INHIBITION OF GIBBSITE CRYSTALLIZATION: ADSORPTION OF THE GLUCONATE ION

Beckham, K*, Clarke, P & Cornell, R
Alcoa World Alumina, Technology Delivery Group, Kwinana, Western Australia

Abstract

Gibbsite crystallization kinetics have been measured in synthetic Bayer liquors in the presence of sodium gluconate, a known inhibitor of gibbsite growth and nucleation. The kinetics data have been fitted using a kinetics model (Kubota and Mullin, 1995) that assumes Langmuir adsorption of the impurity to the crystal surface and an effectiveness factor that allows the adsorbed impurity to block more of the growth surface than it physically covers. The crystallization kinetics and supporting evidence imply that the gluconate ion is not chemisorbed to the gibbsite surface. At 70°C, the Langmuir adsorption constant is evaluated as 770 ± 50 L mol^{-1} and the effectiveness factor as 1.51 ± 0.05. From examination of electron micrographs, it is seen that crystal growth is inhibited on both the basal and prismatic planes, in contrast to what occurs with typical Bayer organics. Gluconate adsorbs preferentially to the "birth and spread" sites and this Langmuir adsorption constant is specific to the active growth sites. Hence, the measurement of an adsorption isotherm by measuring the impact upon the growth kinetics better addresses the question of how much of the growing surface is covered by an adsorbing organic.

1 Introduction

Crystallization is an important step within the Bayer process, requiring understanding of its fundamentals within each unit operation, but particularly for gibbsite (γ-$Al(OH)_3$) precipitation. With an increasing focus upon process control, especially with the use of models and simulations, it is important that the data used to create them is both accurate and complete. However, the complexity and number of components within Bayer liquor mitigates against total measurement and instead the industry has used a few model compounds to approximate the 'real world'.

Gibbsite precipitation is a relatively slow process, even in an ideal system free of impurities. However, the presence of inorganic and organic species within Bayer liquor serves to slow further the crystallization process. Two mechanisms can be assigned: the solubility of aluminate within the liquor is altered and hence the crystallization driving force is altered, or the impurity interferes with the crystallization process, by inhibiting either growth or nucleation.

The gluconate ion ($HOCH_2[CH(OH)]_4CO_2^-$) is not only a strong complexant of aluminium in solution (Watts & Utley, 1956), but it is also strong inhibitor of gibbsite growth and nucleation (Coyne et al., 1994; Rossiter et al., 1996; Rossiter et al., 1998; Watling et al., 2000). Very low levels will stabilize green liquor for several days. It therefore has the potential to provide much information about the rate and mechanism of gibbsite crystallization in the presence of hydrate-active organics.

Inhibition of crystallization reactions is not restricted to the Bayer process. There is an extensive literature that addresses this issue (for example Sangwal 1993 and references therein). While a significant portion deals with changes in crystal morphology caused by impurities, some examines the impact of impurities upon the rates of nucleation and growth. Various mechanisms are hypothesised; the general feature being the adsorption of the impurity onto the crystal surface and the pinning or blocking of growth (Sangwal, 1993; Kubota and Mullin, 1995).

In order to control production and sizing, the precipitation circuits in all alumina refineries, whether continuous or batch, use seeded crystallization, under conditions that favour agglomeration and subsequent crystal growth. For this reason, the current work describes the results of an investigation into the effect of different concentrations of gluconate on the rate of crystal growth and on the ensuing gibbsite morphology. One of the main aims of this work was to explore the implications of applying adsorption models to gibbsite crystallization kinetics and to use the crystallization kinetics to measure the adsorption process.

2 Theory

In the absence of crystal growth inhibitors, the rate of crystal growth is typically given by an equation of the form:

$$- dC/dt = k_C A_T [(C - C^*)/C^*]^g \quad (1)$$

where k_C is the crystal growth rate, A_T is the crystal surface area per unit volume, C is the concentration of the crystallizing substance, C* is its solubility and g is the crystal growth rate exponent. It should be noted that this equation is only an engineering approximation and that it does not take into account the change in solution volume that occurs during gibbsite crystallization.

For the growth of gibbsite, where surface integration is believed to be the rate-controlling step for the reaction

$$[Al(OH)_4]^- (aq) \rightarrow [Al(OH)_3] (s) + OH^- (aq) \quad (2)$$

Equation 1 may be modified as follows

$$- dC/dt = k_C AT (ln \{C [OH^-]^* /(C^* [OH^-])\})_g \quad (3)$$

where C is now the aluminate concentration, C* is its solubility, $[OH^-]$ is the free hydroxide concentration and $[OH^-]^*$ is the free hydroxide concentration when C = C*. The advantage of this modification is that the consequences of a changing molar ionic strength are compensated for and the logarithmic term better captures the activity of the reacting species (Ilievski, 2001).

In the presence of additives, the rate of crystal growth can be affected. If the additive adsorbs to the surface and blocks crystal growth sites, then the rate of growth will be dependent upon the number of sites not blocked. To correlate the additive concentration and the number of blocked sites, the Langmuir adsorption model is most commonly used. It is assumed that the additive is in quasi-equilibrium with the surface and that the coverage is given by the following equation:

$$\theta = K_L C_{add} /(1 + K_L C_{add}) \quad (4)$$

where θ is the fraction of surface covered, C_{add} is the concentration of additive and K_L is the adsorption equilibrium constant. Equation 3 is further modified as follows:

$$- dC/dt = k_C^0 (1 - \theta) A_T ln(\{C [OH^-]^* /(C^* [OH^-])\})^g \quad (5)$$

where k_C^0 is the rate constant for the additive-free system. The dependency of the rate constant upon the additive concentration is given by:

$$k_C /(k_C^0 - k_C) = 1/(K_L C_{add}) \quad (6)$$

Thus, a plot of $k_C /(k_C^0 - k_C)$ against $1/C_{add}$ should be linear with zero intercept and slope of $1/K_L$. The non-linear form of this equation is:

$$k_C = k_C^0 /(1 + K_L C_{add}) \quad (7)$$

An alternative adsorption mechanism is provided by the Freundlich equation:

$$x /m = K_F C_{add}^{1/n} \quad (8)$$

where x is the amount adsorbed on mass m of absorbent, and K_F and n are constants. For a fixed seed charge, the crystallization rate will be given by:

$$k_C = k_C^0 (1 - K_F C_{add}^{1/n}) \quad (9)$$

A third alternative is provided by Kubota and Mullin (1995). They propose that the impact of an impurity is a product of its coverage and its effectiveness at blocking crystal growth. The coverage is given by a Langmuir relationship and the relative rate of crystallization is modified by an effectiveness factor:

$$G / G^0 = 1 - [\alpha K_L' C_{add} /(1 + K_L' C_{add})] \quad (10)$$

where α is the effectiveness factor. For $\alpha = 1$ we have the general Langmuir case, while if $\alpha > 1$, the surface can be blocked with respect to crystal growth without the impurity having to completely cover the surface. Equation 10 can be modified in turn

$$k_C = k_C^0 (1 - [\alpha K_L' C_{add} /(1 + K_L' C_{add})]) \quad (11)$$

Using either Equation 7, 9 or 11, we can treat k_C^0 as an unknown in addition to either K_L or K_F and n or K_L' and α and include the rate constant measured at zero concentration in the data set.

3 Experimental

The experimental procedures have been described previously (Cornell et al., 1999). Synthetic liquor was prepared using analytical grade reagents: sodium hydroxide, sodium carbonate, sodium chloride, sodium sulfate and sodium acetate. Aluminium hydroxide (C-31C Alcoa, Arkansas USA, <0.003% Si, 0.009% Fe) was used to prepare synthetic liquor and as a source of gibbsite seed crystals.

Supersaturated solutions were prepared by digesting aluminium hydroxide into caustic liquor at 143°C using an autoclave. Prior to use, the supersaturated solutions were 'SGA cleaned', to remove any calcium that would inhibit crystal growth. Gibbsite seed crystals were prepared by wet-screening C-31C to recover the +45 µm fraction and subsequently growing the crystals in slightly supersaturated caustic aluminate solutions to grow out surface irregularities. The seed crystals had a mean particle size (D50) of 90 µm measured using a Malvern MastersizerX and a surface area of 0.06 m^2/g as measured by B.E.T. with nitrogen using a Micromeritics Gemini III 2375.

Batch crystallizations were carried out in Teflon® reactors (one litre working volume) having inverted cone bases and baffles and stirred using an axial impellor at 280 rpm. The reactors were immersed in water baths and temperature was controlled to within ± 0.1°C. The reactions were monitored by continuous measurement of the solution conductivity using a toroidal conductivity probe. Samples were taken at intervals for liquor analysis by titration to calibrate the conductivity data.

Conditions were chosen such that crystal growth was the predominant crystallization mechanism; the start A/TC ratio was 0.60, temperature was 70 ± 0.3°C, and the gibbsite seed concentration was 100 g/L. Prior to the addition of the pre-heated seed crystals, solid sodium gluconate was added to the reactors and allowed to dissolve.

The smoothed conductivity data were analysed to calculate the aluminate and caustic concentrations which were subsequently sub-sampled at one-hourly intervals to generate the de-supersaturation curves. The growth rate exponent was set to a value of 2.8 and the de-supersaturation curves were analysed by a proprietary algorithm to calculate the crystal growth rate.

Samples for scanning electron microscopy were washed then coated with platinum before being scanned using a JEOL JSM6400 instrument.

4 Results and Discussion

Crystallization Kinetics

Liquor concentrations were total caustic (TC ≡ NaOH): 200 g/L as Na_2CO_3, total alkali (TA ≡ NaOH + Na_2CO_3): 228 g/L as Na_2CO_3 with the other liquor components (NaCl, Na_2SO_4 and $NaCH_3COO$) chosen to have concentrations similar to those of an Alcoa alumina refinery in Western Australia. Sodium acetate is included as a model compound contributing to total organic carbon and total soda. It has been shown in unreported test work that the additional liquor components only contribute to ionic strength and have no primary impact upon gibbsite crystallization rate constant.

For the de-supersaturation kinetics conducted at constant seed charge and varying gluconate concentration, the resultant de-supersaturation curves are shown in Figure 1. The fitted crystallization rate constants are shown as a function of initial gluconate concentration in Figure 2. Equations 7, 9 and 11 have been optimized to fit the rate constants according to each adsorption model, the resultant modelled equations are shown in Figure 2 and the model parameter estimates and confidence intervals are shown in Table 1. Because the Freundlich equation is semi-empirical, it is not useful to assign units to KF and n.

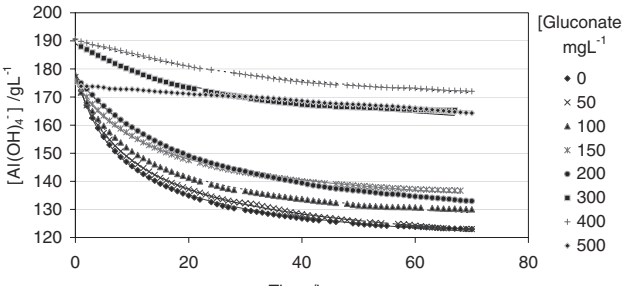

Figure 1. Aluminate de-supersaturation data as a function of time in the presence of varying concentrations of sodium gluconate. Initial TC 195–205 gL^{-1} (as Na_2CO_3), gibbsite seed 100 gL^{-1}, 70°C. Fitted curves shown for g = 2.8.

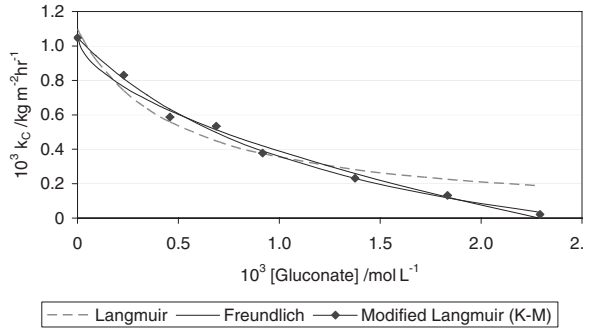

Figure 2. Crystal growth rate as a function of sodium gluconate concentration. Initial TC 195–205 gL^{-1} (as Na_2CO_3), gibbsite seed 100 gL^{-1}, 70°C and g = 2.8.

Table 1. Parameter estimates and 95% confidence intervals for Langmuir, Freundlich and modified Langmuir (Kubota-Mullin) adsorption models fitted to crystal growth rate data for initial TC 195–205 gL^{-1} (as Na_2CO_3), gibbsite seed 100 gL^{-1}, 70°C and g = 2.8.

Model	Parameter	Estimate
Langmuir	k_C^0 /kg $m^{-2}hr^{-1}$	(1.10 ± 0.15) x 10^{-3}
	K_L /L mol^{-1}	(2.10 ± 0.74) x 10^3
Freundlich	k_C^0 /kg $m^{-2}hr^{-1}$	(1.06 ± 0.06) x 10^{-3}
	K_F	28.5 ± 1.3
	n	1.82 ± 0.02
Modified Langmuir (Kubota-Mullin)	k_C^0 /kg $m^{-2}hr^{-1}$	(1.05 ± 0.04) x 10^{-3}
	K_L' /L mol^{-1}	770 ± 50
	α	1.51 ± 0.05

No correction has been made to the solution concentration of gluconate for the quantity adsorbed to the surface. Coyne et al. (1994) estimate that a gluconate molecule would occupy 5.2×10^{-19} m^{-2}. For the seed charge used, the total seed area is 6 m^2 L^{-1} and total coverage by gluconate would consume 0.019 mmol L^{-1}, equivalent to 4.2 mg L^{-1} sodium gluconate. On this basis, we conclude that the quantity adsorbed to the surface is a small fraction of the total in solution and no correction is required.

It is apparent from Figure 2 that both the Freundlich equation and the modified Langmuir (Kubota-Mullin) equation both provide a reasonable fit to the observed rate data, in contrast to the general Langmuir equation. For the Freundlich isotherm equation, the value of n is indicative of the strength of adsorption; the larger its value, the greater the strength of adsorption. The Freundlich isotherm equation is derived by assuming a heterogeneous surface and adsorption at each type of site follows the Langmuir equation. The model doesn't require equal probability of adsorption across all surfaces.

The Kubota-Mullin adaptation of the Langmuir isotherm proposes that the adsorbed impurity has a stereochemical impact, dependent upon the shape, size or orientation of the impurity. For values of $\alpha > 1$, the impurity effectively blocks more of the growth surface than actually covered by the impurity. Kubota and Mullin ascribe this to pinning of the growth step.

At least two further observations can also be made. Firstly, the rate of adsorption of gluconate to the surface is fast compared to the rate of crystallization; there is a dynamic adsorption equilibrium (Kubota et al., 1997). Secondly, there is no requirement that gluconate is chemisorbed to the surface. While not obvious from Figure 1, the infinite time aluminate concentration is the same as the calculated equilibrium solubility for each concentration of gluconate. If gluconate were chemisorbed to the surface, we would expect that the de-supersaturation curves would tail off to an aluminate concentration in excess of the equilibrium concentration. In addition, the fit of a crystallization growth model to the de-supersaturation data would require a term to describe the loss of growth surface to the chemisorbed impurity.

A separate test in which gibbsite seed was contacted with 500 mg L^{-1} sodium gluconate for two days and then filtered without washing and resuspended in a fresh synthetic liquor, also indicated that gluconate was not chemisorbed. For this unwashed "poisoned" seed, the rate of crystallization was essentially the same as that for the control and there was no induction time. If the gluconate were chemisorbed, we would expect that the rate of crystallization would have been significantly reduced. Using Equation 4, we calculate that 65% of the surface would have been covered originally, equivalent to 2.72 mg L^{-1} sodium gluconate. Upon re-suspension, re-establishment of the quasi-equilibrium would result in effective coverage of just 1.5% of the gibbsite surface and a growth rate indistinguishable from that of the poison-free system.

In measuring the adsorption of gluconate, tartrate, mannitol and other organics onto gibbsite, Coyne et al. (1994) had to contact the organic-containing liquor with a large quantity of high surface area gibbsitic solid (Hydral 710B) and then calculate the coverage by measuring the change in concentration of the organic. They then correlated the adsorption isotherm data with kinetics measured at a fixed concentration of impurity using seed crystals much the same as used in this study. This approach suffers from several disadvantages: there is a requirement to know a priori the amount of the organic adsorbed at saturation; the surfaces of the two types of solids are assumed to be similar; and the adsorption sites are assumed to be the growth sites. The question for which we actually require an answer is: 'what is the coverage of the active growth sites by the adsorbing organic?' The approach used in this study has addressed that specific question.

5 Electron Microscopy

There was little apparent difference between the control system and that with 50 mg L^{-1} sodium gluconate (Figure 3(b), 3(c)). Using the Langmuir equation, we calculate that 15% of the surface is covered and 23% is blocked. Some spreading of terraces on the basal plane was noted at 100 and 150 mg L^{-1} sodium gluconate, but definite effects only became apparent at sodium gluconate concentrations above 200 mg L^{-1} (Figure 3(d)). Under these conditions there was considerable spreading of very thin overlapping terraces on the basal plane and in addition, outgrowths of hexagonal plates tilted with respect to the basal plane. At this concentration we calculate that 40% of the surface is covered and 63% is blocked. An interesting feature was the absence of the bevelled edges (112) and (101) planes which were well developed in the control system (Figure 3(b)). This implies that the basal and prismatic planes are affected to a greater extent than are the bevelled edges.

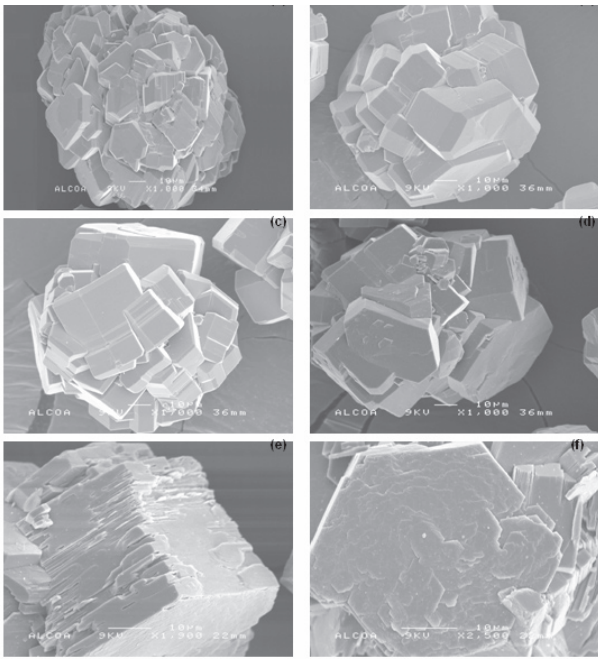

Figure 3. Electron micrographs of gibbsite crystals grown in the presence of sodium gluconate: [*left to right*] (a) seed crystal; (b) crystal after 50 hours in the absence of gluconate; (c) crystal after 50 hours with 50 mgL^{-1} sodium gluconate; (d) crystal after 50 hours with 200 mgL^{-1} sodium gluconate; (e), (f) crystals after 50 hours with 500 mgL^{-1} sodium gluconate.

The effect of 500 mg L^{-1} sodium gluconate on the appearance of gibbsite was dramatic (Figure 3(e), 3(f)). Although precipitation appeared to have slowed almost to a standstill, growth features were evident on some of both the basal and prismatic faces indicating interaction with the entire surface; 65% of the surface is covered and 97% is blocked.

On some of the basal planes there was more extensive spreading of thin irregular overlapping terraces (Figure 3(e)). These terraces moved out from the centre towards the sides of the hexagon; the irregular edges indicate step pinning due to the adsorption of impurities. In addition, well developed crystallites emerge at low angles from the surface of the crystal; these appear to have nucleated at certain specific sites, presum-

ably induced by the presence of the impurity. Some of these crystallites have bevelled edges.

On some of the prismatic planes (Figure 3(f)) many piled up steps can be seen parallel to the basal plane; they correspond to extensions of the terraces on the basal plane and probably represent growth layers pushing between blocked sites. In addition, distinct spiral regions – probably centres of screw dislocation growth (possibly induced by the gluconate) were noted on some of the prismatic faces. It appears that outgrowths of layers and spiral regions occur on alternate prismatic faces – namely (100) and (110).

As the distorted growth on certain crystal faces indicates, gluconate interacts with the growing crystal (the ability of this compound to stabilise liquor indicates that it also interferes with homogeneous nucleation) and affects growth on all crystal planes. Unlike organic compounds such as tartaric acid, gluconate does not induce the formation of needles (Seyssiecq et al., 1999; Paulaime et al., 2003) or hexagonal platelets (Watling, 2000). Nor does it appear to discriminate between the prismatic and basal faces as do typical Bayer organics (Freij and Parkinson, 2005). It may be this attribute that contributes to its marked ability to stabilize liquor.

From considering the low saturation coverage calculated by Coyne et al. (1994) and the high coverage of growth sites calculated in this study, we hypothesise that the gluconate is adsorbing to active growth sites in preference to the total available surface. A 'birth and spread' model is proposed for growth on the basal planes (Watling, 2000; Freij and Parkinson, 2005). If hydrate-active organics such as gluconate have a strong selectivity for the kinks created after the birth of a growth site, they will have a significantly greater impact upon gibbsite growth than their adsorption isotherms would indicate if measured by conventional methods. Thus, the Langmuir adsorption constant obtained in this study is specific to the active growth area, not to the total surface area.

This targeting of specific sites upon the gibbsite surface can also explain the very strong inhibitory effect of calcium upon gibbsite growth (Cornell et al., 1999). If calcium preferentially adsorbs to the active growth sites and is subsequently chemisorbed, a Langmuir adsorption constant much greater than that for gluconate will be the result as the rate of desorption will be much less than that for gluconate. If the calcium ions pin all the birth centres then there will be no crystal growth until all the calcium is included into the crystal lattice.

The reverse of this mechanism could also explain why organics such as 3-hydroxybenzoate are readily detected in hydrate (Picard et al., 2002), but have little impact upon gibbsite crystallization kinetics. If these organics adsorb onto the gibbsite surface but do not block the active growth sites, they could be overgrown into the lattice structure without impacting significantly upon the growth rate. Hence, it could be possible for some compounds to have a large adsorption constant, as measured by conventional techniques, be readily measured in the gibbsite crystals but have a small impact upon gibbsite growth kinetics.

6 Conclusions

Gluconate is a potent impurity, inhibiting gibbsite crystallization on both the basal and prismatic planes. It is adsorbed according to a Langmuir adsorption isotherm but each adsorbed molecule blocks more of the active growth surface than it physically covers. Gluconate shows a strong selectivity for the kinks created after the birth of a growth site and has a significantly greater impact upon gibbsite growth than its adsorption isotherm would indicate if measured by conventional methods. Thus, the measurement of the adsorption isotherm by measuring the impact upon the growth kinetics better addresses the question of how much of the growing surface is covered by an adsorbing organic.

References

Cornell, R.M., Pannett, D.S., Sullivan, N.S., Clarke, P.C. and Bailey, C.M. (1999) "Precipitation of gibbsite; Development of a new rate equation", 5th Int. Alumina Quality Workshop, 154–161.

Coyne, J.F., Wainwright, M.S., Cant, N.W. and Grocott, S.C. (1994) "Adsorption of hydroxy organic compounds on alumina trihydrate", Light Metals, 39–45.

Freij, S.J. and Parkinson, G.M. (2005) "Surface morphology and crystal growth mechanism of gibbsite in industrial Bayer liquors", Hydromet., 78(3-4), 246–255.

Ilievski, D. (2001) "Development and application of a constant supersaturation, semi-batch crystalliser for investigating gibbsite agglomeration", J. Crystal Growth, 233(4), 846–862.

Kubota, N. and Mullin, J.W. (1995) "A kinetic model for crystal growth from aqueous solution in the presence of impurity" J. Crystal Growth, 152, 203–208.

Kubota, N., Yokota, M. and Mullin, J.W. (1997) "Supersaturation dependence of crystal growth in solutions in the presence of impurity" J. Crystal Growth, 182, 86–94.

Mullin, J.W. (1993) "Crystallization", 3rd Edn, Butterworths, London.

Paulaime, A-M., Seyssiecq, I. and Veesler, S. (2003) "The influence of organic additives on the crystallization and agglomeration of gibbsite", Powder Technol., 130(1–3), 345–351.

Picard, F., Audet, D., Boily, H. and Larocque, J. (2002) "Identification of hydrate active organics (HAO) present in spent Bayer liquors by state-of-the-art analytical methods", 6th Int. Alumina Quality Workshop, 46–53.

Rossiter, D.S., Fawell, P.D., Ilievski, D. and Parkinson, G.M. (1998) "Investigation of the unseeded nucleation of gibbsite, $Al(OH)_3$, from synthetic Bayer liquors" J. Crystal Growth, 191(3), 525–536.

Rossiter, D.S., Ilievski, D., Smith, P.G. and Parkinson, G.M. (1996) "The mechanism of sodium gluconate poisoning of gibbsite precipitation", Trans IChemE Part A, 74, 828–834.

Sangwal, K. (1993) "Effect of impurities on the processes of crystal growth", J. Crystal Growth, 128, 1236–1244.

Seyssiecq, I., Veesler, S., Pèpe, G. and Boistelle, R. (1999) "The influence of additives on the crystal habit of gibbsite", J. Crystal Growth, 196(1), 174–180.

Watling, H., Loh, J. and Gatter, H. (2000) "Gibbsite crystallization inhibition 1. Effects of sodium gluconate on nucleation, agglomeration and growth", Hydromet., 55(3), 275–288.

Watling, H. (2000) "Gibbsite crystallization inhibition 2. Comparative effects of selected alditols and hydroxycarboxylic acids", Hydromet., 55(3), 289–309.

Watts, H.L. & Utley, D.W. (1956) "Sodium gluconate as a complexing agent in the volumetric analysis of aluminum compounds" Anal. Chem., 28(11), 1731–1735.