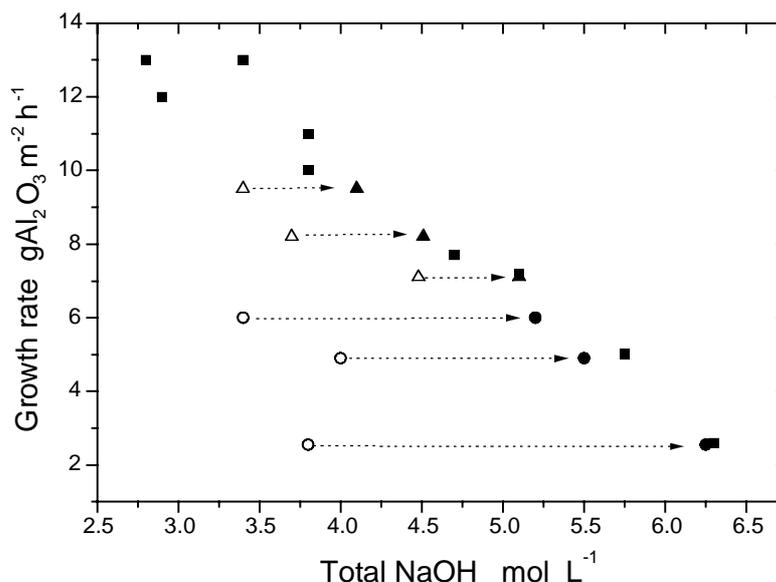


Figure 1 — A plot of growth rate recorded at an initial $\beta = 1.56$ and 70.0°C. A/C was adjusted to give the same initial starting supersaturation for each liquor. Growth rate was measured for the initial almost linear portion of the precipitation curve and no fitting assumptions were made. Filled squares are for liquors containing caustic only and show the expected effect of caustic concentration on precipitation rate. Open triangles and circles show the effect on precipitation rate of adding various amounts of either sodium perchlorate or sodium chloride, respectively. Arrows lead from these data to filled points at the equivalent NaOH concentration required to match the sodium contribution of the salts. There is good agreement with the NaOH-only trend indicating that the concentration of the sodium ion has some bearing on the precipitation rate (and therefore, the mechanism).

adsorption of the two cations on the 001 face (Na^+ adsorbs more strongly than K^+). The caustic concentration effects on gibbsite growth rate are well known. We conducted a series of measurements on the corresponding effects on gibbsite morphology.

Dimensions of 10 crystals were taken from SEM images of each of the products of each experimental run and averaged to give the values in Table 1. Crystals were unagglomerated in most cases but where agglomeration was significant some dimensions were approximated.

A general principle of crystal growth is that slower growing faces dominate the morphology. Therefore, blocky crystals have a slower growing 001 (hexagonal) face than prismatic faces, when compared to needle-like crystals. The data in Table 1 indicate several trends:

- At lower caustic concentrations, the crystals are longer and the prismatic faces dominate.
- Gibbsite grown in potassium aluminate solutions generally has an even greater length to width ratio, with relatively greater growth along the C-axis.
- In K-aluminate liquors an increase in caustic concentration appears to retard growth along the C-axis, reducing the l:w ratio. An increase in supersaturation appears to enhance growth on both the hexagonal and prismatic faces, but more so the prismatic.
- In Na-aluminate liquors an increase in caustic concentration does not seem to retard growth along the C-axis but promotes growth of the prismatic faces.
- Substitution of 25% of KOH in a liquor with NaOH resulted in morphology expected for Na-aluminate liquors (showing the relatively stronger effect of Na^+).

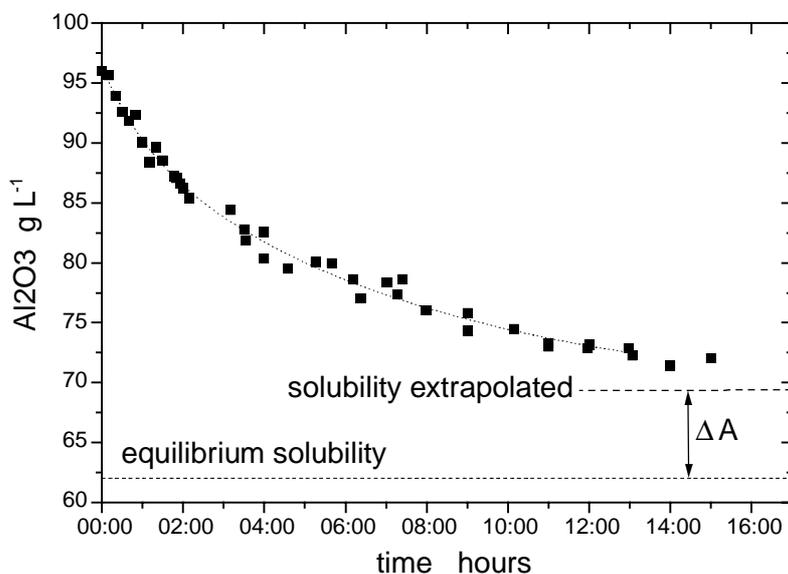


Figure 2 — A desupersaturation curve for seeded sodium aluminate liquor at 70°C. Dots represent measured alumina concentration in the liquor and the dotted line shows an extrapolation based on a fit to the data. The extrapolation indicates that the “fitted solubility” is approximately 69 g L⁻¹, whereas the measured solubility (after 4 weeks) is 62 g L⁻¹.

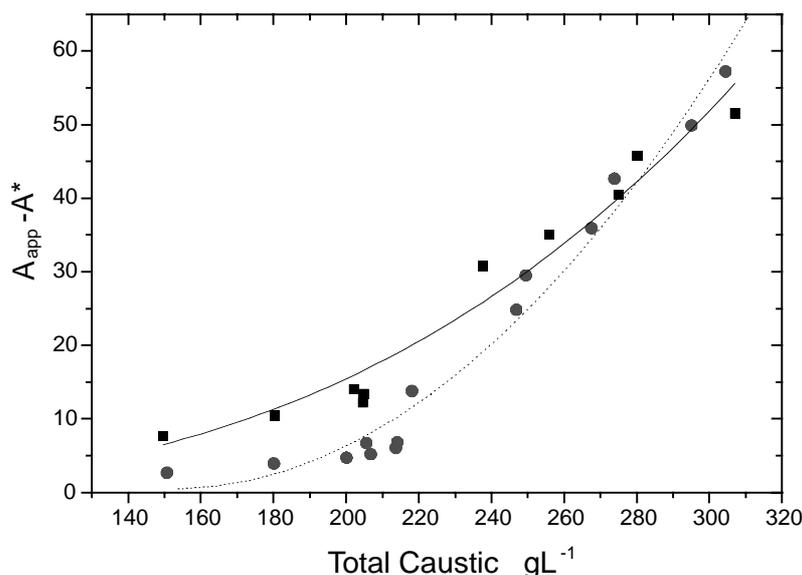


Figure 3 — The difference between the apparent (fitted) equilibrium alumina concentration (A_{app}) and the measured equilibrium value (A^* , obtained after at least 4 weeks, plotted as g L⁻¹ Al₂O₃) is plotted against total caustic (expressed as g L⁻¹ Na₂CO₃). Batch experiments were conducted in pure sodium aluminate (■) and pure potassium aluminate (●) liquors at 70.0°C and seed with 200 g L⁻¹ of coarse hydrate seed.

Table 1 — Liquors were made up to the required start supersaturation, β , and caustic concentration, C, heated to 70.0°C, seeded with a few crystals of gibbsite and tumbled at temperature until appreciable nucleation had occurred. Crystals were then washed in hot deionised water, dried and examined in the Scanning Electron Microscope. The data here represents the average measured lengths and widths for crystals nucleated and grown during each experiment. The 0.8/200* experiment is one in which 25% of the KOH was replaced by NaOH.

β / C	K-aluminate liquor			Na-aluminate liquor		
	<i>l:w</i> ratio	Length / Width μm	% K ₂ O in Al ₂ O ₃	<i>l:w</i> ratio	Length / Width μm	% Na ₂ O in Al ₂ O ₃
1.5 / 100	8.0±0.5	15 / 1.9	0.019	3.0±0.5	15 / 5	0.062
1.8 / 100	5.2±0.9	30 / 5.8	—	3.2±0.3	18 / 5.6	—
2.2 / 100	4.5±0.9	40 / 8.9	0.037	1.9±0.2	20 / 10.5	0.068
1.5 / 200	2.5±0.1	12 / 4.8	0.051	1.2±0.2	8 / 6.7	0.079
2.2 / 200	2.4±0.6	13 / 5.4	0.191	0.8±0.1	12 / 15	0.215
1.8 / 200*	1.1±0.2	13 / 12	0.104			0.065
1.5 / 300	2.0±0.1	11 / 5.5	0.035	1.0±0.1	8 / 8	0.093
1.8 / 300	1.1±0.1	10 / 9.1	0.077	1.2±0.1	20 / 17	0.126
2.2 / 300	0.9±0.1	8 / 8.9	0.323	1.0±0.2	11 / 11	0.342
1.5 / 400	1.0±0.2	5 / 5	0.042	1.0±0.2	5 / 5	0.117
1.8 / 400	0.9±0.3	10 / 11	0.231	1.0±0.1	20 / 20	0.406

3. Results and Discussion

3.1 Na⁺ effects on growth at constant supersaturation

At constant start supersaturation, the rate constant for gibbsite growth decreases as sodium ion concentration increases. Veessler and Boistelle have claimed that once supersaturation is normalised using β there is no caustic dependence. It is not clear why that study found a different result to the present study, but other evidence (eg [16, 29]) indicates a caustic dependence.

This suggests that sodium ion adsorption onto the gibbsite surface controls the rate of integration.

3.2 Driving force: is there a critical supersaturation?

Critical supersaturation, as described by Veessler and Boistelle [32], appears to be some manifestation of a metastable range, which is a function of caustic concentration. It is possible to measure equilibrium solubility of gibbsite in Bayer liquor to high levels of accuracy, and yet the measured thermodynamic solubility seems inadequate to describe the driving force. Some allowance for apparent solubility needs to be made. The difference between the rapid approach to the apparent solubility and the measured thermodynamic solubility suggests separate growth mechanisms. The rapid growth of interest in alumina refining seems to tend towards an A_{app} somewhat higher than the A^* measured after dissolution, or long slow precipitation, typically several weeks. A^* may be a poor baseline measure for calculating driving force in precipitation. A_{app} appears to be a better measure and this is legitimized by its dependence on caustic concentration in the liquor, in line with common observations of the effect of caustic concentration on precipitation rate.

3.3 Morphology as a probe of surface integration

An interpretation of the observations in Table 1 is that even a low level of Na⁺ has a retarding effect on growth in the C direction (i.e. on the hexagonal face). Higher levels of K⁺ are needed to provide the same level of blocking, and this is consistent with observations and predictions that the equilibrium constant for Na⁺ adsorption on gibbsite is an order of magnitude greater than for the adsorption of K⁺. The observations are consistent with a mechanism where

the cation is involved in the growth mechanism, most likely as a moderating influence. Prestidge [8] has shown that whereas even low concentrations of Na⁺ have a profound effect on the surface charge of gibbsite, 2 to 5 times higher concentrations of K⁺ are required to elicit the same effect. It seems reasonable to attribute the caustic concentration effects shown in Table 1 to differential cation adsorption at lower caustic concentrations. It is interesting that the effect of caustic concentration on cation incorporation roughly corresponds to the same effect on morphology, indicating a strong mechanistic link with cation adsorption.

Similar observations have been made in our laboratory when high temperatures are used. High growth temperatures at moderate caustic concentrations result in the lengthening of gibbsite crystals and this is thought to be due to lesser Na⁺ adsorption at higher temperature (as is predicted by any adsorption model).

4. Conclusions

The present study has examined some of the more recent attempts made to understand the growth mechanism of gibbsite in Bayer liquors. It is concluded that the mechanism is complicated. The following are considered important associated issues:

4.1 Physical mechanisms

- A well-behaved spiral type mechanism at low supersaturations. The rate law is approximated by a simple square dependence on supersaturation.
- A birth & spread nucleation mechanism that is described in part as a power of supersaturation (e.g. Eqn. 9). Growth in this regime is rather variable as the rate of surface nucleation and spread appears to be dependent on many uncontrollable factors. This type of mechanism dominates in agglomeration tanks. It is not at all clear what triggers a transition from one growth mechanism to the other.
- The range of supersaturations available within the mechanistic zones is too small to allow differentiation between the many growth rate equations that are available. The quality of fit is much the same for all of the equations presented in the literature but depending on supersaturation and impurity concentrations, some fit some data sets better than others.

4.2 Speciation

- Speciation has been studied extensively and the most authoritative experimental work suggests that it is quite simple. The concentrations of the aluminium species correlate in a general way with growth phenomena, but there are no clear links to any single species.
- The literature contains a number of computational and theoretical approaches to speciation in synthetic Bayer liquors and these are far more complicated, including many species that might play a part in precipitation. In most cases there is no experimental evidence for these species or alternative, simpler, explanations for the observations that suggest their existence.

4.3 Interfacial phenomena

- A number of different studies indicate that the gibbsite surface, particularly the 001 (hexagonal) face, has a high concentration of adsorbed Na^+ .
- Further, the surface seems to have an adsorbed layer many molecular diameters thick. Some studies have claimed that this layer is composed of polymeric aluminate species but this is not necessarily the case, as the phenomenon can be explained in terms of simple coulombic attraction in a water deficient environment (essentially multiple ion pairing). The adsorbed layer appears to be sensitive to solution concentrations of cations in particular but also anions.

4.4 But what is the mechanism?

Although there are many unanswered questions surrounding the growth mechanism, there is sufficient data to form a hypothesis for gibbsite growth. One of the key parts of this mechanism relates to the "missing alumina" or *apparent solubility* as shown in Figure 3. Together with an apparently anomalous adsorbed layer which is affected by both cation and caustic concentration, an image emerges of gibbsite surfaces being shielded from the liquor. Growth and morphology therefore become functions of the properties of the adsorbed layer, rather than the liquor (although liquor properties govern the properties of the layer). Apparent solubility, as shown in Figure 3, might therefore be linked to the equilibrium solubility of aluminate species in the adsorbed layer, rather than in liquor.

The strength and thickness of the layer is likely to be a function of sodium ion concentration (sodium ions adsorbing strongly onto the gibbsite surface and participating in ion pair formation), caustic concentration (OH^- strongly ion pairs with Na^+) and aluminate ($\text{Al}(\text{OH})_4^-$ participates in clustering associations with Na^+). Thus, one

expects that high sodium ion concentrations will stabilize the layer to some extent and retard precipitation and that hydroxide ions will assist in building a thicker, more stable layer. Higher aluminate concentrations will contribute to the strength/thickness of the layer. It is expected that the layer would be dynamic and in equilibrium with liquor species.

As the layer itself is likely to be rich in aluminate species, this is the most likely source of growth units for the gibbsite. At low supersaturations, monomer addition to gibbsite from the adsorbed layer would proceed as dictated by thermodynamics around surface defects. Replenishment of the layer's aluminate would proceed by transfer from the liquor, and outward diffusion of released OH^- . At higher supersaturations, and when the adsorbed layer is much higher in aluminate concentration, it is likely that the energetics are such that nucleation is favoured, either in the adsorbed layer (with subsequent attachment to the gibbsite), or that the gibbsite surface promotes nucleation. In the case of low supersaturation growth, sodium ion incorporation is unlikely as sodium ions are able to diffuse away from the growth areas. At high supersaturations, spontaneous nucleation and attachment to the surface may be trapping sodium ions and preventing their escape.

The hypothesis is consistent with all observations but the many assumptions still need to be rigorously tested. For example, observations of an adsorbed layer of significant thickness and viscosity has only been made by one research group, and not under a wide enough range of conditions to adequately correlate with growth and morphology phenomena. In addition, a competing "polymeric fuzzy interface" hypothesis has not been fully tested. A fundamental rate equation may not be easy to produce and in any case may not perform better than existing rate laws in all situations. What may be more useful is a better understanding of factors which affect driving force and an appreciation of the limitations on rate laws which are brought about by mechanistic changes.

Acknowledgements

The authors would like to thank companies who sponsored the AMIRA P380B, P380 short extension and P625 projects (collectively; Alcoa, Billiton, Comalco, Nabalco, Pechiney, QAL, Worsley) and the AJ Parker CRC for Hydrometallurgy for funding selected parts of this work. Also, thanks to Dean Ilievski (CSIRO), Gordon Parkinson and Andrew Stanley (Curtin), Alistair Gillespie and Angus Hartshorn (Comalco), John Cleaver (QAL) and Lyndon Armstrong (Alcan) for enthusiastic discussions on the topic from time to time.

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