MICROSCOPIC AND MACROSCOPIC OBSERVATIONS OF VARIABILITIES IN THE GROWTH RATES OF GIBBSITE CRYSTALS

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ABSTRACT

The aim of this study was to elucidate, at the molecular level, mechanisms of gibbsite crystallization, by measuring directly the growth rates of the individual faces of single gibbsite crystals. It was found that the growth rates of individual crystal faces varied with time, and from one crystal to another. The causes of this variation were also investigated, by examining the effects of solution preparative history. The results imply that the rate limiting steps in crystallization involve the formation of one or more aluminium containing species in solution. Addition of selected organic compounds was found to inhibit the growth of specific crystal faces, which leads to the formation of gibbsite crystals with different morphology; at the same time, they showed a strong effect of inhibiting agglomeration.

KEY WORDS:
Gibbsite, Crystal Growth, Morphology, Agglomeration, Microscopy

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1.0 INTRODUCTION

In assessing the quality of alumina, the quality of its precursor prior to calcination, gibbsite (aluminium trihydrate), has to be considered. The quality of the hydrate can be defined in terms of its particle size, morphology and mechanical strength and incorporation of soda and organic materials. The crystallization rate of gibbsite is very slow and is further impeded by the presence of some organics in the Bayer liquor. It is the aim of this work to elucidate the microscopic mechanisms operating during the crystallization of gibbsite. The longer term view is to assess the feasibility of accelerating the growth process whilst controlling product quality. Studying the effect of poisoning specific faces will also contribute to our mechanistic understanding.

The growth rate of gibbsite has been reported to be between 1 and 2 μm/hour, depending on the concentration of the liquor (White and Bateman, 1988). These growth rates were obtained as the differences in mean particle size diameters in a bulk crystallization experiment. The purpose of the *in-situ* microscopic study reported here is to measure the growth rates of the individual faces of single gibbsite crystals. Since the atomic structures of the different crystal surfaces differ, a difference in the relative growth rate of these crystal faces is to be expected. Variations in the relative growth rates of these faces will result in changes in morphology of the gibbsite crystals; these changes in the morphology can also be used as an indirect probe of the mechanism of crystallization.

Results from the microscopic studies showed variations in the growth rates, which led to the macroscopic investigations. The effect of seed drying on growth rates and induction times has been reported by Smith and Woods (1993), who claim that induction time is the time taken for re-activation of the seed surface; while Ni and Romanov (1975) claim that induction time is a property of the liquor. Ilievski et al. (1989) have shown that by using active seed, the induction time is reduced, but not eliminated. The effect of liquor history on induction time was thus investigated as part of the macroscopic studies in this work.

Gibbsite crystals precipitated in the Bayer process are usually agglomerates of diamond and hexagonal shaped crystals. Gibbsite grown from a synthetic liquor in the laboratory were of a similar morphology. The crystal faces of the hexagonal and diamond shaped gibbsite have been identified as the (001) basal face, and the (110) and (100) prismatic faces. The (110) face is longer than the (100) face in the diamond shaped crystals, indicating a difference in the growth rates between the (100) and (110) planes for these crystals (Lee et al, 1996).

Certain organic molecules are known to inhibit gibbsite crystallization, reportedly by a surface controlled mechanism (Armstrong, 1993; Grocott and Rosenberg, 1988). Organics that selectively inhibit the growth of a particular face can therefore be used as probes for characterizing the aluminate species in the crystallization process.

2.0 NOTATION

The notation used are those of North American alumina industry, where A is the alumina concentration in g/L Al_2O_3, C is the total caustic concentration expressed as equivalent g/L Na_2CO_3 and S is the total caustic and carbonate concentration, again expressed as equivalent g/L Na_2CO_3. The alumina to caustic ratio, A/C, is the ratio of alumina concentration to caustic concentration.

3.0 EXPERIMENTAL

3.1 *In Situ* Optical Microscopy

3.1.1 Preparation of seed suspension

Synthetic liquor (C 200 , A/C 0.650) was prepared by dissolving aluminium wire (99.9%) in sodium hydroxide solution (AR Grade); it was filtered twice through a 0.2μm pore size membrane and allowed to stand for 16 hours in a water bath at 80°C. The solid content in suspension in this solution, after ageing, was determined gravimetrically by filtration of a known amount through a 0.2μm pore size membrane, washing with hot deionised water and drying at 80°C for 30 minutes.

3.1.2 Preparation of liquor

Another synthetic liquor was prepared as described in Section 3.1.1 (identical concentration). The filtered solution was allowed to stand in a 80°C water bath for 15 minutes, to ensure that the liquor was hot when the seed was added, thus preventing cooling induced nucleation.

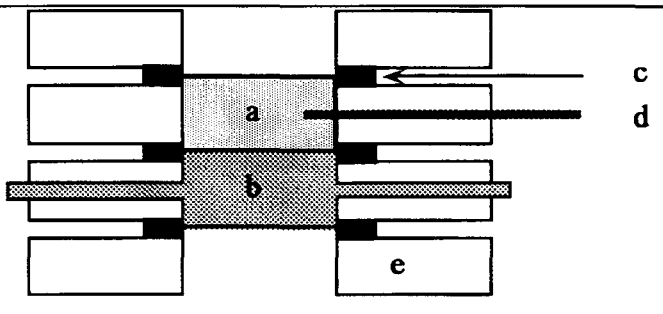
3.1.3 *In situ* cell configuration and crystal growth experiments

Hot seed suspension was added to hot liquor to obtain a final solid concentration of 5ppm. The liquor was transferred to the *in-situ* cell (Figure 1), preheated to 80°C.

The growth of gibbsite nuclei was recorded on a Nikon Labophot-2 optical microscope fitted with a video camera connected to a Macintosh computer. Images were recorded every 30 minutes and the length normal to the crystal faces measured. The growth rate of the crystal face, in microns per hour, at a particular time, was calculated by equation 1.

$$\text{Growth Rate} = \frac{\text{Diameter } (t_2) - \text{Diameter } (t_1)}{2 \times (t_2 - t_1)} \times 60 \qquad (1)$$

where t = time (minutes)



a : *in-situ* cell chamber, 10mL
b : circulating hot water
c : cover slips and o-rings; separating the chambers
d : temperature probe
e : stainless steel body

Figure 1: *In situ* optical microscopy cell

3.2 Effect of Liquor History

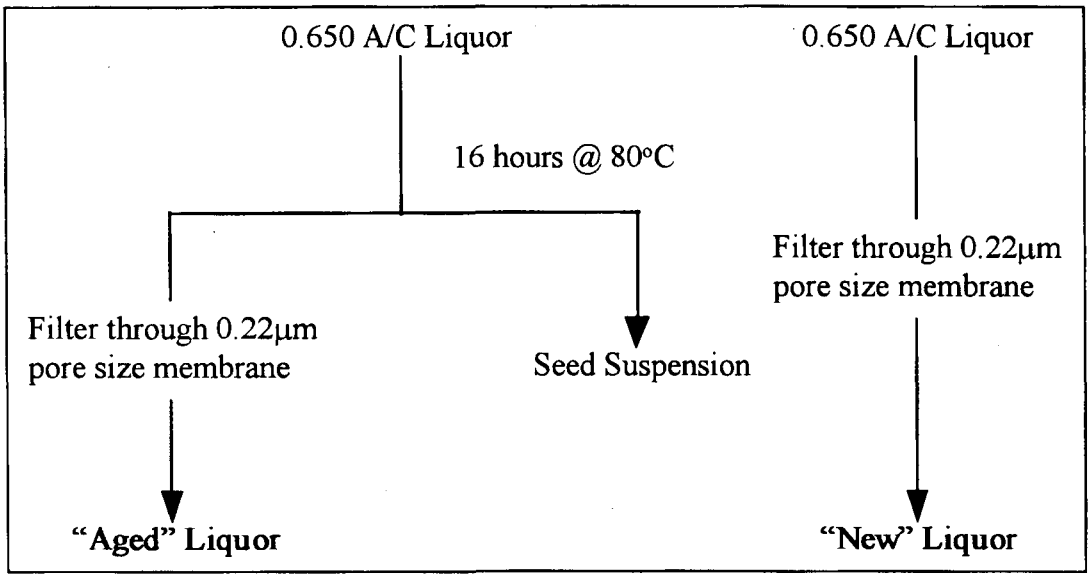


Figure 2: Schematic of liquor preparation to examine the effect of liquor history

The experimental procedures for the liquor and seed preparation are as described for the *in situ* optical microscopy (Section 3.1). Two solutions (aged liquor and new liquor, see Figure 2) containing 5ppm solids were tumbled in a water bath at 80°C. Samples for liquor analyses were taken after 0, 30, 60, 90, 120, 240, 360, 480 and 1440 minutes. The exit liquor was analysed for alumina and caustic concentrations.

3.3 Effect of Organic Compounds on the Morphology of Gibbsite Crystals

Organic compounds, dissolved in water, were added to a concentrated liquor of sodium aluminate that had been filtered through a 0.45μm membrane to remove any solid gibbsite. The final liquor composition was C 200, A/C 0.700, with 10mmol/L organic. The solutions were tumbled in a water bath at 80°C for 95 hours. The organics examined were catechol, sodium gluconate, sodium tartrate (D,L), xylitol and arabinitol.

The precipitate was collected by filtration through a 0.45μm membrane, washed with hot deionised water and air-dried at room temperature. The solids were characterised using powder X-ray diffraction to determine the major phase present and scanning electron microscopy to examine the morphology of the crystals formed.

4.0 RESULTS AND DISCUSSION

4.1 *In Situ* Optical Microscopy

Typical images obtained for the growth of a single gibbsite crystal with time are given in Figure 3. The growth rates of the (110) and (100) faces have been measured, but the exact nature of the surface activity of the (001) face is unknown, because this face is always perpendicular to the direction of viewing. Under identical experimental conditions, differences in growth rates were observed for apparently identical crystals, the differences ranging from no growth to a growth rate up to 5 μm/hour.

Because of the small volume of the *in-situ* cell, the liquor analysis could not be carried out directly on the liquor in the cell. Measurements were therefore made on a parallel batch of liquor prepared and treated under identical conditions. Within the period of observation, microscopically, the growth rate was observed to increase while macroscopically, the A/C ratio decreased. Generally, in Bayer liquors,

the higher the A/C ratio, the higher the level of supersaturation. If the A/C ratio is taken to be an indicator of the level of supersaturation, then the increasing growth rate with time is unexpected according to classical crystallization theories, where the growth rate can be expressed as a positive function of supersaturation for a range of mechanisms operating.

Figure 4 is a typical graph of the growth rates of the different faces of a gibbsite crystal. Although the trends observed were the same (initial induction time or period of slow growth, followed by an increase in growth rates), the absolute values for these rates varied between crystals. In some cases, the crystals did not grow, while in others, the crystals dissolved.

While liquor supersaturation decreases with time, decreasing the crystallization driving force, the growth rates of the crystal faces continue to increase (Figure 4). It is reasonable to expect that the growth rate will level off and ultimately decrease with time, but this was not observed experimentally due to excessive nucleation which obscured the view of the crystal being studied after approximately 10 hours (see Figure 3).

Three factors may be responsible for the observed results. First, it is known that the seeded growth of gibbsite follows an induction period which is ascribed to the activation of the seed surface (Smith and Woods, 1993). It is possible that beyond the induction period, further surface activation continues, effectively increasing the growth rate despite the decrease in A/C. Secondly, it is possible that there are species which are involved in the rate limiting step of the growth process and which are distinct from the dominant bulk species. The former could be increasing in concentration with time despite the overall decrease in the A/C, thus providing a greater driving force. Finally, it is also possible that one or more species exists in the liquor that acts as an inhibitor to crystallization. If these inhibitors were surface active, during the course of crystallization their concentration in solution would decrease, and hence a corresponding increase in the growth rate of gibbsite would be expected.

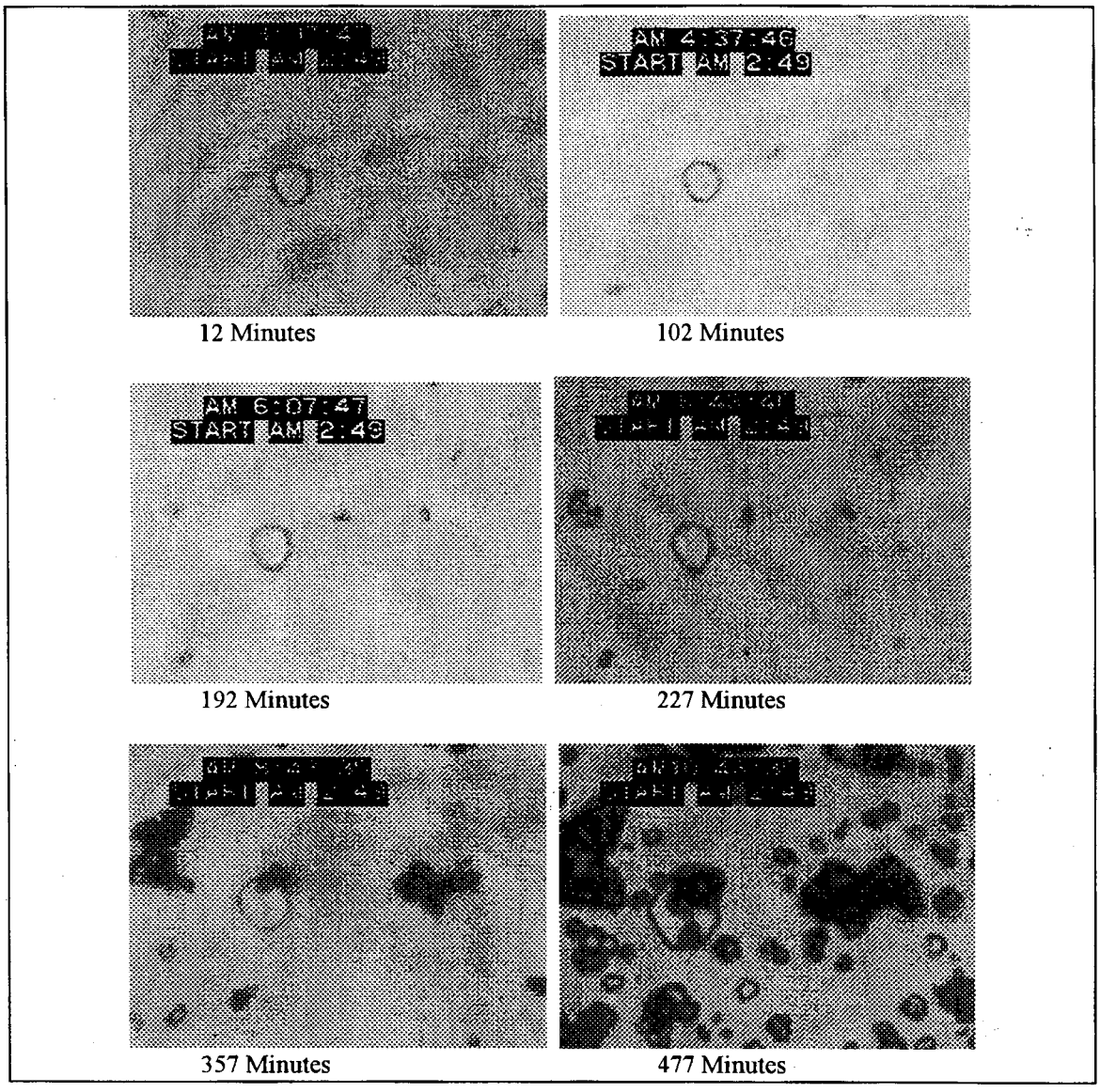


Figure 3: Images of Growing Gibbsite Crystals. Full scale = 125μm

In order to help clarify this, the effects of liquor history were studied in macroscopic experiments.

4.2 Effect of Liquor History

The results of the investigation into the effect of liquor history on precipitation rates in seeded systems are given in Figure 5, which is typical of three independent experiments. If the change in A/C ratio is taken to be a measure of the amount of gibbsite precipitated,

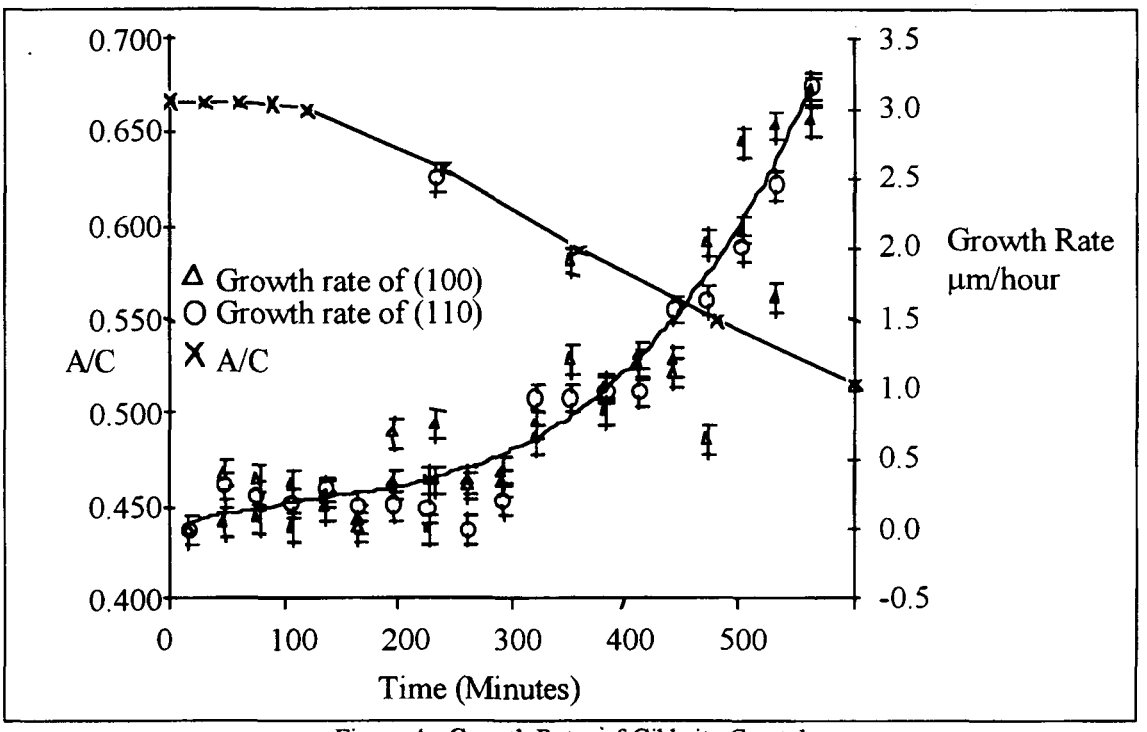


Figure 4: Growth Rates of Gibbsite Crystal

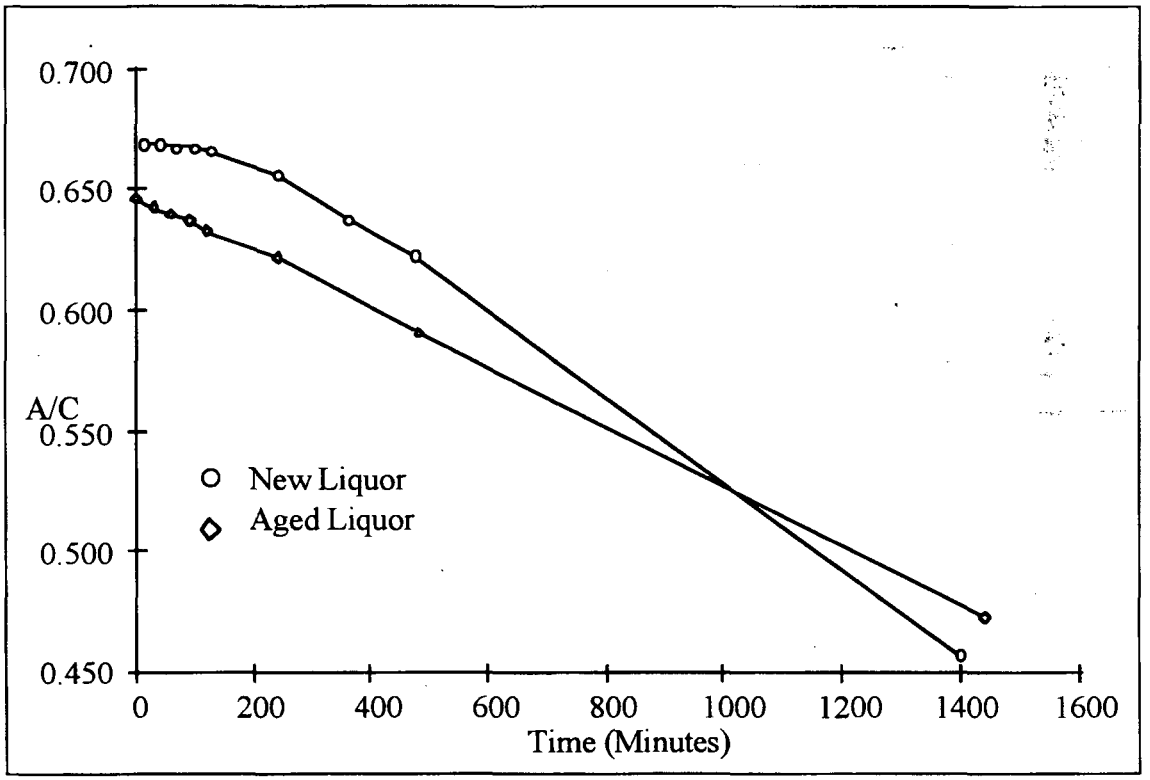


Figure 5: Effect of Ageing Liquor on the Rate of Change of A/C in The Presence of Seed

then the "new" liquor has an induction time of approximately 120 minutes followed by a period of growth. Ilieveski et al. (1989) have shown induction time to have an inverse relationship with A/C, in that with a higher A/C a shorter induction time is obtained. In these experiments, although the "aged" liquor started with a lower A/C, no induction time was observed. Since the seed used in both these cases is "active", the induction time observed in the "new" liquor may be ascribed to some liquor restructuring in the presence of gibbsite crystals; for example, an increase in the concentration of one or more species involved in rate limiting crystallization steps. After approximately 200 minutes, the rate at which A/C decreases in the new liquor is greater than that of the aged liquor. This could be due to

the higher amount of fine nuclei or seed present in the liquor, caused by autonucleation during the induction period.

4.3 Effects of Organic Compounds on the Morphology of Gibbsite Crystals

By quantifying the way in which organics with different stereochemistry interfere with the normal route of crystal growth (as evidenced by growth rates, crystal sizes, morphologies, purity etc.), inferences can be made at the molecular level about processes which occur in the pure system.

Selected organic compounds were examined for their effects on unseeded (homogeneous) gibbsite crystallization. XRD analysis confirmed that the precipitate formed was gibbsite. Comparative data for the effects of these compounds on yield and soda content in seeded precipitation experiments have been reported (Armstrong, 1993; Grocott and Rosenberg, 1988), whereas the thrust of the present work is to characterize their effects on the morphoplogy.

The concentration of organic molecules used was insufficient to complex all the aluminium in solution. The observation that in the presence of certain molecules some gibbsite crystal faces grow, whilst others do not, strongly implies that the mode of action of the organic molecules is to bind to specific growth sites and hence reduce the rate of deposition of gibbsite. The reduction in yield observed for all cases implies that it is the inhibition of growth on specific crystal faces that led to the changes in morphology; however, the converse action, namely the increase in growth rates of certain faces in the presence of organic molecules (which could lead to the same observed changes in morphology) cannot be ruled out at this stage, and is difficult to differentiate experimentally given the wide range of growth rates observed between individual crystals in our liquor.

The gibbsite crystals precipitated from pure liquor consisted of agglomerates of hexagons and diamond shaped crystals. The presence of chamfered faces (112) was also observed in these crystals (Figure 6a). As a comparison, Figure 6b is a micrograph of refinery produced gibbsite - C31, showing agglomerates of hexagons and diamond shaped crystals without the chamfered faces.

With the addition of catechol, the morphology of the crystals changed to that of single elongated hexagonal prisms, indicating preferential inhibition of the growth of the (110) and (100) faces. The absence of the chamfered face was also noted in these crystals (Figure 6c). The crystals obtained from liquors containing gluconate and tartrate were of similar morphology to those obtained in the presence of catechol (Figures 6d and 6e). The reason for the selective inhibition of the (110) and (100) faces is not known at present.

Xylitol and arabinitol are two isomers of the group of C5-polyols in which there is a hydroxyl group at every carbon atom. The addition of arabinitol to the liquor resulted in crystals with larger basal faces, indicating preferential poisoning of the (001) face (Figure 6f). The addition of xylitol to the liquor resulted in the formation of crystals of two different morphologies. Fine, elongated hexagonal needles were obtained as well as agglomerates of hexagons and diamonds (similar to those formed in a refinery) (Figure 6g and 6h). The importance of stereochemistry is indicated by the different effects induced by xylitol and arabinitol.

Almost all the organic additives tested lead to a marked reduction in agglomeration compared to the control samples. This observation further strengthens the proposition that the organic molecules are surface active, and are thus disrupting the normal surface processes that lead to deposition of material between crystal, cementing them together into an agglomerate.

5.0 CONCLUSIONS

- It is known from classical crystallization theories that crystal growth rates are a function of supersaturation. Some results of the present work are not consistent with this, and the difference is believed to be linked to the induction period.

- Growth rates of gibbsite crystals vary widely from experiment to experiment. On a microscopic scale, apparently identical seed crystals would probably have different defects which would in turn affect their growth rate. Thus, for example, internal lattice strains can strongly influence crystal growth rates (Sherwood and Shripathi, 1993) and the presence of surface defects can either enhance or decrease the rate of adsorption of solute species, depending on their nature. This variation would not be observed in macroscopic or bulk studies because average growth rates are measured.

- Although the seed used in this study was "active", an induction period was found, followed by an increase in growth rates with time. In this case, the induction period was ascribed to changes in liquor properties with time, a suggestion supported by the greater induction period observed with "new" compared to "aged" liquor. However, further investigation along these lines is required to determine the absolute values of induction time and growth rates and to clarify the role of other factors (for example the presence of other potential nuclei) in producing the observed result.

- Addition of certain organics may selectively inhibit growth of a specific crystal face. The importance of stereochemistry is indicated, but the reason for this selective inhibition is not yet known, and care needs to be taken to allow for the effects of partial decomposition that may have occured in some of the molecules during the course of the experiment.

- The organic molecules studied show a strong effect of inhibiting agglomeration, indicating that their mode of action is to modify crystal surface processes; this has implications for alumina refinery operation, where the role of naturally occuring, as well as added organic species in affecting product size distribution needs to be considered.

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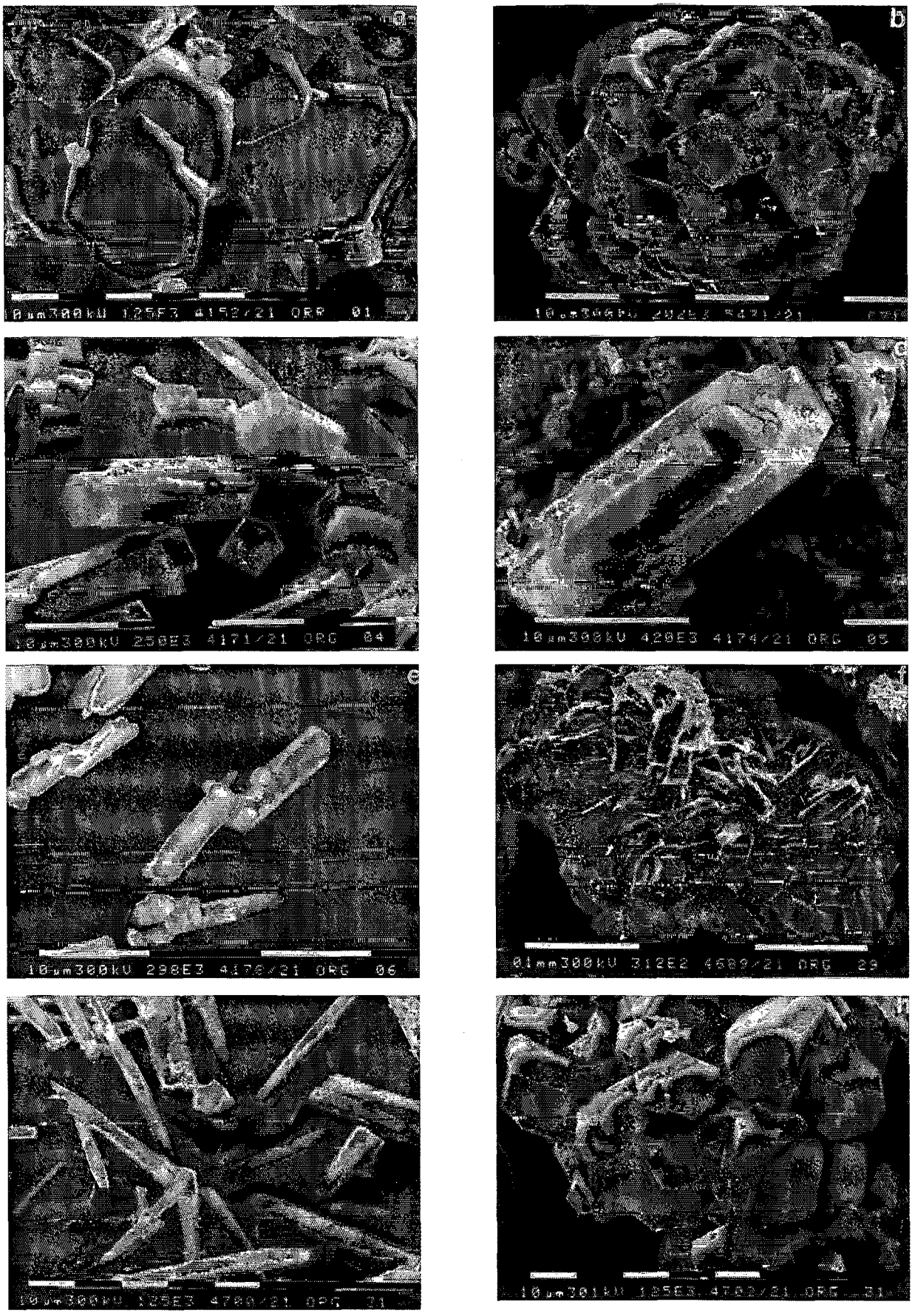

Figure 6: Effect of organics on the morphology of gibbsite crystals (a) control; (b) C31; (c) catechol; (d) sodium gluconate; (e) sodium tartrate; (f) arabinitol; (g) & (h) xylitol .