SODA IN ALUMINA.

POSSIBLE MECHANISMS FOR SODA INCORPORATION

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A mechanism is proposed to explain the incorporation of sodium into aluminium hydroxide during the hydrate precipitation stage of the Bayer process. The proposed mechanism also explains the effect of variables such as temperature and aluminate supersaturation.

The mechanism for soda incorporation into the hydrate crystal structure involves the trapping of sodium ions in a growing layer of gibbsite. These sodium ions do not come directly from Bayer liquor. Rather, they result from the polymerisation of sodium aluminate that occurs during the hydrate precipitation reaction. If the sodium ions are not allowed sufficient time to diffuse away from the growing hydrate surface, they can be incorporated into the hydrate crystal structure, thereby giving rise to soda in alumina.

The proposed sodium incorporation mechanism also provides an understanding of how process liquor impurities can affect soda levels in hydrate. Compounds sharing the common characteristic of relatively acidic, adjacent hydroxyl groups were found to significantly increase soda concentrations in hydrate. These types of impurities are found in Bayer liquors.

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1 INTRODUCTION

1.1 The Need For Low Soda Alumina

Soda is the main impurity in alumina produced from Bayer refineries (apart from residual water). Given that aluminium hydroxide is precipitated from concentrated sodium hydroxide solutions, it might be considered surprising that typical soda in alumina levels are only 0.2 - 0.6% by weight Na_2O.

Nonetheless, it is desirable to produce alumina with soda levels at the lower end of this typical range. Modern smelters generally calculate their break-even point for soda in alumina at 0.35% Na_2O (Sang, 1988). As smelter technology improves and as older smelters are replaced, the incentive will become greater for alumina producers to meet this low soda level. Furthermore, some markets (e.g. catalysts, catalyst supports, refractories, electro-ceramics) require even lower soda levels.

There is a complete lack of knowledge of the fundamental mechanisms controlling the amount of soda incorporated into hydrate. If more efficient soda reduction processes are to be developed then it is necessary to understand these mechanisms.

A small number of studies have examined factors affecting soda incorporation by hydrate. The most recent is that by Sang (1988) which also serves as a good review of the current state of understanding of factors affecting soda in hydrate.

1.2 Notation And Abbreviations

TC, TA: Total caustic (sodium hydroxide plus sodium aluminate) and total alkali (sodium hydroxide plus sodium aluminate plus sodium carbonate) expressed as the equivalent concentration of sodium carbonate. The units are g Na_2CO_3/L.

Hydrate: Alumina trihydrate [$Al_2O_3.3H_2O$] or more correctly, aluminium hydroxide [$Al(OH)_3$].

Soda: Sodium in hydrate or alumina (in any form). This is expressed as % Na_2O by weight on an alumina basis throughout this paper.

A/TC: Ratio of aluminate concentration (g Al_2O_3/L) to total caustic concentration.

1.3 Forms Of Soda In Hydrate

Some of the soda in alumina is derived from imperfect washing of hydrate feeding calciners or kilns. This washable portion of soda in hydrate will be ignored in this paper since it generally constitutes only a small proportion of total soda in alumina. Furthermore, methods for control of this source of soda are generally well known.

There are three other possible forms of existence for soda in hydrate particles.

A. As occlusions or pockets of trapped liquor within hydrate crystals or agglomerates.

B. As individual sodium and hydroxide ions trapped within the hydrate crystal lattice.

C. As sodium ions substituting for protons in the gibbsite structure.

It has been clearly shown (Wefers, 1965; Sang, 1988) that soda in hydrate does not exist (to any measurable extent) as pockets of mother liquor - either in single hydrate crystals or in agglomerates. Therefore, soda in hydrate must exist as either trapped or substituted sodium ions. It has been suggested by Eremin (1980) that sodium substitutes for protons in the gibbsite crystal lattice whereas Wefers (1962) suggests that sodium ions occupy sites between adjacent layers of hydroxide ions in the gibbsite crystal.

2 HYDRATE PRECIPITATION MECHANISM - THE ESSENTIAL LINK

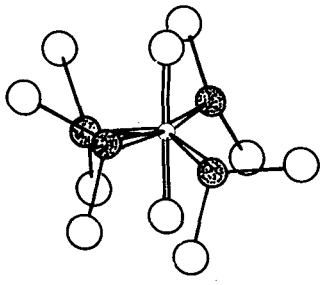
Sodium is incorporated into the hydrate structure during the precipitation reaction. Therefore, the key to control of soda concentrations in hydrate lies in control and understanding of hydrate precipitation chemistry. It is pointless to attempt to understand soda incorporation without first examining the fundamental mechanisms of the conversion of seeded Bayer liquors into gibbsite.

Now, as stated above, sodium is incorporated into hydrate on the **atomic** or **molecular** scale and not as pockets of liquor. Recognition of this fact is essential to an understanding of soda incorporation. Therefore, the corresponding understanding of the hydrate precipitation mechanism must also be at the molecular level.

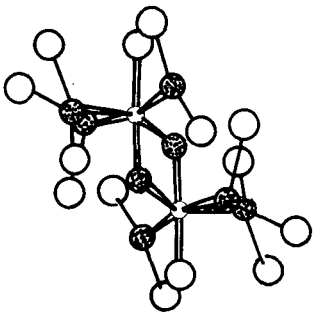
2.1 Mechanism For Hydrate Precipitation

There have been a large number of studies concerned with the precipitation of hydrate from Bayer liquors. However, very few of these have attempted to examine the molecular processes occurring in solution or at the surface of the hydrate seed particles. Whilst hydrate crystallisation is an apparently simple process, the reaction is actually very complex and is not well understood (Overbey and Scott, 1978). However, a recent study (Zambo, 1986) has advanced the understanding of the nature of aluminium-containing species found in pure Bayer liquors. In this study, the existence

of a number of important species was proposed. Two of these are shown in Figure 1.



$[Al(OH)_4.2H_2O]^-.8H_2O$



$[Al_2(OH)_8.2H_2O]^{2-}.12H_2O$

Figure 1: Molecular structure of two aluminium containing species in Bayer liquor (reproduced from Zambo, 1986). The accompanying Na^+-containing species have been omitted for clarity.

The main aluminium-containing species present in Bayer liquor is $[Al(OH)_4.2H_2O]^-.8H_2O$ (Figure 1). The negative charge on this ion is associated with the positive charge on $(Na.4H_2O)^+$. [In Bayer liquor, all of the "free" sodium and hydroxide ions actually exist as $(Na.4H_2O)^+$ and $(OH.4H_2O)^-$ (Zambo, 1986)].

During the hydrate precipitation reaction, two monomeric $[Al(OH)_4.2H_2O]^-.8H_2O$ ions combine to form the hydroxyl bridged dimer $[Al_2(OH)_8.2H_2O]^{2-}.12H_2O$ (Figure 1). It has been suggested that ions containing up to six or more aluminium atoms {e.g. the hexamer $[Al_6(OH)_{24}]^{6-}.24H_2O$} also form in solution. However, most of the structuring of the Al-containing species probably occurs on the hydrate seed crystal surface. The surface energy of seed crystals promotes the formation of the highly ordered polymers, eventually leading to the formation of gibbsite.

Omitting water molecules (whether coordinated or only associated), the gibbsite formation reaction can be summarised as shown in Equation 1. It can also be schematically summarised as shown in Figure 2.

$$n\{Na^+ [Al(OH)_4]^-\} \quad \text{-------->} \quad [Al(OH)_3]_n + n(Na^+ OH^-) \qquad (1)$$

The reactions shown in Equation 1 and Figure 2 occur partly in solution but mostly at the growing gibbsite crystal surface. It is known that the precipitation of gibbsite is surface reaction controlled (White and Bateman, 1988; Brown, 1972). The slow reaction steps probably involve the formation (at the seed surface) of aluminium-containing polymers of increasing structure. As demonstrated in Figure 2, the formation of these increasingly ordered species on the seed surface also requires the release of sodium and hydroxide ions. The fate of these "released" ions forms the basis for the proposed model for soda incorporation into hydrate.

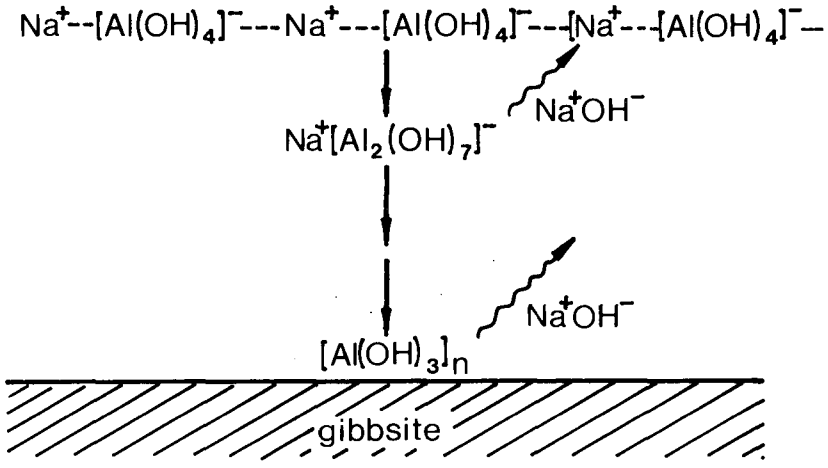


Figure 2: Schematic representation of the gibbsite formation reaction.

3 PROPOSED MECHANISM FOR SODA INCORPORATION INTO HYDRATE

It has been suggested (Wefers, 1962) that some sodium is necessary for the stabilisation of gibbsite relative to bayerite. This may be correct since there is some evidence (Wefers, 1962; Kodama and Schnitzer, 1980; Violante and Violante, 1980; Van Straten et al., 1985) to show that bayerite is the more stable form of $Al(OH)_3$. If it is assumed that the presence of some sodium is necessary to stabilise gibbsite then the question must be asked, "How much sodium is necessary to stabilise gibbsite?".

Fortunately, it is apparent that only small amounts of sodium are required to stabilise gibbsite relative to other forms of $Al(OH)_3$. For example, soda levels of less than 0.1% are easily produced (Lindsay and Kinsman, 1965; Ohkawa et al., 1985) under appropriate precipitation conditions. However, for industrial-scale production of smelter grade alumina, these precipitation conditions for low soda alumina production are either difficult to attain or are uneconomical. Alumina producers must implement more efficient ways in which to reduce the soda content of hydrate below current levels to be able to meet market demands. In order to do this (as stated earlier) it is important to establish the mechanism by which soda is incorporated into the hydrate crystal.

3.1 Previous Soda Incorporation Mechanisms

It was stated above that the concentration of sodium necessary to favour the formation of gibbsite over other $Al(OH)_3$ forms is only a small fraction of the soda typically found in smelting grade alumina. How or why does the remaining soda find its way into the gibbsite crystal?

Although there are a number of studies of factors affecting soda incorporation into gibbsite (Sang, 1988 and references therein) there has only been one which proposed a mechanism for soda incorporation into hydrate (Ohkawa et al., 1985).

It was suggested that hydrate grew over "micropockets" of liquor, thereby trapping the soda in "overhangs" on the crystal surface. However, this is not consistent with the evidence of Sang (1988) who showed that other impurities in the liquor were not incorporated into hydrate particles (even under conditions of severe agglomeration). Furthermore, this proposed mechanism does not reflect the molecular processes by which hydrate growth occurs. Hydrate does not grow by the deposition of large "building blocks" capable of trapping liquor. Rather, it is thought to grow by the polymerisation of molecular Al-OH species at the surface of the seed crystal (Zambo, 1986) (see also Equation 1 and Figure 2).

3.2 Proposed Mechanism

The mechanism proposed for the incorporation of soda into gibbsite is based upon the molecular mechanism for hydrate precipitation described in Section 2.1. The proposed soda incorporation mechanism is not claimed to be rigorously correct. It is only meant to be a descriptive theory of the means by which sodium is incorporated into the hydrate structure during the precipitation reaction. As such, it does not in itself provide a fundamental mathematical model for soda incorporation. However, it may provide a useful basis for the development of such a model. More importantly, it does enable an understanding of how various precipitation factors can affect the concentration of soda in hydrate. This in turn provides the basis for investigation of logical and economical methods to reduce the soda content of alumina as opposed to the *ad hoc* approaches employed in the past.

Using the schematic diagram in Figure 2 as a basis for the soda incorporation model, it is apparent that we should not look for factors that cause soda to **enter** the growing hydrate particles. We should instead be investigating how the released sodium hydroxide is **prevented from leaving** the growing $Al(OH)_3$ surface.

Very simply, the pictorial description of the proposed soda incorporation model is as follows:

> During hydrate crystallisation, Al-OH species associate at the hydrate seed surface. In order to form gibbsite, these Al-OH species must polymerise. This polymerisation initially produces higher molecular weight polymers which form a semi-ordered or "gel-like" layer at the gibbsite surface. The by-products of the polymerisation are sodium and hydroxide ions.
>
> The soda released during the increased structuring of this growth layer, is at lowest energy when located in the liquor. Consequently, diffusion processes tend to cause the soda to migrate out of the growth layer and into the surrounding liquor. Diffusion rates in the liquor are far greater than the rate of growth of the hydrate particle. However, the rate of diffusion of hydrated sodium and hydroxide ions through the semi-crystalline growth layer will be less than the corresponding diffusion rates in liquor.

It is proposed that some of these sodium and hydroxide ions may not have sufficient time to diffuse out of the growth layer before it is converted into gibbsite. Therefore, they will be incorporated into the gibbsite crystal and will report as soda in alumina.

This model does not distinguish between proton substitution and Na^+OH^- entrapment.

Much more complexity could be added to this description of the proposed soda incorporation model. However, the important consequence of this description is that *factors which affect the rate or effectiveness of the soda diffusion will affect the concentration of soda in hydrate and the resultant alumina.* These factors are discussed in some detail in the following sections.

4 EXPLANATION OF FACTORS INFLUENCING HYDRATE SODA

Many factors have been empirically linked to the formation of hydrate with relatively high soda levels. However, no satisfactory description has been given as to why these factors cause high soda concentrations in gibbsite. The following sections are an attempt to provide an understanding of how each factor might cause high or low soda concentrations in hydrate.

4.1 Temperature

It has long been recognised (Lindsay and Kinsman, 1965) that an increase in the temperature at which hydrate precipitation occurs will reduce the soda content of hydrate. However, increased temperature also produces decreased aluminate supersaturation. This too is a factor which affects the soda content of hydrate (see Section 4.2). Some studies have been published of the independent effects of temperature and supersaturation. One study (Sang, 1988) concluded that temperature had no effect upon the soda content of hydrate and stated that any perceived temperature dependence could be entirely explained by changes in aluminate supersaturation. Other studies (Ohkawa et al. 1985, Wefers, 1965) drew the opposite conclusion.

Using the descriptive model for soda incorporation, it is possible to predict a relationship between hydrate soda and precipitation temperature. As temperature is increased, the diffusion rate of ions increases. Therefore, it is expected that lower soda concentrations would be achieved at higher temperature since the soda would be able to diffuse more rapidly out of the growing hydrate layer.

Work in our laboratories has confirmed this relationship. At a constant aluminate supersaturation and under typical hydrate precipitation conditions, a 10°C increase in the temperature can produce up to a 0.2% (Al_2O_3 basis) decrease in the incremental soda concentration.

4.2 Aluminate Supersaturation

It has been known for some time (White and Bateman, 1988 and references cited therein) that the growth rate of $Al(OH)_3$ is proportional to the square of aluminate supersaturation (equation 2).

$$\text{Growth} \propto (C - C^*)^2 \qquad (2)$$

where C = *aluminate concentration and*
C^* = *equilibrium aluminate concentration*

It follows that the thickness of the new hydrate forming on the outside of the seed crystal increases with the square of the aluminate supersaturation. Correspondingly, some of the soda released by structuring in this growth layer will have a greater distance to diffuse before it can escape into the liquor. Therefore, high growth rates can cause more soda to be trapped in the hydrate crystal.

In fact, it has been established in our laboratories and elsewhere (Ohkawa et al., 1985; Sang, 1988;) that the soda content of hydrate is proportional to the hydrate growth rate.

$$\%Na_2O \text{ in hydrate} \propto \text{Growth} \propto (C - C^*)^2 \qquad (3)$$

This hydrate growth rate could be expressed as the specific precipitation rate (SPR) for hydrate and therefore:

$$\%Na_2O \text{ in hydrate} \propto \text{SPR} \qquad (3)$$

where *SPR is the specific precipitation rate*
and *SPR* = *(g Al_2O_3 precipitated)/(m^2 seed area)/hour*

4.3 Other Factors

Precipitation temperature and aluminate supersaturation are two of the most important influences upon soda concentrations in hydrate. Among other factors which have been described as affecting soda are - hydrate agglomeration, seed size and density, caustic concentration, sodium oxalate, inorganic impurities and organic impurities. Organic impurities are very important and are discussed separately in Section 5.

4.3.1 Agglomeration.

Plant experience (Howard, 1988) indicates that conditions favouring high agglomeration also produce higher soda alumina. However, agglomeration generally requires high SPR. Therefore, it is not surprising that agglomerating conditions favour the production of high soda alumina. It should be stressed again that the higher soda content of hydrate formed under agglomerating conditions is not due to liquor inclusions (Sang, 1988) but is a consequence of the high hydrate growth rate or SPR.

4.3.2 *Seed*

The amount and size of hydrate seed participating in the precipitation reaction have also been investigated as factors affecting soda incorporation into hydrate. Sang (1988) found that increased quantities of seed reduced soda but that seed size had no effect. Ohkawa et al. (1985) found no influence of seed upon soda incorporation.

The proposed model for soda incorporation predicts that surface area should have an effect upon soda incorporation. At higher seed charges and smaller seed sizing, the surface area available for hydrate growth is larger. Therefore, over a finite precipitation time, the average SPR will be smaller throughout the precipitation period. This, in turn, causes lower average growth rates. This allows the sodium ions to diffuse more readily out of the growing hydrate layer, thereby leading to lower hydrate soda concentrations. Results from our laboratory work are summarised in Table 1 overleaf.

Table 1: Effect of hydrate seed charge and size upon soda in hydrate.
The hydrate was grown from pure sodium aluminate (TC 180, A/TC 0.65) at 65°C for 90 hours.

Seed Charge (g/L Al_2O_3)	**Mean Seed Size**	**Surface Area** (m^2/L)	**%Na_2O in New Hydrate** (±0.006%)
6.6	50*um*	0.73	0.376
3.3	10*um*	2.6	0.251
6.6	10*um*	5.3	0.223
33	10*um*	26	0.223

As predicted from the soda incorporation model, the data in Table 1 reflect some form of dependence of hydrate soda upon seed size and charge. This is also borne out by plant experience which has shown that an increase in precipitator tank seed concentration from 200 to 300 g/L caused up to a 0.05% decrease in the hydrate soda concentration.

4.3.3 *Caustic Concentration*

Recent studies (Sang, 1988; Ohkawa et al., 1985) have concluded that caustic concentration of liquor has no significant influence upon soda incorporation into hydrate. The model proposed in this paper for soda incorporation indicates that soda diffusion may be inhibited by the presence of higher liquor caustic concentrations (Fick's law of diffusion through a porous layer), thereby leading to higher soda levels. However, it is also known (White and Bateman, 1988) that increased caustic concentration reduces the hydrate growth rate. Therefore, this influence may counteract the effect of reduced diffusion rates, resulting in no net change in soda levels.

4.3.4 *Oxalate*

It has been shown experimentally (Sang, 1988) that under agglomerating conditions, the presence of fine sodium oxalate can contribute substantially to the hydrate soda content. Plant experience confirms this. However, the mechanism for soda incorporation proposed in this paper does not deal with soda contamination by oxalate, which proceeds by a different pathway. Briefly, oxalate can contribute to the total level of soda impurity by precipitating as fine needles of sodium oxalate which are physically incorporated into hydrate particles. This may be seen more clearly by referring to Figure 3.

At one refinery which was experiencing contamination of the seed hydrate by fine sodium oxalate, the alumina soda concentration increased by 0.1%. The source of this added soda was from incorporation of solid sodium oxalate into the hydrate crystals.

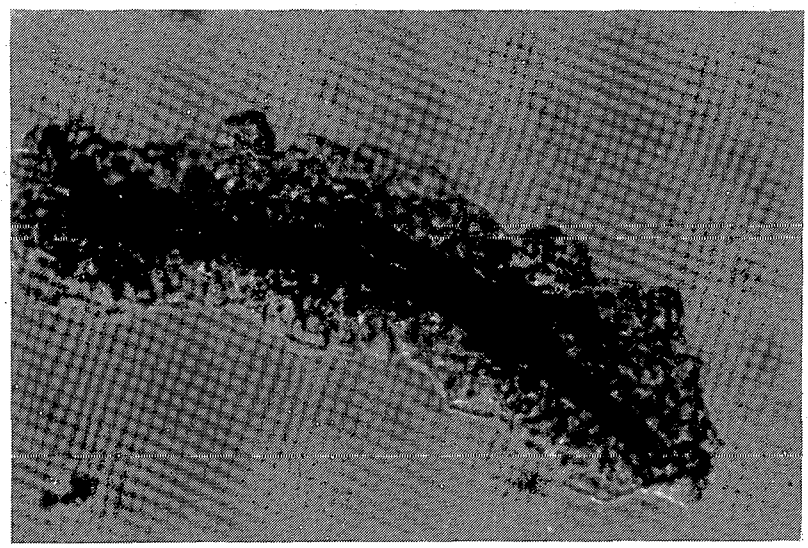


Figure 3: Sodium oxalate contamination (dark coloured needles) in a hydrate particle (pale crystals).
This photograph was obtained by optical microscopy after immersing contaminated hydrate in aniline.

4.3.5 *Inorganic Impurities*

Only one study has been published (Sang, 1988) in which the effect of inorganic impurities (e.g. sodium carbonate, sulfate and chloride) was studied. Their influence upon hydrate soda was found to be insignificant. This has been borne out in our work, the results of some of which are shown in Table 2.

Table 2: Effect of inorganic impurities upon hydrate soda. The hydrate was grown from sodium aluminate (TC 180, A/TC 0.65) at 65°C for 90 hours. Hydrate seed was 6.6g/L of 10*um* material.

Impurities (added to pure sodium aluminate solution)	**%Na_2O in New Hydrate** ($\pm$ 0.006%)
Nil	0.223
Na_2CO_3 (55g/L), Na_2SO_4 (11g/L) and NaCl (22g/L)	0.219
NaF (5g/L)	0.246

Clearly the carbonate, sulfate and chloride have no significant effect upon soda levels in the hydrate. The results also suggest that added sodium ion has no effect. However, the presence of fluoride does increase hydrate soda. The reasons for this are unclear, but it may be related in some way to the strong affinity between aluminium and fluoride ions.

5 EFFECT OF ORGANIC IMPURITIES UPON SODA IN HYDRATE

The one factor remaining which has not been discussed in relation to the proposed soda incorporation model is the effect of organic impurities in Bayer liquor.

Bayer liquor contains a wide range and large amount of organic impurities (Guthrie et al., 1984). Typical concentrations range up to 40 g/L as total organic carbon (TOC). It is common to express the concentration of organic impurities as TOC. However, since they are present as sodium salts, their concentration is in fact as high as 100g/L. Thus, organic impurities constitute a very large part of the dissolved solids in Bayer liquors.

It has long been recognised (Lindsay and Kinsman, 1965) that the organic impurities in Bayer liquor can exert a significant effect upon soda incorporation into hydrate. Despite this, few studies have directly examined the effect of organic impurities.

5.1 Previous Studies

Sang (1988) examined the effect of commercial humic acids upon hydrate soda. Unfortunately, one would not expect these humic acids to resemble the humic acids (or other organics) found in Bayer liquors. Nonetheless, some interesting observations were made in this work. It was found that humic acids in concentrations up to 0.25g/L increased the soda content of hydrate. However, above a this concentration, no increase in effect was observed. No comment was made on the origins of this plateau. However, it seems to imply a surface dependent phenomenon such as an adsorption of the humic acid on the hydrate. If Langmuirian (or similar) adsorption occurred, then above a certain concentration, no significant further adsorption of humic acid would occur. This would correspond to the lack of soda dependence upon humic acid concentration above the observed limiting value of 0.25g/L.

It was also noted that the relatively small impact of the added humic acid did not account for the large difference in the soda level of hydrate precipitated from synthetic and Bayer liquors.

5.2 Bayer Liquor Versus Synthetic Liquor

In our tests, a synthetic liquor was prepared to exactly match a plant liquor in every way except for the absence of impurities. The aluminate supersaturations of the two liquors were also matched by adjusting the dissolved aluminate concentration. Blends of the synthetic and plant liquors were prepared and hydrate was precipitated from the liquors. The soda content of the hydrate produced from these liquors is shown in Figure 4.

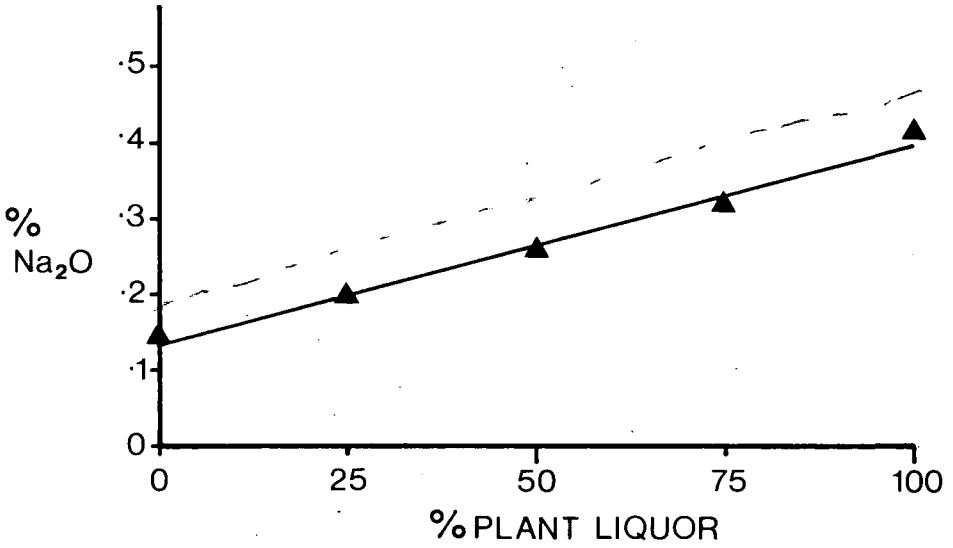


Figure 4: Soda content of hydrate precipitated from blends of plant and synthetic liquors.
The conditions were 65°C, 90 hours, 6.6g/L of 10μm seed.

This graph clearly demonstrates a strong relationship between soda in hydrate and the amount of organic impurities present in liquor.

5.3 Mechanism Of Influence Of Organic Impurities

As part of the proposed soda incorporation model, it has been stated that soda incorporation is a surface dependent phenomenon (i.e. soda diffusion through a growth layer). How then might organic impurities affect this process?

We propose that certain organic impurities adsorb on the growth layer of hydrate seed. The presence of these adsorbed impurities can affect hydrate soda in two ways.

Firstly, they might inhibit the outward diffusion of soda, thereby causing higher soda retention in the hydrate. Secondly, they may reduce the available hydrate seed surface area (i.e. seed "poisoning"). This latter effect would cause the average growth rate on the non-poisoned hydrate growth sites to be higher for longer periods of time (i.e. high local SPR). The high local growth rate would lead to higher soda in alumina.

These hypotheses are depicted pictorially in Figure 5.

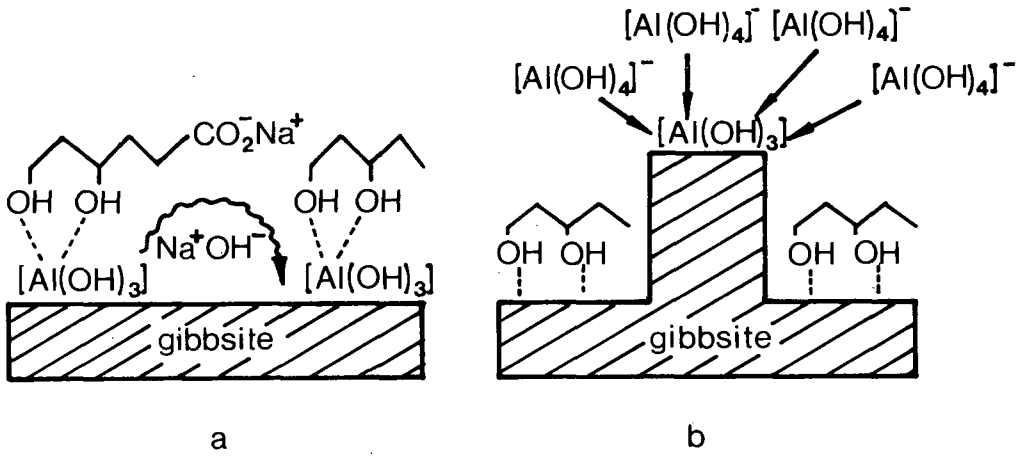


Figure 5: Mechanisms for the influence of organic impurities upon soda incorporation.
a) Inhibition of soda diffusion.
b) Surface poisoning.

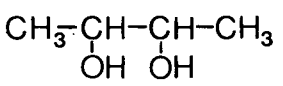
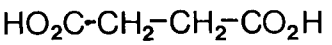
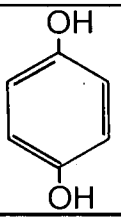
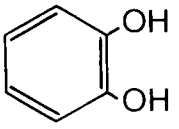
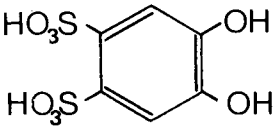
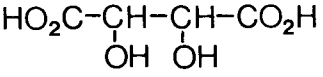
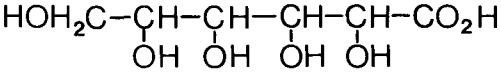
Evidence supporting these hypotheses of surface-mediated dependence of hydrate soda upon organic impurities is given below.

5.4 Impurities That Cause High Soda In Hydrate

If the hypotheses above are correct, then only organic impurities which can adsorb at the hydrate-liquor interface will affect hydrate soda levels. Furthermore, only trace concentrations of these impurities would be necessary to cause elevated soda concentrations in hydrate.

Aluminium coordination chemistry dictates that organic species with adjacent, acidic hydroxyl groups will have a strong affinity for the gibbsite surface. Eight simple organic impurities were selected for evaluation of their impact upon hydrate soda levels. They were each added to separate bottles of seeded synthetic liquor at equimolar concentrations and hydrate was then grown from the liquor. The compounds used and the results of the analyses of the hydrates are shown in Table 3.

Table 3: Effect of various organic impurities upon incorporation of soda into hydrate.
The precipitation conditions were 65°C, 90 hours, 6.6g/L of 10*um* seed. Each organic impurity was added as its sodium salt at a concentration of 0.015M (e.g. 0.33g/L for sodium gluconate).
The hydrate yield in each test was almost identical.

Impurity Name	**Impurity Structure**	**% Increase In Hydrate Soda** (+ 5%)
Nil	-	0 %
2,3-butanediol		7 %
Succinic acid		8 %
Hydroquinone		11 %
Catechol		40 %
Tiron		54 %
Tartaric acid		65 %
Gluconic acid		127 %

It has been postulated that organic impurities cause high soda concentrations in alumina by physical incorporation of the sodium salt of the impurity into the hydrate particle (Sato and Kazama, 1971). This view is clearly incorrect. As can be seen from Table 3, the concentrations of organic impurities are too low to account for the increase in soda. For example, even if all of the sodium gluconate was consumed by the hydrate, it would still only account for 14% of the soda contained in the freshly precipitated hydrate.

Furthermore, we have shown in other work (Grocott, forthcoming publication) that the gluconate is only adsorbed onto the surface of the hydrate and is not strongly incorporated into the crystal structure.

The organic impurities in Table 3 are arranged in ascending order of their ability to adsorb onto an aluminium hydroxide surface. Clearly, this is also the order of their ability to cause increased soda incorporation into hydrate. Organic impurities possessing only carboxylic acid functionalities (e.g. succinic acid and most Bayer liquor organics [Guthrie et al., 1984]) would not be expected to strongly adsorb onto hydrate. However, organic impurities with adjacent, acidic hydroxyl groups would be expected to adsorb strongly. This accounts for the trend in soda levels observed in Table 3.

Furthermore, the organic impurities with multiple acidic hydroxyl groups would be expected to adsorb most strongly. This adsorption would be further enhanced if the impurities possess a high molecular weight and low hydrophilicity (e.g. some humic and fulvic acids). Substances fulfilling these criteria exist in Bayer liquors. There is NMR evidence for the presence of phenols (e.g. catechol) in Bayer liquor (Grocott, forthcoming publication). Polyhydroxy organics similar to gluconic acid have already been identified as a constituent of hydrate seed surfaces (The, P.J., 1980).

Since these types of organic impurities adsorb strongly on hydrate they would not be expected to build up to high concentrations in Bayer liquor. However, only trace amounts of these substances are required (e.g. 0.33g/L of sodium gluconate) to substantially increase hydrate soda. Clearly, the bulk of Bayer liquor organics has little or no impact upon hydrate soda levels.

6 FUTURE DIRECTIONS IN SODA RESEARCH

The model proposed in this paper for soda incorporation into hydrate provides a basis for future research. It has not been generally possible to develop mathematical models for prediction of soda contamination in hydrate. This study provides an opportunity for the development of soda models based upon the **mechanism** of soda incorporation into hydrate. Clearly however, this is an area requiring considerable work.

More significantly, this study has demonstrated the importance of hydrate surface chemistry and the role of certain types of organic impurities in determining hydrate soda levels.

Current strategies for reducing hydrate soda levels can add considerable cost to the production of smelting grade alumina. Novel, cost-effective processes must be sought. This will only occur after further developing an understanding of soda incorporation chemistry. Alcoa of Australia Ltd will be pursuing research into discovering the types of compounds responsible for increased soda in hydrate. Work will also be carried out on the corresponding hydrate surface chemistry. Processes for negating or removing these "active" impurities will then be developed.

7 CONCLUSIONS

The proposed mechanism for sodium ion incorporation into gibbsite provides a plausible molecular description of the process by which soda arises in alumina. The proposed model is not only consistent with experimental observations of soda-influencing factors but also provides an understanding of their mode of action.

The major factors affecting hydrate soda levels (temperature, alumina supersaturation and organic impurities) can now be understood. With further research, this may lead to processes by which soda levels in hydrate can be more economically reduced to levels required by modern smelter technology.

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