

GALLIUM INCORPORATION INTO PRECIPITATED GIBBSITE

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^{*} current address Alcoa of Australia, Hope Valley Road, Kwinana, Western Australia 6167[#] Alcoa of Australia, Hope Valley Road, Kwinana, Western Australia 6167ABSTRACT

Gallium in precipitated gibbsite is a future product quality concern for alumina producers in Western Australia. This work was undertaken to establish the mechanism of gallium incorporation into gibbsite, and to develop a model to determine the level of gallium uptake from synthetic Bayer liquors.

It has been shown that -

- Isomorphous substitution is the most likely mechanism of incorporation, although there was a surprisingly low upper limit to the level of incorporation that could be achieved (~2 mole%).
- At levels of gallium in the liquor of <1800 ppm, the concentration of gallium in precipitated gibbsite is dependent on the concentration of gallium in the liquor, and virtually independent of other precipitation parameters. The relationship of gallium in the precipitated gibbsite to the level in the liquor is given by

$$(Ga/Al)_{pp1} \times 10^6 = K \times Ga_L \text{ (ppm } Ga_2O_3 \text{ in liquor)}$$

where for our system $K=0.266$.

KEY WORDS

Gibbsite Precipitation, Gallium Inclusion

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1.0 INTRODUCTION

The efficiency of smelting aluminium from alumina depends critically on the levels of some inorganic impurities in the feedstock material. Levels of these impurities in the alumina may be traced back to inclusions into gibbsite as it is precipitated from Bayer liquor. The commonest impurity in gibbsite, and the one that has received most attention, is sodium (Armstrong, 1993). Modern smelting technologies are less tolerant of sodium and the push is on for lower and lower sodium levels in the alumina.

Another impurity that is often included during gibbsite precipitation is gallium. Presently levels of gallium in alumina are not considered a problem by smelters, but gallium has been targeted as a future product quality concern, especially for alumina produced in Western Australia where gallium levels in the bauxite are especially high. It is possible that in the future, we will be examining gallium levels in gibbsite as closely as we do sodium levels today.

Gallium enters the Bayer circuit with the bauxite. The exact nature of the gallium in the bauxite is not known, but there are very few gallium minerals, and it is probable that gallium substitutes for aluminium in the alumina bearing minerals (Hill Roy and Osborn, 1952). Several gallium analogues to aluminium oxides are known, but interestingly, no stable hydroxides of gallium (analogous to say gibbsite) have been reported (Hill Roy and Osborn, 1952).

The fate of gallium in the process is also somewhat unclear. If it is associated with the iron minerals, it will exit, undigested with the mud. If gallium is associated with the alumina minerals, then the majority is likely to be liberated into the liquor. Some of it will precipitate with the gibbsite and some will accumulate in the liquor. It is the rising levels of gallium in some refinery liquors, and hence in the precipitated gibbsite, that gives rise to the quality concern.

There are at least four possibilities for the mechanism of gallium inclusion into gibbsite -

- Adsorption of gallium ions onto the growing gibbsite surface
- Entrapment of pockets of liquor (containing gallium) into the crystal structure of gibbsite
- Separate crystallisation of gibbsite and a gallium solid which agglomerate to a single compact (this we will term coprecipitation)
- Isomorphous substitution of atomic gallium for aluminium in the structure of gibbsite.

Adsorption is the mechanism favoured for the inclusion of soda into gibbsite, and entrapment of liquor is an earlier, now discarded theory for the same inclusion. Coprecipitation is the likely mechanism for the presence of sodium oxalate in precipitated gibbsite. Isomorphous substitution has been suggested before for the incorporation of gallium into gibbsite (Yatsenko and Demenev, 1960) although no direct evidence was presented.

The objectives of the current work are -

- 1 Establish the most likely inclusion mechanism
- 2 Develop a model to predict the levels of gallium inclusion

2.0 EXPERIMENTAL

2.1 Materials and synthetic liquor preparation

Sodium hydroxide and sodium carbonate were AR grade (Ajax Chemicals). Gibbsite (C31 hydrate, Alcoa Chemicals Division) was used for liquor preparation and for seeding liquors. Liquors were made by atmospheric digestion to a total caustic level (TC) of 180 g/L (Na_2CO_3) and a total alkali level (TA) of 220 g/L (Na_2CO_3) with varying aluminium to produce liquors from A/TC=0.5 to 0.7 (aluminium, A expressed as g/L Al_2O_3). Liquors were passed through 0.45 μm membrane filters before use, and analysis was by an inflection point variation of the standard gluconate titration (Watts and Utley, 1956). Gallium oxide (Sigma Chemicals) was dissolved in caustic to make a stock solution of the same TC and TA and added to the liquor to produce the desired Ga concentration. Dilution of the aluminium by this procedure was of the order of a 2% change in A/TC for a Ga level of 400 ppm.

2.2 Precipitation Tests

HDPE bottles (250 mL) were charged with liquor (200 mL) and gallium stock solution to produce concentrations between 100-1800 ppm gallium (as Ga_2O_3). Two high gallium concentration solutions (50 g/L and 75 g/L Ga_2O_3) were prepared by mixing the gallium oxide with the C31 before digestion (see section 3.2). Solutions were placed into a preheated, temperature controlled bottle roller (Intronics Ltd, 23 rpm). After equilibration, they were seeded and returned to the bottle roller. After the desired time, solids were filtered through a Postlip filter, washed with deionized water and dried at 100°C.

2.3 Analysis of Gallium

X-ray fluorescence (XRF) was used to analyse for gallium in gibbsite. A Phillips model PW1480 X-ray fluorescence spectrometer was used. A Mo X-ray source was set at 90 kV and a current of 30 mA. A fine collimator and a NaI scintillation detector was used. The analysing crystal was LiF(200). The detector angle for Ga radiation was set at 38.8° for Ga K_α .

Gibbsite was mixed with an XRF binder and made into a pressed powder sample, dried at 100°C and run on the XRF. In-house standards of aluminosilicates containing gallium up to 5000 ppm were used to produce a calibration. Concentrations of Ga are reported in this paper as g/L equivalent Ga_2O_3 in precipitated gibbsite (total weight minus seed).

3.0 RESULTS AND DISCUSSION

3.1 Effect of Process Parameters on Gallium Inclusion

The influence of starting Ga in the liquor on Ga in precipitated gibbsite is shown in Figure 1. Gibbsite was precipitated for 96 hours at 60°C from a liquor with a starting A/TC of 0.7, and a seed charge of 50 g/L.

Figure 1 shows a linear relationship between the Ga in the liquor and in the final precipitate. This relationship holds up to 1800 ppm in the liquor, which is far in excess of current plant levels. The degree of atomic substitution (Ga for Al) in gibbsite for our conditions will therefore be given by the relation

$$(\text{Ga}/\text{Al}) \times 10^6 = K \times \text{Ga}_L \text{ (ppm } \text{Ga}_2\text{O}_3 \text{ in liquor)}$$

where for our system $K=0.266$.

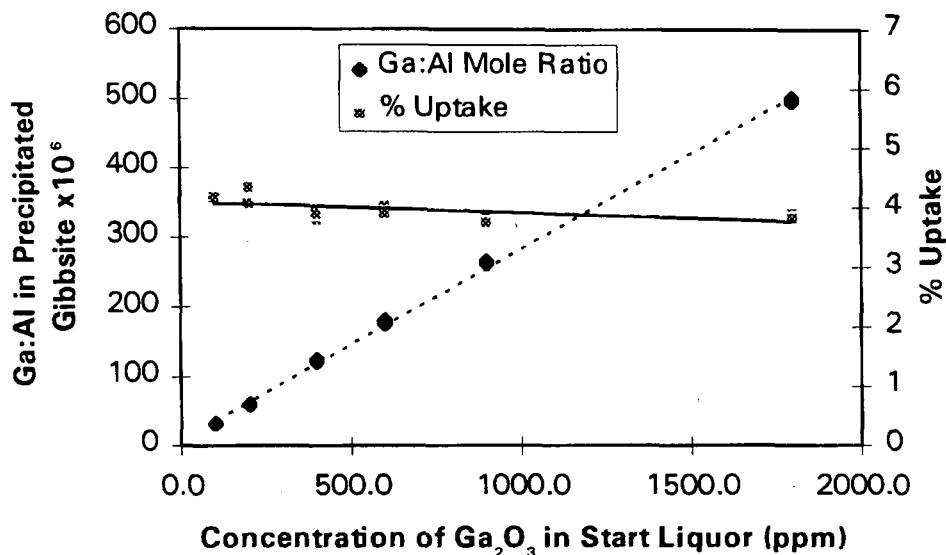


Figure 1: Gallium in precipitated gibbsite and % uptake as a function of starting gallium in the liquor.

Also shown in Figure 1 is the uptake of gallium from the liquor which is almost a constant 4% up to 1800 ppm Ga₂O₃ in the liquor. This constancy is to be expected if the gallium included in the gibbsite is directly proportional to the liquor concentration, and the gibbsite yield after 96 hours is itself constant. The value of 4% uptake is in good agreement with the results of Yatsenko and Demenev (1960), and since the yields of the present experiments (~75-80 g/L (Al₂O₃)) are consistent with those in industry, then subject to the effects of, the same % uptake could be expected to occur across the precipitator bank in a refinery.

The influence of gallium inclusion on gibbsite precipitation kinetics can be seen in Figure 2 which shows the amount of gibbsite precipitated as a function of time for seed charges 50, 100 and 200 g/L and gallium in the start liquor of 0, 200 and 400 ppm Ga₂O₃. Within experimental error, gallium up to 400 ppm in liquor has no effect on precipitation kinetics, except for the initial stages at low (50 g/L) seed charge. At this initial stage, higher levels of Ga depress the rate of gibbsite precipitation, and although the effect is only small (~13% less precipitation after 2 hours at 50 g/L seed) it is outside experimental error. This depression of rate decreases for higher seed charges and for the latter stages of precipitation.

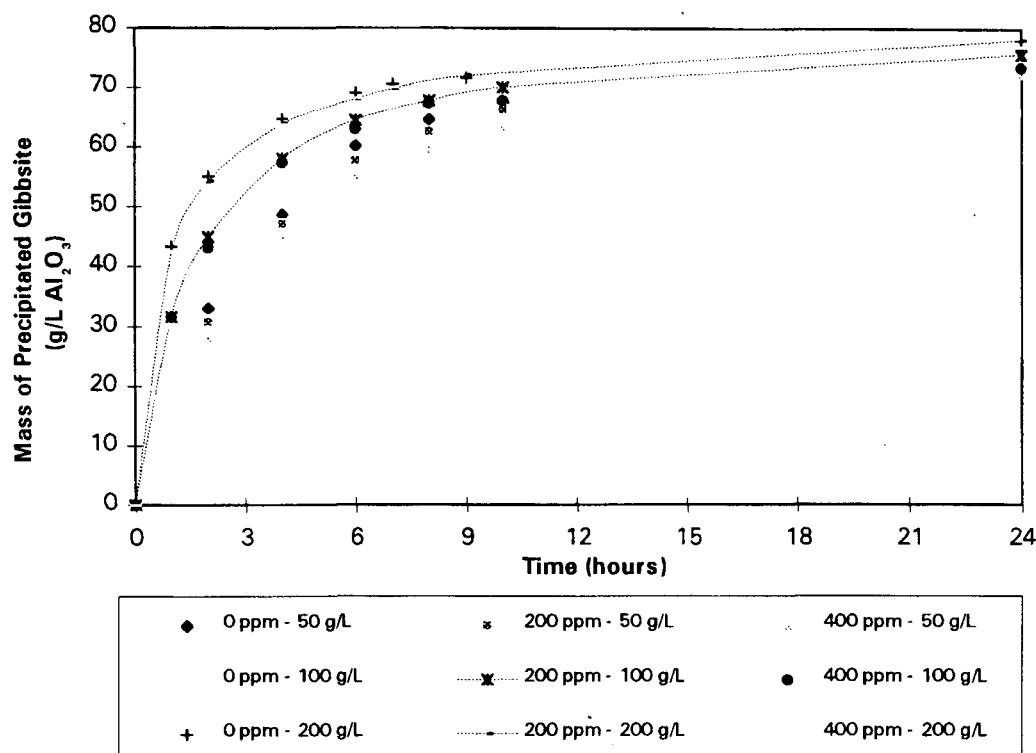


Figure 2: Influence of seed charge and starting gallium concentration in the liquor on gibbsite precipitation.

A single parameter which describes the kinetics of the precipitation process is the linear growth rate which can be defined as the volume flux of gibbsite over unit seed surface area. Its units are $\mu\text{m/hr}$. Figure 3 shows the incorporation of gallium into gibbsite as a function of the linear growth rate for seed charges 50, 100 and 200 g/L, gallium concentrations of 0, 200 and 400 ppm and start liquor A/TC of 0.5, 0.6 and 0.7 (TC constant at 180, temperature 60°C). There are no trends for any of these variables, suggesting that gallium is having no effect on standard precipitation kinetics.

The influence of gallium incorporation on precipitation yield at different temperatures is given in Figure 4. Increasing temperature increases the saturation level of alumina in the liquor and hence decreases the overall yield. It also slows the precipitation and so 24 hours may not be sufficient time to reach maximum yield. The influence of different levels of gallium in the liquor is apparent only at the higher temperatures. The differences are all within experimental error ($\sim 5\%$), but the trend (higher gallium - lower yield) does appear to be consistent.

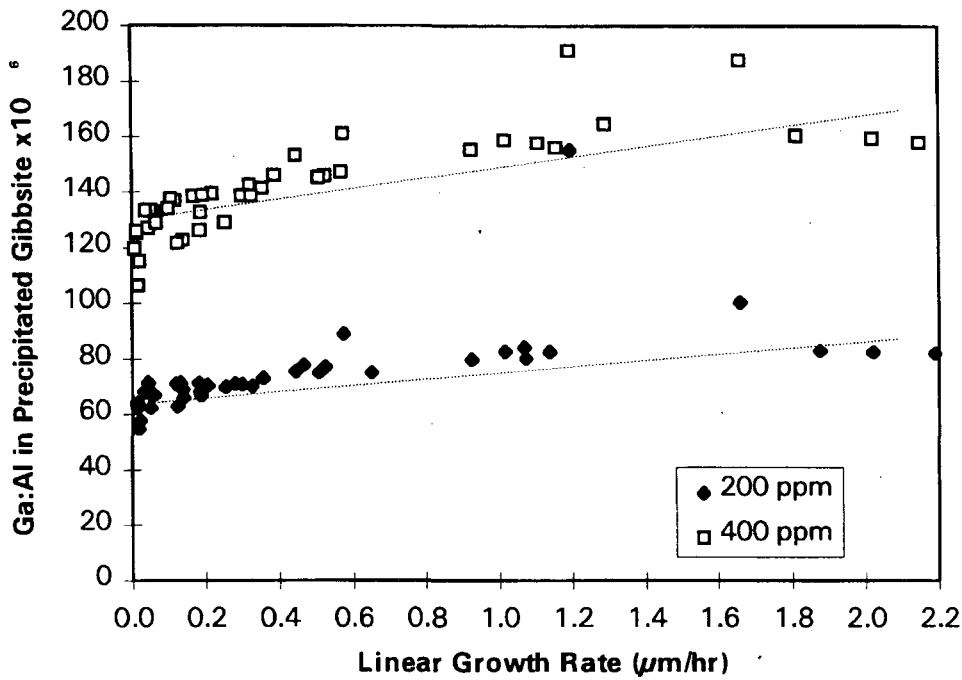


Figure 3: Effect of gibbsite precipitation rate on gallium inclusion for all data (varying temperature, superaturation and seed charges).

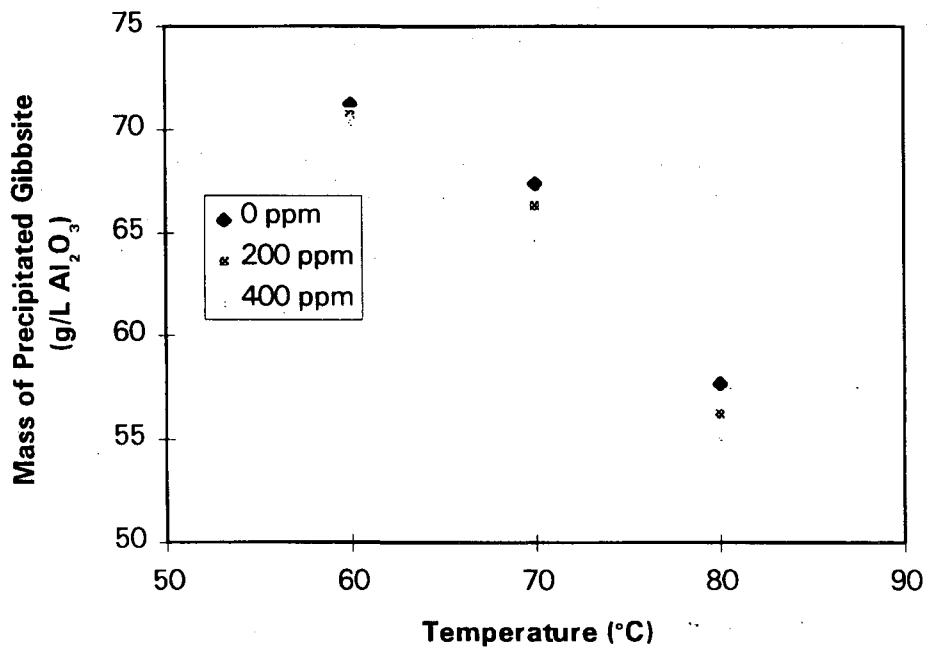
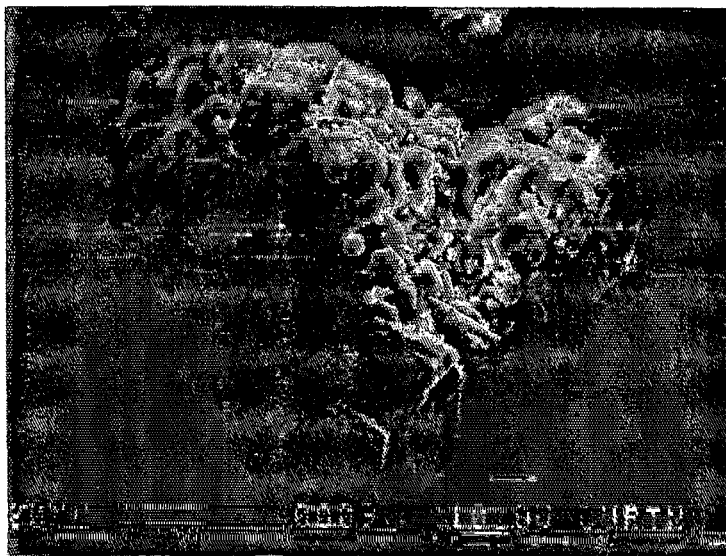
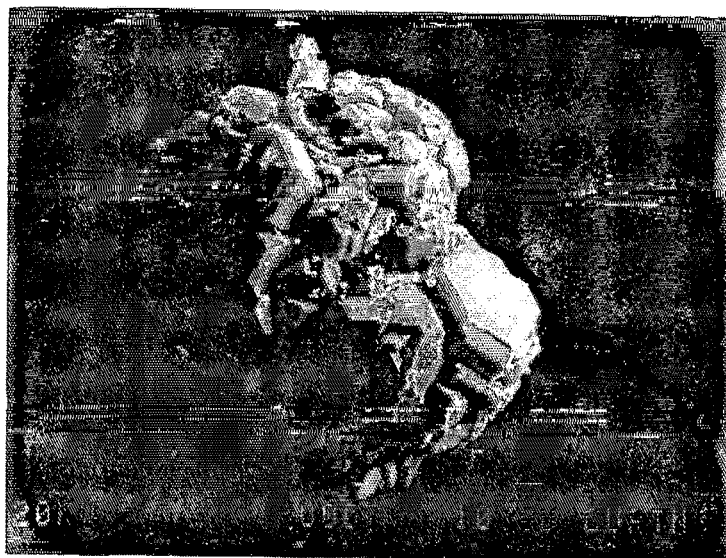


Figure 4: Effect of temperature on gallium incorporation.

(a)



(b)



(c)

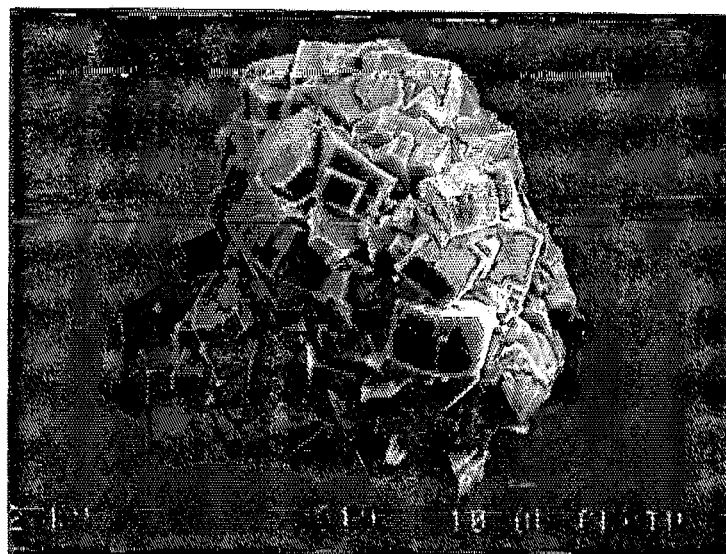


Figure 5: Morphology of crystals grown with varying levels of gallium - (a) no gallium, (b) 0.25 mole % Ga_2O_3 and (c) 2 mole% Ga_2O_3 .

3.2 Mechanism of Gallium Incorporation

Preparation of two high gallium content gibbsites were attempted. In the first, a solution with A=100 g/L and Ga₂O₃=50 g/L was seeded with gibbsite (50g/L) and left at 60°C for two weeks. The total gallium content of this material was 0.25 mole % which corresponded to 0.75% gallium in the precipitated material. An example of the resulting crystals is shown in Figure 5 (b) (For comparison, Figure 5(a) shows a typical crystal grown under the same conditions without gallium).

The second high gallium product was made from a solution of A=72 g/L and Ga₂O₃=72 g/L (~at the limit of solubility by the atmospheric preparation process). Only a small amount of seed was added (0.25 g/L) to start the crystallisation which was left for two weeks at 60°C. The resulting crystals (Figure 5(c)) contained 2 mole% Ga₂O₃ and this represented the maximum level of incorporation achieved in this study.

A sample of the 2 mole% product was set in resin, sectioned and analysis performed in a Jeol JSM-35C SEM. Figure 6 shows a backscatter image of a sectioned particle showing a darker section in the centre. An X ray spectrum across the particle (not shown) indicated that the edges of the particle were higher in gallium than the centre. From this we believe that the centre represents a seed particle, around which the high gallium gibbsite has grown (since the seed concentration was small in the preparation, this particle may be atypical). An X-ray dot map of the same particle shows that aluminium is distributed evenly throughout the particle. Gallium is also evenly distributed around the outside of the particle and sparse in the centre.

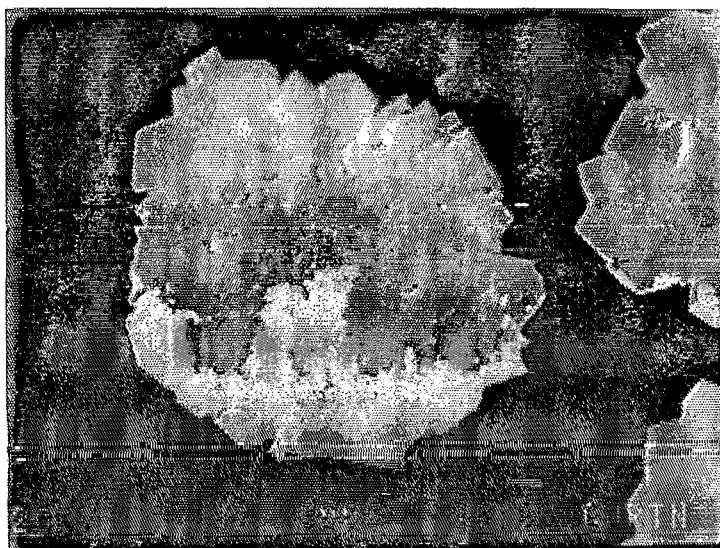


Figure 6: Backscattered image of a sectioned particle of high gallium incorporated (2 mole%) gibbsite.

There is no evidence from the micrographs or the X-ray maps of a coprecipitated phase or entrapment of mother liquor (which would show up as uneven gallium distributions).

The effect of two organic compounds on the incorporation of gallium is shown in Figure 7.

From Figure 7 it is apparent that citric acid has no effect on gallium incorporation, and that such incorporation is mildly suppressed by the presence of tartaric acid. This is in marked contrast to the effect that tartrate has on the soda incorporation where increases of soda inclusions of 65% result from the presence of 0.015M tartrate in the liquor (Grocott and Rosenberg, 1988).

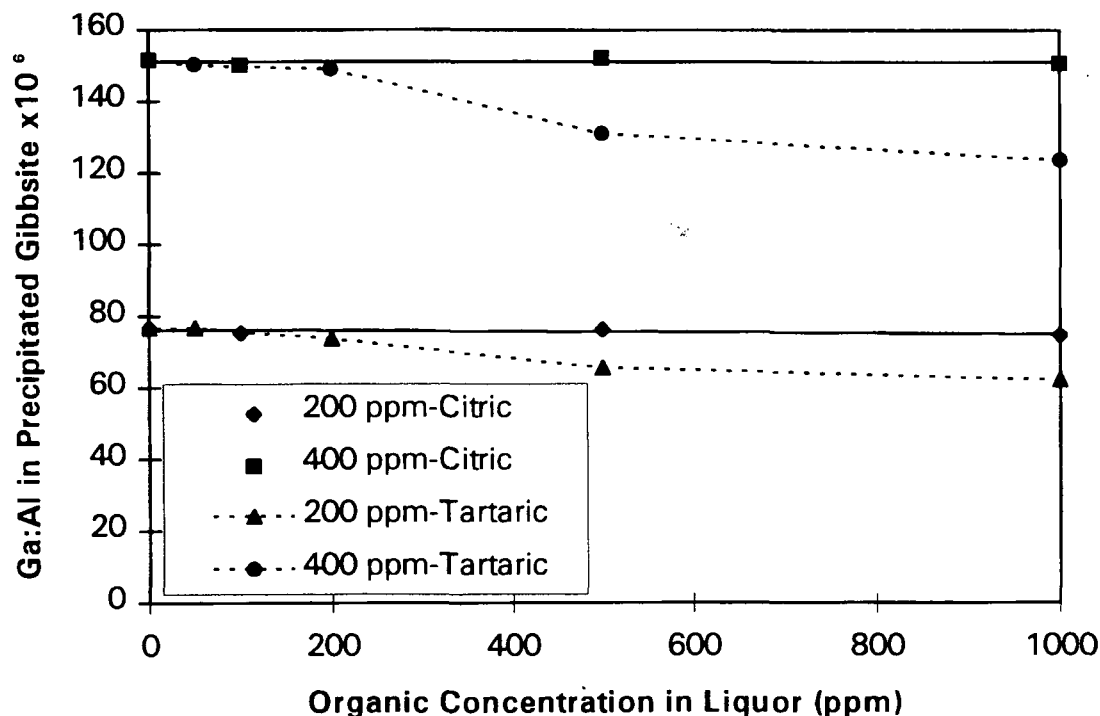


Figure 7: Effect of model organic compounds in the liquor on gallium incorporation.

It is believed that soda is incorporated into gibbsite through adsorption onto the surface and that the blocking of surface crystallisation sites by tartrate results in higher levels of soda on the surface, and ultimately into the gibbsite structure. The fact that gallium does not show the same behaviour in the presence of tartrate indicates that adsorption is not the method by which gallium is included. This conclusion is supported by the linear relationship of incorporation to the concentration of gallium in the liquor (Figure 1). Such a relationship would not be likely if adsorption was the inclusion mechanism.

This leaves isomorphous substitution as the most likely mechanism of incorporation. On the basis of its charge and radius, the gallium ion is well suited to substitute for aluminium in the gibbsite structure (ionic radius of Ga^{3+} is 62 pm compared to Al^{3+} of 53.5 pm). A change in the unit cell dimensions calculated from XRD analysis is usually taken as definitive evidence for such a mechanism, but in this case the level of substitution (2 mole%) is too low to make a measurable difference (a minimum of ~10 mole % substitution would be needed to see a significant change in the unit cell). The reason why there is such a small upper limit to substitution is at present still unclear.

4.0 CONCLUSIONS

- The degree of incorporation of gallium into precipitated gibbsite is directly proportional to the level of gallium in the liquor (up to 1880 ppm Ga_2O_3 in liquor) and unrelated to other precipitation parameters (temperature, aluminium supersaturation or seed charge).
- The morphology of gibbsites containing increasing levels of gallium show a decrease in fines and an increase in the regularity and blockiness of the crystals.
- The direct relation between gallium in liquor and gallium in precipitated gibbsite, the evenness of gallium distributed in the solid and the absence of coprecipitation (of different phases) suggest that isomorphous substitution is the most likely mechanism for incorporation, although the maximum incorporation achievable (2 mole%) was unexpectedly low.

ACKNOWLEDGEMENTS

The assistance of Ian Barrow and Lindsay Pescud at the Chemistry Centre (WA) with the gallium determinations by XRF is gratefully acknowledged.

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