The Impact and Control of Organic Compounds in the Extraction of Alumina from Bauxite

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INTRODUCTION

Australia is the Western world’s largest producer of alumina, supplying one third of total needs. Western Australia’s South-West has the greatest concentration of alumina production in the world, with a current annual production rate in the region of 6.8 million tonnes per annum, 20 per cent of the total produced to market economies. The value of this production in 1989-90 was 2.34 billion dollars, a very significant contribution to the economy of the State (1). This is despite the fact that the bauxite from the Darling Range is the lowest grade that has ever been commercially exploited, and despite the geographical isolation of the region. It is therefore of great importance to the National and State economies that this industry retain its competitive edge, particularly in the current times of economic downturn. One essential ingredient of this competitiveness is technology and innovation, which can be assured by the commitment of the industry to an active program of Research and Development, with support from the public sector as appropriate.

Organic contamination of the process liquor is a general problem to alumina refineries. The problem is greatest in Western Australia, due to the combination of a uniquely low-grade ore with among the highest levels of contained organic matter. The impact on the productivity of the liquor is substantial, representing an overall production loss of at least 20 per cent, or 1.3 million tonnes per annum for the region, equivalent to an entire alumina refinery. Considerable effort is therefore being directed at this problem by the producers. Little input has so far been made from the public sector, although this is expected to improve in the future as the importance of the problem, and the complexity of its practical and academic challenges become more generally recognised.

SOURCES OF ORGANICS

As implied in the Introduction, the greatest source of organics is the bauxite. The remainder enter the liquor as a result of the deliberate addition of process enhancing chemicals, including starch and synthetic flocculants, dewatering aids, defoamers, and crystallisation aids.

Darling Range bauxite is mined in forest areas, and therefore contains relatively large amounts of organic matter. The carbon content of the soil varies with depth, as shown in Figure 1 for a typical mining area in the Worsley lease. The carbon content is highest in the topsoil, which must be quantitatively removed in the mining operation. Carbon generally decreases with depth through the bauxite horizon to the basement clay, due to natural leaching.

THE BAYER PROCESS

In the Bayer process, bauxite is digested in caustic soda solution, at temperatures in the range 140 to 240°C, depending on the nature of the bauxite to be treated and the details of the refinery design. The Alcoa refineries in Western Australia, as well as Gove in the Northern Territory, digest at around 145°C, which is sufficient to dissolve the gibbsite, Al(OH)3, which forms the extractable alumina in their ores. The Worsley refinery digests at a somewhat higher temperature, to achieve a more favourable water balance. Queensland Alumina is an example of a high-temperature plant, operating at above 220°C to dissolve the Boehmite, Al2O3·H2O, in the Weipa ore. Higher digestion temperatures increase the degree of solubilisation of the organic compounds in the bauxite, as well as the rate of breakdown of complex organics to simpler molecules.

After digestion, the residue mud is separated from the aluminate-containing liquor by settling and washing in a counter-current decantation system. The liquor is then passed through pressure filtration to remove the last traces of mud, before being cooled and transferred to Precipitation. In Precipitation, the liquor is held in contact with aluminium hydroxide, or “hydrate”, seed for approximately forty hours, after which time the now spent liquor is heated and returned to Digestion. The precipitated hydrate solids are filtered, washed, and calcined at 1000°C to produce calcined alumina, Al2O3. Details of the Worsley Refinery, for example, are given elsewhere (2).

The process, as shown schematically in Figure 2, therefore features a recirculating liquor loop in which each impurity inevitably builds up to a steady-state concentration at which the rate of input equals the rate of output.

The build-up of organic carbon in the life of the Worsley Refinery liquor is shown in Figure 3. The curve has the expected logarithmic general shape, and steady state was reached after about three years. The current variations about the mean value are dependent on a number of factors, the most important of which are variations in the organic carbon content of the bauxite, and the rate of addition of fresh caustic soda to the liquor.

Organic impurities which enter the liquor are continuously removed by a variety of mechanisms. The most important of these are adsorption to the residue mud, purging with the residue and other liquors, adsorption to the product hydrate and subsequent calcination, and conversion to carbonate in Digestion, followed by removal as calcium carbonate by lime addition. The alumina refineries also practice some form of sodium oxalate removal which, apart from removing the sodium oxalate itself, takes a variety of adsorbed organics out of the liquor.

EFFECTS OF ORGANICS ON THE PROCESS

Overall, the presence of organic impurities in Bayer liquor has a strongly negative effect on the Process. Organics create process difficulties by increasing liquor viscosity, which decreases mud settling rates and particle classification efficiencies in Precipitation, and increases pumping costs. They also raise the boiling point of the liquor, so limiting evaporation efficiencies. The organics are present as sodium salts, and so tie up sodium ions uselessly, increase the ionic strength, and place a limit on achievable caustic concentrations.

By far the greatest impacts of organics on the Bayer Process, however, are in the areas of Precipitation Yield and Product Quality. As the process liquor spends most of its time in Precipitation, owing to the inherently slow kinetics of hydrate precipitation, precipitation yield is the key to overall refinery productivity, a principal determinant of economic viability.

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Fig 1 - Typical carbon profile of a bauxite pit in the Darling Range.

Fig 2 - Bayer process schematic, showing recirculating liquor stream.

Maintenance and improvement of Product Quality are essential to competitiveness in the marketplace.

Yield effects

The overall effect of liquor organics on precipitation yield as calculated for the Worsley Refinery is shown in Figure 4. This plot is based on laboratory precipitation tests which provided the data for the calculation of yields by computer simulation. For the laboratory tests, a synthetic liquor free of organics but otherwise similar in composition to Refinery Liquor was prepared. This was blended with Refinery Liquor in various proportions to give liquors with a range of organic carbon levels from zero up to the full amount in Refinery Liquor. The presence of the organics has negative effects on both the rate constant and the equilibrium aluminate ion concentration approached after extended reaction time (3).

These results are consistent with the findings of Bird et al (4), who found the reduction in yield to be linear with concentration.
ORGANIC COMPOUNDS IN EXTRACTION OF ALUMINA FROM BAUXITE

ORGANIC CARBON IN PLANT LIQUOR

Fig 3 - Buildup of organic carbon in the Worsley liquor since startup.

EFFECT OF ORGANICS ON PRECIPITATION YIELD

Fig 4 - Overall effect of organics on precipitation yield.


<table>
<thead>
<tr>
<th>ORGANIC SPECIES</th>
<th>% INHIBITION per millimole</th>
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<tr>
<td><strong>A. ACID ANIONS</strong></td>
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<tr>
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<td>TARTRATE</td>
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<td>OXALATE</td>
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<tr>
<td>ETHANE DIOL</td>
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<td><strong>3. AROMATICS</strong></td>
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<td>HYDROQUINONE</td>
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for the liquor at the Reynolds Metals Co Sherwin Refinery in Texas, albeit with a different proportionality constant, as would be expected. The Texas Refinery processes a wide range of bauxites, from Jamaica, Africa, South America and Australia, in a high temperature process. The inference is therefore that the linear dependence holds generally. This then implies that benefits are to be gained from removal of the full spectrum of organics from the liquor, and that the degree of such benefit is in direct proportion to the fraction of organics removed.

Soils, and therefore bauxites, contain a complex mixture of organic compounds arising from plant and animal materials in various stages of degradation. Digestion in caustic soda in the Bayer Process results in dissolution of a portion of the soil organics, and further degradation of them by a variety of oxidative and non-oxidative processes. This leads to a wide variety of process impacts, depending upon the properties, such as surfactant activity and adsorption behaviour, or ability to form complex ions with aluminium, of the compounds concerned.

Investigations of the effects of individual organic compounds on precipitation yield indeed show that there are correlations between the structure of organic molecules and their effect on precipitation yield. From the results given in Table 1 it can be seen that compounds with adjacent hydroxyl groups are the most powerful precipitation inhibitors. The basis of the inhibition mechanism therefore appears to be related to the ability of these compounds to form complexes with aluminium. Because inhibition occurs at concentrations much lower that could be accounted for by complexation in solution we can conclude that these compounds have the ability to strongly chemisorb to the surfaces of the hydrate seed crystals (4). Sodium gluconate, which may be present in the liquor as a degradation product of starch added to promote mud settling (5), is a particularly effective inhibitor. This property of gluconate is used to prevent aluminium hydroxide precipitation in the analytical procedure for determining aluminate by titration (6).

**Particle size effects**

Particle size distribution is one of the most critical product quality parameters for alumina. In particular, it is necessary to control the level of very fine (45-55 microns) material present to the lowest practicable values. It has been shown that specific organics promote the formation of fine particles by secondary nucleation during hydrate precipitation (7). The mechanism of this is presumably inhibition of orderly crystal growth by adsorption at growth sites, which then forces precipitation to occur by nucleation of new crystals on sites not conducive to growth. Compounds which exhibit this effect include sodium acetate, succinate and lactate (7). The special effects of sodium oxalate are treated separately below.

**Impurity effects**

The major impurity in product alumina is Na₂O, which is typically in the range 0.4 to 0.5 per cent. The presence of organics in the liquor has a marked effect on the incorporation of soda from the liquor into the hydrate. Grocott has shown that the organics which most affect soda incorporation are of the same class as those that have the greatest effect on precipitation yield, ie compounds with hydroxyl groups on adjacent carbon atoms (8). This has been rationalised by first assuming that the adjacent hydroxyl structure enables chemisorption to the growing hydrate surface. If we then suppose that the diffusion of sodium ions away from the growing hydrate surface is involved in the
(a) Inhibition of Sodium Diffusion

(b) Surface Poisoning

Fig 5 - Inhibition of sodium diffusion and surface blocking by organics can cause reduced precipitation rates, higher soda contamination, and dendritic growth. (After Grocott (8)).

Rate Determining Step, then inhibition of sodium diffusion by the presence of the adsorbed organics would at once reduce the reaction rate and increase the rate of incorporation of soda into the growing crystal. This is illustrated schematically in Figure 5, which is taken from Grocott's paper (8).

Most other impurities, such as calcium and titanium, are quantitatively removed from the liquor in Precipitation. Therefore organic effects in Precipitation have no influence on the amount of impurities that are incorporated in the product. Complexation of calcium and titanium can, however, increase the solubilities of these metals in the liquor, and in this way organics can increase the amounts in the product.

Effects of sodium oxalate

Sodium oxalate occupies a special place in Bayer liquor chemistry. Oxalate is generally present in bauxite, but most of the oxalate that is found in the Process is produced by degradation of more complex organics during the Digestion step (9). Sodium oxalate dissolved in the liquor has no significant effect on any aspect of the Process, but the limited solubility of oxalate in caustic soda solution leads to the crystallisation of sodium oxalate in the cooler parts of the circuit. Unless specific steps are taken to prevent it, this means that sodium oxalate will co-precipitate with hydrate in Precipitation. In fact, this is done deliberately in many refineries as the first step in the oxalate removal process (2,10).
The increased fines generation is as a result of both a reduction in the efficiency of the agglomeration of fine particles into larger aggregates, and the nucleation of hydrate single crystals on oxalate surfaces. This latter effect, which is illustrated in Figure 6, occurs only if the oxalate surface is contaminated by adsorption of other, high molecular weight, organic compounds (9).

An extension of this phenomenon leads to increased rates of formation of scales on the walls of vessels and pipes. Precipitated oxalate has a tendency to attach to metal surfaces, where it can then form nucleation sites for hydrate. Mature hydrate particles also have a tendency to attach to oxalate crystals. All of these attachments appear to be made via surface active organic contaminants which readily adsorb to the various available surfaces.

An example of oxalate-induced scale formation is shown in Figure 7. This sample was taken of scale in the early stages of formation in a laboratory simulation. The way in which hydrate particles have nucleated on the oxalate and are then meshed together is evident. Such composite scales are difficult to clean, because normal caustic cleaning solutions are too concentrated to dissolve the oxalate, whereas the hydrate is insoluble in water. A compromise of a weak caustic solution, if sufficiently hot, forms a solvent which will attack such scales.

The attachment of oxalate to hydrate also interferes with particle size classification by elutriation, an essential part of the preparation of seed hydrate for Precipitation. Elutriation depends upon segregation of particles by free settling according to Stokes’ Law. The presence of oxalate tends to prevent hydrate particles from behaving as individual entities, by physically attaching them together, as is illustrated in Figure 8.

SPECIATION OF ORGANICS IN BAYER LIQUORS

The complexity of the organic matter in bauxite, which consists of humate and fulvate, lignin, cellulose and protein material, means that there is an enormous range and diversity of organic compounds in Bayer liquor. Since the pioneering work of Lever (11), use has been made of a variety of chromatographic techniques for the separation and identification of these species. Guthrie et al employed gas chromatography / mass spectrometry to separate and identify the low and medium molecular weight fractions (up to 90, and 90 to 300 MW), and gel permutation chromatography for the higher molecular weights (above 300 MW). This enabled them to identify 35 compounds in the low to medium molecular weight ranges, mainly aliphatic and aromatic acid anions and some amines. Approximate proportions of the compounds within ranges of molecular weights were obtained for the higher molecular weight compounds (12).

The compounds in the liquor are produced from the soil components by a variety of oxidative and non-oxidative mechanisms, mostly in Digestion. Most of the carbonate and oxalate in liquor are the result of oxidative degradation of more complex molecules. It has been shown, however, that oxalate is also produced non-oxidatively (9). The vent gases from Digestion contain ammonia and amines, as well as hydrogen and methane. The latter suggest decarboxylation reactions of the type shown in Figure 9.

The exact composition of a Bayer liquor is a function of the bauxite source, the digestion temperature, and other factors, so each individual Plant liquor is different. Because of this, and the challenging analytical problems, unravelling the details of the organic components of Bayer liquor is an active area of research.

REMOVAL AND CONTROL OF ORGANICS

A great variety of methods has been proposed for the removal of organics from Bayer liquors. Only those which are in use or have been shown to be technically feasible will be considered here.
Causticisation

All alumina plants have a need to remove carbonate from the liquor. This is done in the "causticisation" process, in which calcium carbonate is precipitated, returning caustic (hydroxide) to the liquor, thus indirectly removing organics which have been degraded to carbonate in Digestion. Causticisation is best carried out in a dilute liquor stream at close to 100°C, to minimise the extent of the competing reaction, the formation of tricalcium aluminate (13).

Oxalate removal

Most Bayer plants practice the selective removal of sodium oxalate. There are a number of different processes in use for this. The method patented by Sumitomo (14), and practiced by Alcoa and others, consists of cooling Spent Liquor after the hydrate precipitation step, and crystallising the oxalate from solution by addition of sodium oxalate seed. This has the advantage of avoiding oxalate co-precipitation with hydrate, but is of low efficiency and requires large equipment. A possible improvement to the method involves changing the morphology of the precipitated oxalate from individual needles to spherical agglomerates, minimising the filtration equipment required. The morphology change is achieved by choosing the correct liquor and process parameters, employing a "pipeline nucleator", or using chemical additives to promote nucleation and to reduce the stabilising effects of the humate compounds in the Bayer liquor (15).

The Kaiser seed wash method (16) is more efficient and less capital intensive, but suffers the disadvantages of oxalate co-precipitation. These disadvantages can be reduced by the application of chemical additives, in particular surfactants to reduce the degree of interaction of oxalate with hydrate and to increase the tendency of the oxalate to agglomerate. Humate removal agents such as poly dialyl dimethyl ammonium chloride (17) or magnesium salts (18) can also be of assistance by reducing the oxalate stability of the liquor, so increasing oxalate precipitation rates. This strategy must be approached with caution, however, as increased oxalate precipitation can have a very negative impact on the precipitation process (9).

Liquor burning

The most effective method for the removal of the full spectrum of organics is the Liquor Burning Process of Showa Denko (19,20,21), which is currently also being practiced by Alcoa at Kwinana (22). In this method, a side stream of Spent Liquor is treated. First, the liquor is evaporated to about twice the initial concentration. A source of alumina, which may be either calcined alumina or hydrate, is added, to adjust the alumina to soda molar ratio to unity. The slurry is dried and pelleted, and then calcined to sodium aluminate in a rotary kiln operating at around 1000°C. This quantitatively removes all of the organic material as CO_{2}. The sodium aluminate is then dissolved in Spent Liquor to recover the soda and alumina values, and to produce a pregnant liquor suitable for sending to Precipitation. Treatment of a one per cent sidestream in this way can be expected to reduce the organics load in the liquor circuit to about one third of its initial value in three years.

The Liquor Burning Process as described here is a variant of the Sinter Kiln Process previously used by both Reynolds Metals and Alcan (23), in which liquor is calcined with bauxite as the source of the alumina required to satisfy the stoichiometry.
Rising energy costs in the 1960s meant that these processes were no longer economically viable. In common with the Sinter Kiln method, the Showa Liquor Burning Process is also energy intensive, and suffers from the disadvantages of high capital investment and maintenance requirements, and materials handling difficulties.

Solution oxidation methods

A variety of schemes have been proposed for the removal of organics from Bayer liquors by oxidation. Methods such as electrolysis (24), and the use of oxidants such as peroxyde (23) and manganese dioxide (25) have been investigated but not applied in industrial practice. All solution oxidation suffer from the disadvantage that the oxidation is not quantitative, so that the most readily oxidisable compounds are broken down into a variety of more stable compounds. Under vigorous oxidising conditions, the main product is sodium carbonate, which then has to be removed from the solution by causticising with lime. The other main product is sodium oxalate, which also has to be removed separately.

The method of high temperature oxidation with molecular oxygen has been developed in Germany (26), and is in operation at the YAW Alumina Plant. In this method, a temperature of 700°C is required, with the addition of a copper catalyst to maximise the breakdown to carbonate (27). Even so, significant quantities of oxalate and other of the more electrochemically stable organics are formed. The process is relatively hazardous, as there is the possibility of the formation of explosive gas mixtures (28).

The Dawsonite process

Carbonation of a liquor sidestream to form sodium dawsonite, NaAl(OH)$_3$CO$_3$, has been employed as a means of purging impurities from Bayer Liquor (29). The Dawsonite is precipitated, filtered, and then redissolved into the liquor circuit. The filtrate, which contains all of the soluble impurities, including the organics, is discarded. This process has the advantage of offering a means of purging all impurities, organic and inorganic, from the liquor. It is, however, expensive to run, requiring the injection of CO$_2$ which is subsequently removed from the liquor by causticising with lime. The purging of the waste stream also presents difficulties, as this has to be done in an environmentally acceptable manner.

Chemical additives

Magnesium Oxide has been used as an additive to Bayer liquor to remove the higher molecular weight compounds (18). This has been claimed to improve precipitation rates, liquor physical properties, and mud handling. It certainly reduces the amount of highly coloured materials in the liquor, which improves the whiteness of the precipitated hydrate, and important parameter in hydrate prepared for sale as such.

Poly diethyl dimethyl ammonium chloride has been used as a more economical method of achieving a similar result (17), although it does not appear to remove as broad a spectrum of organics as MgO. Some Plants have claimed success in the application of this, particularly where the main aim is to control hydrate whiteness. Attempts to employ it for more general process improvements have not been uniformly successful, however, due either to the destabilising effect on oxalate (9), or the formation of tar which precipitates which interfere with filtration (28).

Barium-salt can be used to remove a broad range of impurities from liquor, including carbonate and organics (30). The barium is recycled by calcining to barium aluminate which is redissolved into the liquor stream. The process is cumbersome and expensive, however, and with the added disadvantage of the hazardous nature of barium, it is not generally practiced.

Bauxite roasting

Low temperature calcination, or roasting, of the bauxite feed has been tested as a means of removing the organic carbon input to the Bayer Plant (31). For gibbsite bauxites, the main danger of this is the partial dehydration of the soluble gibbsite to the less soluble boehmite phase, or total dehydration to highly insoluble alumina, such as corundum. By careful control of the temperature, residence time, and ambient humidity, however, it is possible to dehydrate the gibbsite quantitatively to chi alumina, a soluble form (32). This offers total organics removal, as well as other advantages such as reduction in the water introduced to the Bayer circuit, and the conversion of goethite to haematite. The goethite to haematite conversion both releases alumina in Digestion and produces a mud with much superior settling properties. Despite these advantages, the process is not generally used, because of its high capital cost and energy intensiveness.

REFERENCES

1. 1991. The Western Australian Economy, Department of State Development, Western Australia, March.


