Organic compounds in the processing of lateritic bauxites to alumina Part 2: Effects of organics in the Bayer process

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A B S T R A C T
This review is the second of a series examining the history and current state of knowledge of the science related to organic compounds in the Bayer process for the extraction of alumina from lateritic bauxites. The series of reviews provides a compilation of the information available from the public literature, and critical analysis of the research that has been carried out in this area in the past 50 years. It points the way to future opportunities for research to assist in mitigating the high costs that organics impose on the industry globally ($500 Mpa in Australia alone). Part 2 provides unique insights into the effects on the Bayer process of organic compounds in the liquor.

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1. Introduction

It was noted in Part 1 of this review series that organic matter contained in bauxite is the main source of the organic compounds in Bayer process liquors which cost the Australian alumina industry alone in excess of $500 m (US$520 m) per year (Power and Loh, 2010). This estimate is consistent with figures provided by Teas and Kotte (1980) for a range of other bauxites. It was further noted that:

• Organic compounds build up in the recirculating process liquor to concentrations determined by a complex interaction of inputs, outputs and reactions;
• The presence of organic compounds leads to increased raw materials usages, reduced production efficiency and lower product quality;
• Mitigation of the effects of organic compounds requires the installation of additional processing equipment which increases capital and operating costs; and
• Volatile organic compounds emitted from digestion and other parts of the refinery process may raise environmental and health concerns.

It is the purpose of Part 2 of the review series to provide a systematic compilation of the current state of knowledge and research into the effects that organic compounds have on the Bayer refinery process. Part 2 examines the effects that organics have on the physical and chemical nature of the liquor, specific effects on the productivity of the liquor through adsorption to the surfaces of precipitation seed and the formation of complexes with the aluminate ion, effects on the purity, particle size distribution and other physical properties of the product alumina, scale formation on the surfaces of vessels and pipes, and the production of volatile gases including hydrogen.

2. Liquor properties

2.1. Solution composition and nomenclature

The first step of the Bayer process is the digestion of aluminium hydroxide minerals by reaction with caustic soda. Digestion of aluminium tri-hydroxide (gibbsite) for example, consumes hydroxide as follows:

\[
\text{Al(OH)}_3 + \text{OH}^- \rightarrow [\text{Al(OH)}_4^-]^{-}
\]  

This causes a reduction in the “free caustic” (OH⁻) concentration in the liquor by binding one OH⁻ ion (“bound caustic”) for each Al unit dissolved. Bound caustic is released later in the process, when this equation is reversed to recover pure Al(OH)₃ in the precipitation stage of the Bayer process circuit. The sum of the free caustic and bound caustic is used by Bayer process operators as a measure of the overall causticity of the solution, and is given the title “total caustic” with the symbol “TC”, or simply “C” (shaded box, Fig. 1). The convention within the industry is to express TC in units of its sodium carbonate equivalent (rather than moles), hence:

\[
\text{TC} = [\text{OH}^-] + [\text{Al(OH)}_4^-], \text{expressed as equivalent g/L Na}_2\text{CO}_3
\]  

The chemistry of the formation of organic compounds in Bayer process digestion due to the degradation of complex organic materials in
Fig. 1. Schematic representation of distribution of species in a Bayer process liquor, and summary of nomenclature (adapted from Smith (2011)). Note: TS, TA, TC and TOS are expressed as equivalent g/L Na₂CO₃.

The only sodium ions that are useful to the Bayer process are those associated with hydroxide and aluminate anions, i.e. the “caustic” or TC portion highlighted in Fig. 1. The remainder which is “tied up with” (i.e. provides charge balance for) carbonate, organic acid anions and inorganic anions, provides no value and is a technical and economic burden on the liquor.

2.2. Physical properties

Knowledge of the physical properties of the liquor is essential for the chemical engineering design and operation of hydrometallurgical operations such as Bayer process refineries. For example, values of liquor density and viscosity are fundamental to the design of the vessels and pipes, agitators, pumping systems, and solid/liquid separation systems including settlers, filters, cyclones and centrifuges that are used in refineries. The boiling point elevation and specific heat of the liquor are important to the design and ongoing efficient operation of heating and cooling systems required for digestion, flashing and evaporation, all of which are essential unit processes in Bayer process refineries (Dewey, 1981).

In general, the parameters which have been found to have the most influence on the physical properties of Bayer liquors are the total soda (TS) and alumina contents, with TS having the dominant impact. Teas and Kotte (1980) estimated that 10 g L⁻¹ of any impurity increases the liquor density by approximately 1%, but noted that this does depend to some extent on the nature of the impurity. Nicolas (1986) concluded that knowledge of the ionic strength of plant liquors was sufficient to enable prediction of the main effects of impurities on the properties of the liquor. He proposed that the contribution of organic compounds to the ionic strength may be calculated using a “carbon number”, n, which is defined as the mean number of carbon atoms in the mixture of organic anions per sodium ion required for charge balance in the solution. The ionic strength associated with the organics can then be calculated using the following equation (note that there is a typographical error in the original paper which is corrected here):

\[ I = 0.5 \times m \times \left\{ \frac{1}{n} + \left( \frac{N}{n} \right)^2 \right\} \]  

(4)

Where:

- \( I \) ionic strength of solution
- \( m \)  molality of carbon in solution
- \( n \) average number of carbon atoms per sodium ion (“carbon number”)
- \( N \) average number of carbon atoms per organic anion

This is consistent with Dewey’s (1981) finding that the boiling point rise of Bayer process solutions could be accurately estimated from knowledge of the ionic strength of the solution. He also found that this enabled the heat of vaporisation of Bayer liquors to be calculated by rigorous thermodynamic relations with the aid of an equation of state for water or the steam tables. Some uncertainty was assigned to the effect of the organic compounds present, not in relation to the assumption that it was the ionic strength that was important, but in relation to how to estimate their contribution to the ionic strength. The
difficulty lay in determining the number of acid groups per mole of carbon with the techniques for chemical analysis available at the time; this is a straightforward matter with the analytical techniques now available (Power et al., 2011b). It is interesting to note that Dewey found a significant difference between liquors from plants operating high temperature (>200 °C) and low temperature (143 °C) digestion. The low temperature liquor was found to be much less oxidised (i.e. fewer acid groups) than the high temperature liquor, which meant that a given level of organics in the high temperature liquor had a greater effect on boiling point rise than the same level of organics in the low temperature liquor (Dewey, 1981).

Nicolas (1986) proposed the following empirical correlation (in which concentrations are expressed in g L⁻¹, and D and D₀ are the solution densities, respectively with and without impurities, in g cm⁻³) for the effect of organic compounds on liquor density:

\[
D = D₀ + 10^{-3} \times \left( \left[ Na₂CO₃ \right] + \left[ NaCl \right] + \left[ Na₂SO₄ \right] + 0.7 \times \left[ TOC \right] \right)
\]  (5)

This equation implies that the contribution of organics can be also reduced to a parameter related to ionic strength for the purpose of calculating their contribution to liquor density. The equation is also consistent with the earlier observations of Teas and Kotte (1980).

Königsberger et al. have recently published a series of papers reporting the development of a thermodynamic model for calculating the effects of impurities on liquor properties (Königsberger et al., 2005a, 2005b, 2005c, 2006). The model is based on Pitzer equations (Pitzer, 1991), and at the time of writing included ten components (water plus sodium hydroxide, aluminate, carbonate, sulphate, chloride, fluoride, oxalate, formate and acetate). The ultimate aim of this work is to provide a thermodynamically consistent means for calculating a wide range of solution properties, including heat capacities, enthalpies, entropies, densities, water activities, activity coefficients, vapour pressures and boiling point elevations, as well as solubilities of various compounds of interest, over the wide ranges of temperature and concentration of interest (Königsberger, 2008).

The authors have concluded that water activity is the key quantity governing the thermodynamic behaviour of concentrated process solutions (Königsberger et al., 2009). Consistent with the conclusions of Nicolas (1986), the overall effect of the presence of organic compounds is therefore qualitatively similar to that of other (inorganic) anions in relation to their effect on the physicochemical properties of the liquor. In order to calculate the effects quantitatively, measurements are required to establish the necessary coefficients for each component and property of interest over a range of conditions, and at elevated temperatures in particular. Some work has been done along these lines. For example, the apparent molar volumes and heat capacities of three dicarboxylates, oxalate, malonate and succinate, have been studied at 25 °C in dilute solutions and extrapolated to high ionic strengths (Tromans et al., 2005). These compounds are important components in Bayer liquors which, according to the authors, can be used as model impurities for estimating the overall effects of organic compounds on the properties of the liquor. This suggests that Nicolas’ approach of defining a “carbon number” for individual liquors may, in combination with modern methods of chemical analysis, be worth revisiting as a way of simplifying the estimation of the effect of organics on the physical properties of Bayer process liquors.

3. TOC concentration

The steady-state concentrations of organic compounds in Bayer liquor are the result of a dynamic balance of inputs and outputs, which are complex, notoriously difficult to model in detail, and only scantily reported in the literature (Power and Loh, 2010). Nevertheless, considerable understanding can be gained by making a few simplifying assumptions and applying basic chemical kinetics principles, as follows.

The input of organic compounds to Bayer liquor in modern refineries is almost entirely from the bauxite, but process additives, in particular starch, can also be a significant input if it is used as a flocculent (Solyomár et al., 1996). Organic compounds may exit the refinery liquor by a number of mechanisms, which may be divided into those which are an inevitable consequence of the basic refinery process, and those which are deliberate sub-processes for removal of organics. The main processes in the former category are direct loss of liquor with the bauxite residue or other leakage mechanisms, and conversion to carbonate by oxidation, which occurs mainly in the digestion stage of the process. Deliberate removal strategies include crystallisation and removal of oxalate (by any of a variety of methods), direct pyrolysis (“liquor burning”), and reaction with air or oxygen in a wet oxidiser. These and other methods will be examined in detail in Part 3 of this review series.

The time dependence of the concentration of organic compounds in liquor may be modelled to a first approximation by assuming that the input from bauxite is in direct proportion to the rate of alumina production, and that the volumetric rate of liquor loss is constant. These assumptions lead to the following equation for the rate of change of concentration with time:

\[
di[TOC]/dt = I - L \cdot [TOC]
\]  (6)

In this equation,
- [TOC]: concentration of total organic carbon in liquor (g/L)
- I: rate of input of TOC (g/s)
- L: volumetric rate of loss of liquor (L/s)

If I and L are both constant, the steady-state TOC concentration is simply given by:

\[
[TOC] = I/L
\]  (7)

Fluctuations in [TOC] can therefore be understood in terms of changes in I, L or both. On the other hand, if the TOC concentration is not at steady-state and I and L can be considered as constants, then the rate of change of [TOC] should follow a first-order law. This would be the case, for example, for the build-up of TOC in the liquor of a new refinery, or for the reduction in liquor TOC in a refinery which adds an organic removal process (such as liquor burning).

The former effect is well illustrated by the build-up of TOC in liquor at the Worsley refinery from its start-up in 1984 to a reasonably stable steady-state in 1990–91 (Power, 1991). Over this period, the TOC build-up appears to occur in two distinct stages, as shown in Fig. 2. The TOC concentration follows an initial first-order curve quite closely from start-up until mid-1986 (Stage 1), after which the data suggests that the input of organic compounds increased by about 14% while the output rose by 208%, resulting in a second first-order curve from mid-1986 to 1991 (Stage 2). The increased input in Stage 2 may for example be related to a change in bauxite quality and/or to an increase in plant yield resulting in greater bauxite input and consequent residue volume per volume of liquor, and/or an increase in the amount of starch used per volume of liquor (starch was used as a flocculent until 1993 (Kahane and McRae, 1996)).

The increased output in Stage 2 indicates that the volumetric rate of liquor loss doubled in 1986 and then remained constant at that the new level for the remainder of the period.

4. Liquor productivity

The economics of the Bayer process is strongly influenced by the liquor productivity, which is the degree to which alumina can be brought into solution in digestion according to Eq. (1) and subsequently be removed from the solution by precipitation in the presence of gibbsite seed (Eq. (8)) before it is returned to digestion to again extract alumina.
from fresh bauxite. Typically only about half of the alumina contained in the green (pregnant) liquor is recovered in the precipitation step, the balance remaining to circulate unproductively with the liquor. Hence the precipitation yield, which is the amount of alumina precipitated (as gibbsite) per volume of liquor (at a specified sodium concentration) (Pearson, 1955), is a key factor in the production costs of a refinery (AMIRA, 2001; Teas and Kotte, 1980).

\[
[Al(OH)_4]^− \xrightarrow{\text{SEED}} Al(OH)_3 + OH^−
\]

It has been known since at least the 1930s that organic compounds have a negative influence on Bayer liquor productivity (Volf and Pudovkinoj, 1935; Yamada et al., 1973). There are three main ways in which this may occur. Firstly, the presence of organic acid anions (and the carbonate ions that are present as a result of the oxidative degradation of organic anions) requires an equivalent amount of cations, in particular sodium ions, to maintain charge balance, which reduces the number of sodium ions available to balance hydroxide and aluminate ions. Secondly, organic compounds may adsorb to seed surfaces and affect the kinetics of gibbsite precipitation, which reduces the precipitation yield (see below). Finally, adsorption effects and the influence of crystallisation of solid sodium oxalate can have a major effect on the size distribution of the precipitated gibbsite. This has an indirect effect on precipitation yield because of the measures required to maintain an acceptable particle size distribution.

4.1. Total soda—thermodynamic effect

In order to understand this effect it is necessary to examine the effect of the total caustic concentration, TC, on yield. The digestion stages in alumina refineries are generally designed to extract the soluble alumina phases from bauxite to the point that the liquor is almost saturated in aluminate at the digestion temperature. The goal of the precipitation stage is then to recover as much as possible of that alumina in the form of solid gibbsite by cooling and diluting the liquor, and seeding it with crystalline gibbsite. The maximum possible yield in such a process corresponds to the aluminate concentration being in equilibrium with the solids at the new temperature. This concept is illustrated for a gibbsitic bauxite in Fig. 3, which is adapted from the data of Kotte (1981). The theoretical maximum yield, \(Y_T\), is then the product of the change in ratio, \(\Delta A/TC\), and TC:

\[
Y_T = (\Delta A/TC) \times TC \text{ g/L}
\]

The available \(\Delta A/TC\) decreases slightly as TC rises, however this effect is small in relation to the multiplicative effect (Eq. (9)), so that the theoretical yield is almost exactly proportional to TC, as shown in Fig. 4. For this reason, refineries operate at the maximum possible TC, which is determined by the maximum total soda concentration, TS. The TS includes the soda associated with inorganic and organic impurities as well as hydroxide, so any increase in the concentration of impurities correspondingly reduces the operating TC, which directly reduces the available yield. Because the influence of TC is related to equilibria, this is essentially a thermodynamic effect. The presence of TOC can be thought of as decreasing the carrying capacity of the liquor for aluminate ions.

As an order of magnitude example, the theoretical effect of 20 g/L TOC in liquor is shown in Fig. 4. (20 g/L was chosen as typical of Bayer liquors derived from Australian and Caribbean bauxites, which vary in the range of 10 to 40 g/L (Arnswald et al., 1991; Lever, 1978; Power, 1991; Rosenberg and Healy, 1996; Solymár et al., 1996)). Assuming that 1 g/L TOC is equivalent to 2 g/L sodium carbonate (i.e. a TOS/TOC ratio of 2 (Rosenberg and Healy, 1996)) the loss of theoretical yield caused by 20 g/L TOC is about 9 g/L Al2O3, or 7%.

4.2. Seed poisoning—kinetic effects

4.2.1. Background: general effects of organic compounds

It has been noted that about 90 million tonnes of aluminium hydroxide is produced by precipitation from Bayer process liquors annually (Li et al., 2003), which is probably the greatest rate of production of all precipitates in hydrometallurgy. It is a slow chemical reaction, requiring high seed densities (250 to 1000 g/L), long holding times (24 to 36 h) and low temperatures (the liquor is cooled from about 80 °C to about 60 °C during precipitation) to maximise the yield of product (Newchurch and Moretto, 1990; Pearson, 1955). As such, precipitation is the “rate limiting” stage in the Bayer process, and requires significant investment in tanks, heat exchangers and associated equipment to provide the holding times and temperature profiles necessary to achieve acceptable yields. The
precipitation reaction is therefore of considerable commercial importance, and so has been the subject of extensive research in the past several decades (e.g. see Vernon et al. (2002)).

Lowering the temperature decreases the equilibrium solubility of gibbsite, and so increases the yield provided the residence time is sufficient to overcome the competing effect of a slower reaction rate (Chaubal, 1990). Achieving the best yield outcome requires careful optimisation of conditions, in particular the temperature profile in precipitation.

It has been known since at least the 1950s that impurities in the liquor, both inorganic and organic, can affect precipitation yield considerably (Hudson, 1987). Pearson (1955) reported reductions in precipitation rates in the presence of organic compounds, which he attributed to poisoning of the seed surface. He listed "saponin, gum Arabic, cane sugar and numerous other organic substances containing hydroxyl groups" as effective poisons, but noted that oxalate (which has no hydroxyl groups) is not. Pearson made a number of other insightful observations that have largely stood the test of time. He described the possible modes of action of poisons as broadly falling into three types: (a) general overall slowing of precipitation rate; (b) temporary inhibition, which has since become related to an "induction period"; and (c) permanent inhibition. He observed that type (a) generally appeared to be caused by an elevation of the equilibrium aluminate concentration, i.e. an increase in gibbsite solubility. To quantify the effect he defined a "poisoning factor", which was found to decrease with temperature. This was interpreted as evidence that the poisoning was related to adsorption of impurities on the gibbsite surface. It has been suggested that poisons enter the liquor on contact with bauxite during digestion, but do not generally build up in the liquor to observable concentrations because of a combination of removal processes, in particular continuous degradation to simpler compounds and adsorption to gibbsite (Anderson et al., 2001).

The (1980) reported the identification of numerous organic compounds that were associated (apparently by adsorption) with the fine gibbsite seed at a particular refinery. Of these, glucoisosaccharinate was
singed out for special study. It was found that glucoisosaccharinate, a degradation product of sugars that may be present as a result of the degredation of bauxite organics and/or starch added as a flocculent, had a significant inhibitory effect on precipitation. The (The, 1980) postulated that glucoisosaccharinate was present in trace amounts in the Bayer process liquor and was concentrated at the gibbsite surface by adsorption, where it interfered with precipitation by interacting with aluminate in such a way as to increase the solubility of aluminate at the liquid/solid interface. These and other related results (Solyomár et al., 1996) undoubtedly accelerated the change from starch to synthetic flocculants as the principal settling and fining agents in Bayer process practice (Ryles and Avotins, 1996).

4.2.2. Precipitation mechanisms

A deeper understanding of the role of organic compounds in precipitation requires knowledge of the mechanism(s) of the crystallization of gibbsite. Indeed, the effects of organic compounds can be used as a probe to investigate precipitation, as has been demonstrated the work by Rossiter et al. (1999, 1996) and Watling et al. (2000) on the effects of gluconate in solution during crystallization, and by Beckham et al. (2005) and Loh et al. (2010a) who used measurements of precipitation yield inhibition to estimate the active surface areas of gibbsite seed.

These observations on the actions of poisons highlight the importance of surface chemical reactions in the crystallization of gibbsite. This is consistent with the observed kinetics of precipitation, which shows that it is not a simple first order process, but instead the rate generally depends on the square of the aluminate supersaturation. The first reports of the square law appear to be the equation given by Pearson (1955). A slightly different equation was presented by King (1973), and other variants have subsequently been developed to improve the prediction of reaction rates over wider ranges of solution concentrations, temperatures and seed additions (Cornell et al., 1999; Veesler and Boistelle, 1994; Vernon et al., 1999).

King (1973) interpreted the square law in terms of a proposed pre-equilibrium between the predominant [Al(OH)₄]⁻ species and a dimeric species at the gibbsite surface; using a linear growth model, the slowness of the reaction was interpreted as due to a very low equilibrium concentration of the dimer at the growing solid surface. This appears to be consistent with the hypothesis of a dimeric “growth unit” which has been proposed (Paulaime et al., 2003; Sessieq et al., 1999) based on molecular modelling and crystallographic considerations (the “growth unit” concept in crystallization hypothesises the formation in solution of a fundamental building block of the crystal which can readily be incorporated into the crystal surface (Li et al., 1999; Zhong et al., 1994)). However other authors have proposed different growth units for gibbsite. In particular, Wu et al. (2005) cite the existence of a growth unit of one aluminate ion with two waters attached, and another (energetically preferred) unit with six aluminium ions, based on thermodynamic calculations and in situ Raman measurements. A number of these possibilities, in particular the six aluminium ion growth unit, had been previously suggested by Zambo (1986) based on theoretical analysis of the bulk properties of the solutions.

However, it has also been shown that quadratic dependences of the rate on supersaturation can result from other growth models. At low supersaturation, a quadratic dependence is expected as a result of a spiral growth mechanism dominating the crystallisation rate (Vernon et al., 2002), according to the classical Burton–Carrera–Frank (BCF) model (Burton et al., 1951; Kumar, 2009). In this model, growth occurs at discontinuities (steps) on the crystal surface, and the rate of growth depends on the concentration of such active sites. A consequence of this is that the growth rate is sensitive to any blocking of active sites, for example by adsorption of organic impurities. Because of this, controlled introduction of impurities can be used as a probe to investigate crystal growth, a method which has been used to good effect in studying the crystallisation of aluminium hydroxide (as gibbsite) from alkaline solutions.

At higher supersaturation levels, precipitation by a birth-and-spread mechanism becomes dominant (Brown, 1972a, 1972b; Lee and Parkinson, 1999; Li et al., 2003). This process accelerates the rate of crystallization by secondary nucleation at the gibbsite surface and the consequent production of new growth sites. At still higher supersaturation, macroscopic seed particles may also grow by agglomeration (Iliyevski and White, 1995; Stephenson and Kapraun, 1997). All of these processes are present in modern Bayer precipitation circuits (Tschamper, 1987). The precipitation rate varies as the square of the aluminate concentration irrespective of whether the macroscopic regime is nucleation, agglomeration or growth (albeit with widely differing rate constants), which implies the existence of a common rate determining step at the molecular level.

A number of different models have been suggested to explain the kinetics and mechanism of crystallization of gibbsite. There seems to be a general agreement that growth occurs primarily at kink sites on the surface, but there is less unanimity in relation to the chemical processes which occur there. In particular, consensus has not been reached on the mechanism of the transition from tetrahedrally-coordinated aluminium in the aluminate ions in solution to octahedrally-coordinated aluminium in the solid gibbsite. The simplest model which seems to be consistent with the data available to date is the electrostatic model of Vernon et al. (2002), in which it is proposed that the gibbsite/solution interface behaves as a pair of electrical double-layers (Bard and Faulkner, 1980) in which the negatively-charged gibbsite surface is connected to the (negative) aluminate anions by a layer of (positive) sodium ions, as shown schematically in Fig. 5. In this model, growth may take place at surface discontinuities such as kink sites, by the formation of a new bond between a surface O atom and the Al atom of an aluminate ion in solution, with the simultaneous exit of a sodium ion from the electrical double layer into the solution; there is no requirement for the existence of a hypothetical “growth unit” at trace concentrations, the reaction being between the dominant aluminate ion in solution and the gibbsite surface. While this model may not fully describe all the actual and possible processes at the interface, it nevertheless provides a useful rationalisation of many of the phenomena that have been observed.

Gibbsite grown from sodium hydroxide solutions may display a variety of shapes and sizes. The resultant shape and size distributions are relatively insensitive to crystallization conditions and to traces of inorganic impurities, and are therefore a result of properties inherent in the crystallization process itself. It has been shown that the effects which dominate in the production of this diversity include crystal twinning at the nucleation stage, and accumulation of surface defects and the continuous formation of nuclei during growth (Sweegers et al., 2001). This results in crystals which evolve from thin, rounded hexagons and faceted lozenges into faceted plates and blocks with well-formed basal, prismatic and chamfered faces. Individual crystals are most commonly in the form of hexagonal prisms, which are generally clustered together by either twinning and intergrowth, or agglomeration. The result is illustrated in Fig. 6, which shows a particle of gibbsite product from an alumina refinery. These results are consistent with the theoretical model developed by Fleming et al. (2000), who showed that the dominance of the basal (001) plane may be explained by the lower surface energy afforded by its 6-fold coordination of Al in comparison to 5-fold coordination in the other faces. The growth rate dispersion between crystal facets is a key determining factor in the final shape of each crystal, but for gibbsite precipitation the very mechanism of crystallisation may also be different for different facets: Lee and Parkinson (1999) showed that, with supersaturation above 0.81, birth and spread becomes the dominant mechanism on the basal face whereas spiral growth remains dominant on the prismatic faces.

Also of importance in the understanding of the modes of action of organic impurities is the existence of an induction period in the crystallization of gibbsite. This is observable in batch precipitation tests as an initial period after the addition of seed to a supersaturated liquor, during which the precipitation rate, as observed by the rate of change of aluminate
concentration in the solution, is very low but nevertheless finite (Smith and Woods, 1993). The end of the induction period is marked by a sudden change in the precipitation rate which subsequently follows the expected quadratic law (Vernon et al., 2002). The induction period is characterised by Brown (1972b) as follows: “the (001) seed crystal faces erupt into a sea of potential secondary nuclei simultaneously with the formation of kink sites which can initiate spiral growth which eventually (i.e. at the end of the induction period) becomes the dominant crystallization mechanism. Induction periods are strongly influenced by the presence of calcium ions (Brown, 1988; Gnyra and Brown, 1975; Raty et al., 2004), which are in turn influenced by the organics in solution (see Section 6 below).

The effects that organic anions have on precipitation depend on their chemical structures and on the conditions of precipitation. For example, compounds with two or more adjacent hydroxyl groups tend to inhibit precipitation by surface adsorption, whereas mono-hydroxy compounds tend to adsorb without affecting the precipitation rate. Some compounds affect both precipitation rates and product morphology, while others have little or no effect on either. Various compounds and compound types are discussed in the following sections, starting with gluconate, the best known and most studied of precipitation inhibitors. The majority of the compounds considered are not in fact found in detectable quantities in Bayer process liquors, even though many are expected to be formed during bauxite digestion. This is at least in part because of the very properties that are of interest, e.g. chemical reactivity, formation of complexes with aluminate ions, and adsorption to gibbsite surfaces.

4.3. Effects of specific types of organic compounds

The effects that organic anions have on precipitation depend on their chemical structures and on the conditions of precipitation. For example, compounds with two or more adjacent hydroxyl groups tend to inhibit precipitation by surface adsorption, whereas mono-hydroxy compounds tend to adsorb without affecting the precipitation rate. Some compounds affect both precipitation rates and product morphology, while others have little or no effect on either. Various compounds and compound types are discussed in the following sections, starting with gluconate, the best known and most studied of precipitation inhibitors. The majority of the compounds considered are not in fact found in detectable quantities in Bayer process liquors, even though many are expected to be formed during bauxite digestion. This is at least in part because of the very properties that are of interest, e.g. chemical reactivity, formation of complexes with aluminate ions, and adsorption to gibbsite surfaces.

4.3.1. Gluconate

Certain organic acid anions are known to be capable of stabilising aluminate solutions to the extent of preventing precipitation of gibbsite, even when the solution is neutralised to pH 7. Tartrate and gluconate are particularly effective in this respect, and so formed the basis of the original methods for determining the alumina contents of Bayer process liquors (Watts and Utley, 1953, 1956). In these methods, the organic compound was added in large excess (> 10× on a molar basis, corresponding to 40 g/L in the case of sodium gluconate). The stabilising effect was attributed to the formation of complex ions in which the organic anion replaces one of the hydroxyl groups in the aluminate ion. At lower concentrations, gluconate has been shown to have an effect on precipitation which is much greater than can be explained by
complexation of the aluminite in solution. Rossiter et al. (1996) demonstrated that the presence of 1 g/L sodium gluconate in a sodium aluminite solution containing 110 g/kg Al2O3 resulted in a 50-fold increase in the induction period and an 85% drop in the crystallization growth rate, compared with an expected 0.6% drop in growth rate if the effect were due solely to complexation of the aluminate ion in solution. Electron microscopy of the crystals showed that significant surface roughening occurred during the induction period, corresponding to the formation of new growth sites by secondary nucleation. It was shown that the rate of surface roughening was much less in the presence of gluconate, consistent with the observation of an extended induction period and a lower surface roughening was much less in the presence of gluconate, consistent with the observation of an extended induction period and a lower growth rate. It was concluded that the low growth rate in the presence of gluconate was due to a reduction in the surface area available for crystal nucleation, surface density, and to show that it has strong selectivity for kinks created after the birth of growth sites. At shorter times however, the mechanism of inhibition was by simple blocking rather than a fundamental change in the chemistry of the gibbsite seed itself. Coyne et al. (1989, 1994) showed that a concentration of gluconate sufficient to cover only 3.5% of the total seed surface could be enough to reduce the crystallization rate to almost zero, indicating that gluconate adsorbs preferentially to active growth sites.

These conclusions were corroborated by Beckham et al. (2005), who demonstrated that gluconate interacts with the gibbsite surface by a physical adsorption mechanism that is accurately described by an adsorption isotherm, and that chemisorption is not involved. By inferring the adsorption isotherms from de-supersaturation curves, these authors were able to measure the degree of adsorption to active sites directly, and to show that it has strong selectivity for kinks created after the birth of growth sites. Using a modified Langmuir isotherm, they demonstrated that adsorbed gluconate effectively blocks about 50% more of the growth surface than it actually covers.

By studying gibbsite crystallization under different conditions of supersaturation and seed density, Watling et al. (2000) were able to separately observe the effects of gluconate under conditions that favoured each of the three macroscopically different regimes (nucleation, agglomeration and growth) in turn. The effects were found to be a function of not only crystallization conditions, but also of gluconate concentration in the range 1 to 6 mM (0.22 to 1.31 g/L sodium gluconate). They found that in all cases, the precipitation yield after an extended period (200 h) from the solutions containing gluconate was within 10% of the yield from a pure solution. This is consistent with the observations of Beckham et al. (2005) who interpreted it as evidence that the gluconate acts by a physical adsorption mechanism. At shorter times however, the effects on crystallization were found to be varied and significant. The effects of gluconate as a function of concentration for each aspect of crystallization are summarised in Table 1.

The promoting effect of gluconate on secondary nucleation at low concentrations may be due to partial blockage of growth sites reducing the adherence of nuclei to the surface such that nuclei can become detached, leaving the site available for the formation of new nuclei. At higher gluconate concentrations this effect is overshadowed by a more comprehensive blocking of growth sites.

The significance of even a very small amount of a precipitation inhibitor in the context of a Bayer plant liquor is demonstrated in Fig. 7. An addition of 0.07 g/L carbon (1 mM) in the form of gluconate to a synthetic Bayer liquor (initially containing no carbon) is similar to the effect of all the impurities in a Bayer plant liquor containing about 30 g/L carbon as well as carbonate and other inorganic impurities. This indicates that the majority of the carbon in the plant liquor is not associated with inhibitors (Coyne et al., 1994), a conclusion which has since been corroborated by detailed chemical analysis of Bayer plant liquors. This is to be expected, because the action of inhibitors generally requires that they be adsorbed to the precipitating gibbsite, which means that they are continuously removed and so do not accumulate in the solution. Consistent with this, gluconate has never been detected in Bayer plant liquor to our knowledge, and only minor amounts of a few other polyhydroxy compounds have been found in some liquors, even though they are almost certainly formed during bauxite digestion (Power et al., 2011a).

4.3.2. Aliphatic poly-hydroxy compounds—the aldolts

Aldolts are straight-chain hydroxy-alkanes with a single hydroxyl group on every carbon atom. They have the general formula:

\[ \text{CH}_2\text{OH} - [\text{C}^*\text{HOH}]_n - \text{CH}_2\text{OH} \]

In this formula \( C^* \) denotes a chiral centre, i.e. this carbon atom has two possible stereo-isomers. The first nine in the series of aldolts are

![Fig. 7. Desupersaturation curves for synthetic and plant Bayer liquor, showing the effects of 1 mM sodium gluconate (added at the end of the induction periods indicated by the dashed lines). Redrawn from Coyne et al. (1994).](image-url)
shown in Table 2, in which the chiral centres are highlighted as circles and the first two groups of stereo-isomers are bracketed.

The first mention of hydroxyl groups in relation to the inhibition of precipitation rate appears to have been by Pearson (1955), and The (1980) discovered that glucosaccharinate (which contains multiple hydroxyl groups) is a powerful crystallization inhibitor. Consideration of aluminium co-ordination chemistry led Grocott and Rosenberg (1988) to propose that organic compounds with adjacent hydroxyl groups should have a strong affinity with the gibbsite surface, and correctly predicted that this would increase the incorporation of sodium into the precipitate. Confirmation of the adsorption of such compounds onto gibbsite surfaces, and the effect this has on precipitation rates, was first made by Coyne (1989) and Coyne et al. (1989, 1994) who established equilibrium adsorption isotherms for a number of them. The only compounds that were found to exhibit significant adsorption were those with at least one pair of adjacent hydroxyl groups. Compounds which in addition have one or more carboxylic acid groups were found to adsorb more strongly than those without, and adsorption increased with the length of the carbon backbone. Hence, the order of adsorption strengths of the compounds studied is mannitol (6 carbons) > adonitol (5 carbons), and gluconate (6 carbons) > tartrate (4 carbons). For compounds with multiple hydroxyl groups but no carboxylic acid groups, no adsorption was detected for compounds with less than five carbon atoms.

The degree of yield inhibition was found to depend linearly on the degree of surface coverage irrespective of the identity of the adsorbent, as shown in Fig. 8. The results for mannitol correspond to solution concentrations of 0.1, 0.5, 1.0 and 2.0 mM, for which the surface coverage was confirmed to be a linear function of solution concentration. The solution concentration of the other three compounds was 1 mM. These results are consistent with a simple physical adsorption mechanism in which inhibition results from blockage of active growth sites, as discussed above for the case of gluconate and as indicated by the partial activation of gibbsite seed by treatment with boiling water (Zeng et al., 2007).

Detailed studies have been made of the effects of alditols on gibbsite crystallization, not because they are likely to be present in significant quantities in Bayer process liquors, but because they have proven useful in probing the mechanism of adsorption and hence of inhibition (Smith et al., 1996; Watling et al., 1996).

Smith et al. (1996) found that alditols generally inhibit gibbsite crystallization, and that the degree of inhibition generally increases with carbon chain length. Diols are generally less effective inhibitors, and it was found that compounds with three adjacent hydroxyl groups tended to be the strongest inhibitors. It was also found that stereoisomer ribitol (Table 2).

Degree of inhibition was found to correlate with the relative degree to which these compounds are able to form complexes with metal ions in aqueous solution, measured in calcium acetate buffer solution, as illustrated in Fig. 9 (Angyal et al., 1974). Using NMR and Raman spectroscopy, Smith et al. (1996) confirmed that complexes also exist between the alditols and aluminium in aqueous solution at pH 14. Furthermore, the degree of complexation was found to be qualitatively in the same order as previously reported for (acidic) acetate solutions for the limited number of compounds studied.

These results suggest that the mode of action of the alditols in inhibiting gibbsite crystallization may not be by poisoning of growth sites by direct adsorption of the organic compound, on the basis that the compounds that form stronger complexes would have the lower free concentration in solution, would therefore be expected to be less available for adsorption, and so would be the weaker inhibitors. As discussed above, the mode action cannot be to reduce (by complexation) the amount of aluminate available for crystallization, because the inhibitors act at far too low a concentration for that to be the case. These considerations suggest that it may be the aluminium-
alditol complex, not the alditol itself, which attaches to growth sites and causes them to be deactivated.

For a gibbsite ion to transform to solid gibbsite, two key steps are required: first, the ion must adsorb to the surface, and second, the aluminium species must transition from tetrahedral to octahedral co-ordination in order to become properly incorporated into the solid.

A possible explanation for the powerful inhibiting effect of alditols may therefore be related to stabilization of tetrahedrally co-ordinated aluminium by complexation, as follows: alditols form complexes with aluminium by replacing two or three of the hydroxide groups on the original aluminate ions. This leaves a least one hydroxyl group which can be eliminated to allow the aluminium to bond to a growth site on the surface. Transition to octahedral co-ordination would then be inhibited by the presence of the chelating alditol resulting in the complex blocking the site, as illustrated schematically in Fig. 10. In this way the growth site may become irreversibly de-activated. It has also been found that inhibition is directly related to the acidity of the hydroxyl groups, which is also consistent with the formation of stronger complexes (Grocott and Rosenberg, 1988).

This is consistent with observations on the importance of the stereochemistry of the inhibitor, in particular that compounds with three adjacent hydroxyl groups alternating either side of the carbon backbone are the most potent inhibitors. It is also similar in principle to the proposal by Seyssiecq et al. (1999) based on binding of alcohol groups to a dimeric aluminate “growth unit” which was predicted by molecular modelling to exist at low concentrations in aluminium solutions. The inter-atomic distances between pairs of oxygen atoms in the growth unit were found to be quite similar to the distances between alternate OH groups in polyols (polyhydroxy carboxylic acids and alditols), leading the authors to propose the general structure shown schematically in Fig. 11 for a growth unit to which a polyol has been attached with the elimination of two hydroxyl groups. The unit would then dock onto a gibbsite growth site via remaining hydroxyl groups, leaving the organic ligand facing outwards and effectively deactivating the growth site.

The alternative explanation of direct adsorption of the organic inhibitor to the solid surface is favoured by other authors, by analogy with the case of gluconate and on the basis that octahedral aluminium complexes which form under acidic conditions may be dissociated and form tetrahedral aluminate ions in highly alkaline solutions (Motekaitis and Martell, 1984). Under this model, the relative strengths of inhibitors are seen as resulting from the relationship of the structure and stereochemistry of an inhibitor to its ability to adsorb to the gibbsite surface (van Bronswijk et al., 1999; Watling, 2000), in which the aluminium ions are octahedrally co-ordinated. However from the available information it does not appear to be possible to distinguish between adsorption of the organic compounds themselves and adsorption of an organic/aluminate complex.

Experiments on a series of alditols by van Bronswijk et al. (1999) revealed clear relationships between structure, adsorption and precipitation yield. In particular, the compounds studied were found to fall into distinct two groups based on the key stereochemical characteristic of threo (alternating hydroxyls) or erythro (hydroxyls all on same side), as shown in Fig. 12, in which the behaviour of a group of threo compounds is compared with that of a set of erythro compounds. Each set of compounds showed adsorption increasing monotonically with the number of carbon atoms, with corresponding monotonic decreases in the precipitation yield (shown here relative to the yield in an identical experiment carried out in the absence of organic additives (the “control”), which has been assigned a value of 20 arbitrary units for the purposes of comparison). The effects were significantly greater for the threo group. A more extreme example (not shown) was between the structural isomers xylitol (threo) and ribitol (erythro), which showed adsorptions of 22 units and $2.7 \times 10^{-8}$ mol g$^{-1}$, and relative precipitation yields of 2.2 (11% of the control) and 17 units (85% of the control).

The presence of organic inhibitors affects not only the precipitation yield, but also the shapes and numbers of the particles produced. The exact effects on particle shape are complex and depend on both the nature of the inhibitor and the conditions of crystallization, in particular whether the conditions favour nucleation, agglomeration or growth, although the fundamental (molecular) mechanism of inhibition appears

![Fig. 9](image_url) Degree of inhibition of gibbsite crystallization by alditols at a constant specific dose rate of 0.5 mM m$^{-2}$ as a function of their ability to form complexes with metal ions in acidic solution. Data from Smith et al. (1996) and Angyal et al. (1974).

![Fig. 10](image_url) Schematic representation of an aluminium–alditol complex attached to a growth site. The co-ordination of the aluminium ion by the alditol forces the Al to remain tetrahedrally co-ordinated, preventing it from becoming fully incorporated into the gibbsite phase and irreversibly blocking the growth site (interpreted from Smith et al. (1996)).
to be independent of the macroscopic crystallization regime (Watling, 2000). Under conditions of moderate to high supersaturation, which favour secondary nucleation and agglomeration, crystals grown from pure solutions are agglomerates of blocky hexagonal prisms with chamfered faces as illustrated in Fig. 6. The shapes of the individual crystals within the agglomerates are consistent with theoretical predictions (Seyssiecq et al., 1999; Sweegers et al., 2001, 2002). Crystals become elongated in pure sodium aluminate solutions because the rate of growth on the hexagonal (001) basal plane is mainly by a relatively fast birth-and-spread mechanism, whereas the side faces are characterised by slower spiral growth. Inhibition of the birth-and-spread mechanism by polyhydroxy compounds which block secondary nucleation sites therefore results in the development of flat hexagonal plates (Watling, 2000). It can also cause the formation of dendrites and of individual small particles, as well as reducing the overall size of the main growth particles.

4.3.3. Carboxylates

In neutral or acid solutions many carboxylates have strong interactions with gibbsite surfaces, for example by chemisorption via a reaction analogous to esterification, which is key to their importance in areas such as catalysis and chromatography (Karaman et al., 2001). Low molecular weight dicarboxylates including oxalate, malonate and succinate (which are all generally present in Bayer process liquors) show significant adsorption, but only below pH 9 (Rosenqvist et al., 2003). In strongly alkaline solutions however, it seems unlikely that simple aliphatic carboxylates (i.e. saturated hydrocarbons with carboxyl groups as the only functional groups) have strong interactions with the gibbsite surface. Accordingly, the presence of simple aliphatic carboxylates appears to have little effect on gibbsite precipitation apart from the aggregate effect on the ionic strength of the liquor discussed in Section 4.1.

Thirty-eight carboxylates are commonly present at measurable quantities in Bayer process liquors (Power and Loh, 2010). Twenty-one are simple aliphatics, two have one hydroxyl group and one, tartrate, has a pair of (adjacent) hydroxyl groups. Of these, tartrate is the only one that has been confirmed to be a crystallization inhibitor (Coyne et al., 1994; Nikolic et al., 2008; Paulaine et al., 2003; Power, 1991). Lactate, acetate and succinate have been reported to have significant effects on yield and product particle size distribution under conditions of unseeded precipitation by carbonation of the liquor, apparently due to effects on the induction period (Brown et al., 1986); no such effect has been reported in the context of seeded precipitation however.

The other fourteen compounds are benzene carboxylates, including four with a single (phenolic) hydroxide. The simplest of these, benzoate, is commonly found in Bayer process liquors (Power and Loh, 2010). The effects of benzoate and the three methyl benzoate isomers (o-, m- and p- methyl benzoate (or toluenidate)) have been investigated by Lv et al. (2009), who found that they all reduce precipitation yield and also affect the particle size distribution of the product. The observed order of yield effect was: p-methyl benzoate > benzoate > m-methyl benzoate > o-methyl benzoate. This order was found to correlate with the order of net charge on the carboxylic acid group, on which basis the effect was rationalised in terms of an electrostatic model of the solution/gibbsite interface (see Fig. 5). The presence of p-methyl benzoate has been reported in Bayer liquor at least once (Picard et al., 2002), but to date there do not appear to be any reports of the other isomers.

A number of aliphatic carboxylates with two or more adjacent hydroxyl groups, which are therefore either known or likely to be inhibitors (Bouchard et al., 2005; Loh et al., 2010b; Nikolic et al., 2008; Paulaine et al., 2003; Power, 1991), have been found at low concentrations in at least one Bayer process liquor (Power et al., 2011a). Systematic studies of this class of compounds have shown that they generally inhibit precipitation, and that the trends in inhibitor strength tend to correlate with the trends for the corresponding alditols (Watling, 2000). In order to assess the effect of the presence of the carboxylate group, it is necessary to compare pairs of otherwise identical compounds. Such comparisons indicate that the acid group generally enhances the...
The inhibition effect (Watling, 2000). The differences are sometimes dramatic, as between threitol which is a mild inhibitor, and threonate, which is one of the strongest. In contrast, Paulaine et al. (2003) observed that the alditols were more potent inhibitors than the acids based on a comparison of group of acids which had a maximum of four carbons with a group of alditols which had a minimum of five carbons. However, in this study, the effects of carbon number and stereochemistry appear to have been greater than the effects of the addition of carboxylate groups.

A study of the adsorption behaviour and yield impacts of a group of benzene carboxylates and hydroxy-acids, catechol, and the hydrogenation and oxidation products of catechol (1,2-cyclohexane diol and muconate, respectively) in comparison with gluconate has illustrated a number of interesting features of these compounds (Bouchard et al., 2005). All of those which contain either carboxylate or hydroxyl groups were found to adsorb to the gibbsite surface and to be precipitation inhibitors. According to the Henry constants, the adsorption strengths of phthalate, isophthalate and 2-hydroxybenzoate are almost as great as for gluconate, however all are far less effective inhibitors than gluconate. Catechol (1,2-dihydroxybenzene), which has two adjacent hydroxyl groups, also shows an adsorption strength similar to gluconate, but is a considerably weaker inhibitor. The related compounds resorcinol (1,3-dihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene), in which the two hydroxyl groups are not adjacent, are not yield inhibitors (Power, 1991), consistent with an expected lower adsorption due to the different stereochemistry of the hydroxyl groups. The hydrogenation product of catechol, 1,2-cyclohexane diol, retains the two adjacent hydroxyl groups but does not adsorb and is not an inhibitor, presumably because of the significant change in stereochemistry (from planar to three-dimensional boat and chair conformations). Similarly, oxidation of catechol to muconic acid by opening the benzene ring and oxidizing the hydroxyl groups to carboxylates renders the molecule non-adsorbing and non-inhibiting.

Most of the adsorption measurements reported in the literature are reported as adsorption isotherms measured by contacting test solutions with gibbsite solids, either in a suspension or a column, at room temperature and measuring the uptake of individual organic compounds at equilibrium (Bouchard et al., 2005; Coyne et al., 1994). The Henry constants determined in this way are then compared with the yield from a precipitation test carried out at elevated temperature with a different seed. These experiments have generally demonstrated the importance of adsorption in relation to yield inhibition; in particular, adsorption appears to be a pre-requisite to yield inhibition for any given compound. However the converse is not true (i.e. not all compounds that adsorb are inhibitors), and it has not been possible to compare results quantitatively from one study to another. It has also been suggested that adsorption under precipitation conditions may not always follow the same behaviour as at room temperature (Loh et al., 2010a).

Accordingly, Loh et al. (2010a) undertook a study of adsorption in which the degree of adsorption was measured on the same seed and under conditions as close as possible to the conditions under which yield inhibition was determined. To do this, adsorption was measured by determining the uptake of each organic compound by a gibbsite seed in slurry with sodium aluminate at its equilibrium concentration at the desired temperature. Precipitation tests were then carried out with a supersaturated sodium aluminate solution under the same conditions of seeding and temperature. This work showed that, not only is there no single correlation between adsorption strength and the degree of inhibition, but that adsorption can lead to either inhibition or enhancement of precipitation yield, or to no change at all, depending on the type of compound involved. For compounds containing hydroxyl groups, a comparative study of a small number of aromatic and aliphatic compounds indicated direct correlations between adsorption strength and degree of inhibition. The degree of inhibition per amount adsorbed was greater for aliphatic compounds than for aromatics, and in both cases the effects increased with the number of hydroxyl and/or carboxylate groups present, as summarised in Fig. 13. In most cases the trends are qualitatively similar to those determined previously from room temperature adsorption measurements, but the results from the different studies cannot be compared quantitatively because of the different seed materials used and the lack of comparative information on their specific surface areas, for example. Even so, the results for salicylate (2-hydroxy benzoate) are clearly different. Bouchard et al. (2005) found that the Henry constant for salicylate was similar to that of gluconate, indicating very strong adsorption potential consistent with the observation by Picard et al. (2002) that salicylate appears to have quite a strong affinity for gibbsite under Bayer plant conditions. By contrast, Loh et al. (2010a) found that salicylic acid did not adsorb at all under precipitation conditions and correspondingly did not inhibit precipitation (Fig. 13).

The inhibition effects of three benzene carboxylates were also investigated, and all were found to increase yield. This effect was ascribed to increases in the total surface area of the solids due to enhanced secondary nucleation. No adsorption measurements were made for these compounds in this study, but the results were correlated with the “surface affinity” as defined by Picard et al. (2002), as shown in Fig. 14.

These results indicate that adsorption via paired hydroxyl groups occurs by a different mechanism than adsorption via carboxylic acid groups. As discussed above, the former appears to be associated with direct interactions with aluminium ion, either in growth units or directly at the surface itself, resulting in permanent deactivation of growth sites. On the other hand, the presence of carboxylic acid groups alone appears to result in the formation of an increased number of secondary nuclei that do not adhere to the growth surface, causing an increase in the number of fine particles and hence a greater overall surface area for precipitation.

Further insight into the effects of hydroxy benzoates may be gained from Fig. 15, which has been constructed from data given by Armstrong (1993). This figure summarises data from a set of precipitation experiments carried out in two stages, the first under conditions that favour agglomeration, and the second favouring growth. Yield inhibition in the agglomeration stage is shown as a function of organic compound added; the results have been adjusted to represent the effects of equimolar additions of each compound. Comparing the degrees of inhibition caused by 1,2-dihydroxy benzene and 3,4-dihydroxy benzoate indicates that the addition of a carboxylate group not adjacent to the hydroxyls more than doubles the inhibition, whereas the adjacent carboxylate in 2,3-dihydroxy benzoate increases the inhibition by about 40%. For the hydroxy benzoates with three adjacent hydroxyl groups the inhibition is independent of the positioning of the carboxylate group, and is almost as high as for 3,4-dihydroxy benzoate. These observations support the hypothesis that pairs of adjacent hydroxyls (shown circled) are the main cause of the inhibition effect, and that this effect is magnified by the presence of carboxyl groups.

Further work on 3,4-dihydroxy benzoate demonstrated that it adversely affects all aspects of the precipitation process, by increasing the induction time and decreasing the rates of nucleation, agglomeration and growth (Tran et al., 1996).

4.3.4. Oils, fatty acids and miscellaneous compounds

Oils enter Bayer process liquor by a variety of routes, including as partial degradation products of the organic matter in bauxite, as carriers for process chemical additives and from leakage of lubrication oils from process machinery, for example (Power and Loh, 2010). Fatty acids are present as degradation products of more complex compounds and from the saponification of oils. Any possible direct effects of these compounds on precipitation yield do not appear to have been investigated in detail and have generally been assumed to be negligible, although there are reports that certain fatty acids may be beneficial in ameliorating the effects of inhibitors to some extent (Zeng et al., 2008).

The addition of a crown ether (15-crown-5) to a sodium aluminate solution has been shown to destabilise it towards nucleation and to increase the rate of seeded precipitation (Zeng et al., 2007). This crown ether is an effective complexant for sodium ions (An et al., 1992), so
the effect appears to be related to a reduction in the availability of sodium ions which facilitate the formation of gibbsite solids (Li et al., 2000a, 2000b).

5. Size control in precipitation: crystal growth modifiers (CGMs)

The control of the particle size distributions of the precipitator solids in alumina refineries is crucial for proper operation of the continuous precipitation process to maximise yield and achieve acceptable product quality. Because of the complex nature of the precipitation process, the engineering solutions involved in its optimisation are complex and varied, and are outside the scope of this review. However the influence of organic compounds on sizing and size control can be significant, primarily because certain compounds can inhibit or enhance agglomeration and/or nucleation. Some of these effects have already been mentioned in the context of yield impacts, for example the increases in fines production caused by the presence of benzene poly-carboxylates, which in turn increases the surface area available for precipitation and so increases the precipitation yield (see Carboxylates section). This has a disadvantage, however, because the generation of excessive fine material can lead to a loss of control of the solids due to elutriation, carryover and size classification issues. The countermeasures to this include reducing seed loadings and supersaturation, which limit the precipitation yield. Considerable research effort has therefore been focussed on the development of process additives to facilitate particle size control in precipitation while maximising yield parameters. This has led to a range of formulations generally known as “crystal growth modifiers” (CGMs) (Roe et al., 1988).

The first CGM was an agglomeration aid based on an acrylate/methacrylate copolymer (Roe and Perisho, 1986). This was superseded by a more economical formulation consisting of an ionic surfactant (a fatty acid) dissolved in an oil to produce a cheaper product which achieved similar results (Owen and Davis, 1988). Improving agglomeration has the effect of coarsening the particle size distribution and therefore reducing the available area for precipitation, which of itself would have the effect of reducing yield. However, it is claimed that the improved process control flexibility afforded by the ability to manipulate agglomeration can lead to increases in precipitation yield of the order of 10% with CGM addition rates of less than 25 ppm (Roe et al., 1988).

Many different formulations have since been examined to improve the technical and economic performance of CGMs. A mixture of
carbon content of the liquor. Not all of the organic compounds contribute to this effect; rather, it is due to the presence of a small subset of the organic compounds present. As with the inhibition of precipitation yield, the compounds that have the greatest effect on calcium concentrations are those with multiple hydroxide groups. Consequently, green liquor calcium concentrations tend to be lower in liquors from plants with high temperature digestion than from those with low temperature digestion (The and Sivalakumar, 1985). Tests with sodium gluconate have indicated that the effect is likely to be due to the stabilization (by chelation) of a calcium aluminate hemihydrate species (Rosenberg et al., 2001).

7. Sodium oxalate

Sodium oxalate occupies a special place in Bayer process technology because of problems that its limited solubility can create in the operation of alumina plants (Yamada et al., 1973). The many and various problems caused by oxalate are not always fully understood (Kim and Lee, 2003), but as we will see in this section, much progress has been made.

Although moderately soluble in water (approximately 35 g/L at 25 °C and 65 g/L at 100 °C (CRC, 2011; Dean, 1998; Stephen and Stephen, 1963)), sodium oxalate is less soluble in Bayer liquors by a factor of 20 or more, primarily due to the common ion effect of the sodium. A number of empirical correlations have been derived for the dependence of oxalate solubility on the concentrations of other ions present in Bayer liquors (Bouzat and Philopponneau, 1991; Brown and Cole, 1980; Yamada et al., 1973). More recently, thermodynamic models have been developed which take into account all the main ions in solution, and which can be calibrated to give good correlations for the equilibrium oxalate solubility in actual plant liquors (Beckham et al., 2005; Königsberger et al., 2005b).

In actual plant liquors however, it is generally found that the measured sodium oxalate solubility is significantly higher than predicted from the thermodynamic models. This apparent solubility (The and Bush, 1987) is a function a number of factors, in particular the nature and concentrations of other (high molecular weight) organic compounds in the liquor. It therefore cannot be predicted thermodynamically and must be determined empirically for each liquor and circumstance (Beckham et al., 2005). Apparent solubility does not follow the same trends with concentration as the thermodynamic solubility; for example apparent solubility may increase with TA, as illustrated for particular plant liquor in Fig. 16.
7.1. Oxalate input

The oxalate present in Bayer process liquors is a result of degradation of organic compounds extracted from the bauxite. Estimates of the proportion of the organic content of bauxite which reports as oxalate in single laboratory digestions vary from about 3 to 10 percent (Brown and Cole, 1980; Grocott and Rosenberg, 1988; Lever, 1983). The total oxalate production in a plant will generally be somewhat greater than this because oxalate is also produced by the progressive degradation of organic compounds as the plant liquor cycles through digestion, which may account for around 20% of the ultimate oxalate input to the liquor (Armstrong and Healy, 2006; Power and Tichbon, 1990).

The total oxalate production in a plant will generally be somewhat greater than this because oxalate is also produced by the progressive degradation of organic compounds as the plant liquor cycles through digestion, which may account for around 20% of the ultimate oxalate input to the liquor (Armstrong and Healy, 2006; Power and Tichbon, 1990). Oxalate input varies widely with bauxite source and digestion temperature, as can be appreciated from Fig. 17 in which the oxalate production rates of a range of bauxite types is compared. The measurements were made on samples from bulk standards prepared as broadly representative of the bauxite deposits concerned. The three USSR bauxites are diasporic, the two Jamaica and Wagina Island samples are from mixed gibbsitic/boehmitic karst bauxites, and the remainder represent lateritic bauxites. In all but one case (Darling Range) the oxalate production rate at the higher temperature is equal to or higher than at the lower temperature, markedly so for the Jamaica 1 and Wagina Island samples. Lever’s comment that oxalate production is roughly double at the higher temperature presumably applied to Jamaican bauxites, but he also observed that for Australian bauxites the ratio may be up to a factor of three (Lever, 1983). These discrepancies highlight the limitations of such generalisations and the need for each bauxite to be assessed individually.

7.2. Direct effects: sodium oxalate crystallization

It has been shown that the oxalate anion reduces the rate of growth of gibbsite by adsorbing to growth sites (Kingsley and Wilcox, 1986; Nikolic et al., 2004), but its effect is minor in comparison to that of other more strongly adsorbed anions (Power, 1991). The dominant effects of oxalate

![Fig. 16. Behaviour of apparent solubility in comparison with thermodynamic solubility, for a liquor from a plant treating Australian bauxite (redrawn from Beckham and Grocott (1993)).](image)

![Fig. 17. Oxalate generation rate as a function of bauxite source and digestion temperature (from data in Power and Tichbon (1990)).](image)
are caused by the crystallization of sodium oxalate, and the interactions that occur between sodium oxalate and gibbsite solids.

Uncontrolled oxalate crystallization can be highly detrimental to the operation and economy of Bayer process plants (Power and Tichbon, 1990). For most plants processing lateritic bauxites, the rate of input of oxalate to the liquor is greater than the natural outputs via soluble losses (including to the bauxite residue) and entrainment of solid sodium oxalate with gibbsite product or scale (The and Bush, 1987). The improvements in bauxite residue washing efficiencies that have been achieved in modern plants has had the downside effect of increasing the rate of oxalate accumulation in the liquor. Some form of oxalate removal process is therefore generally operated in order to maintain oxalate concentrations within acceptable levels (Chinloy, 1990; Newchurch and Moretto, 1990; Yamada et al., 1973). Reported studies of oxalate behaviour in the absence of an oxalate removal process are therefore rare. An exception to this is the investigation at the Burntisland plant in Scotland (Brown and Cole, 1980). This was a small plant producing gibbsite and calcined alumina for the chemical industry, which operated for long periods on low oxalate bauxite from Ghana. During these times the plant ran without operating an oxalate removal process, making it possible to observe the “natural” behaviour of oxalate in the Bayer circuit. It was found that the oxalate level in the liquor would rise steadily over a period of about three months to a peak which corresponded to the appearance of sodium oxalate solids co-precipitated with the gibbsite seed and product. Oxalate would then exit the circuit with the product which was calcined to alumina, thus pyrolysing the oxalate and leading to a decline in the concentration of oxalate in the liquor. The liquor oxalate concentration would eventually drop until sodium oxalate crystallization ceased (i.e. the sodium oxalate concentration was equal to the apparent solubility). The soluble oxalate concentration would subsequently increase until it was again sufficiently supersaturated to create the next round of spontaneous crystallization. The oxalate supersaturation/de-supersaturation cycle in this case was found to have a period of about six months. The presence of sodium oxalate solids was detrimental to the quality of the gibbsite product by causing a reduction in particle strength, and increases in both the sodium content and the proportion of material in the finer size fractions. A direct cause and effect relationship was inferred as these product quality parameters were found to vary in parallel with the oxalate cycle. These phenomena have since been observed in many refineries, and are now well known throughout the industry.

Lever (1983) interpreted the metastable behaviour of oxalate as a result of the adsorption of organic “stabilisers” on the surfaces of oxalate crystals, noting the stabilizing effect associated with high molecular weight compounds (“humates”) from the bauxite. He also observed that “humates” tend to co-precipitate with the oxalate, creating an interactive effect in which crystallization of oxalate can result in a lowering of liquor stability by the co-removal of stabilisers. It is the presence of co-precipitated “humates” that imparts the brown colour typical of the sodium oxalate solids found in Bayer process plants.

Sodium oxalate crystals exhibit a variety of morphologies, depending on the conditions of their formation. When grown from neutral solutions they tend to form blocky prismatic shapes, but in sodium hydroxide solutions the crystals are generally acicular (needle-like, see Figs. 18 to 20) due to stabilization of the [110] crystal faces in relation to the [001] faces (Reyhani et al., 2000). Acicular oxalate crystals may agglomerate in a variety of ways to form shapes resembling fans, bow-ties, or balls (spherulites). The most important single factor determining the shapes of the agglomerates appears to be supersaturation, which in turn depends on the presence of organic impurities or additives, such as surfactants, in the solution (Grocott and Harrison, 1996; Power and Tichbon, 1990).

In order to quantify oxalate supersaturation, Lever (1983) introduced a method for measuring the “Critical Oxalate Concentration” (COC), which may be defined as the highest concentration of oxalate that can be achieved in a given solution before spontaneous nucleation of sodium oxalate occurs. An automated method for COC determination which can be used to evaluate the effects on oxalate stability of chemicals added to the liquor, or for routine monitoring the COC of plant liquors, has been described by Hiralal et al. (1994).

An understanding of oxalate stability is important in the operation of Bayer process plants, because the effects of uncontrolled crystallization of oxalate can be severe. This is particularly evident in plants processing bauxites with higher organic contents, in which major operating disruptions leading to significant losses in production and degradation of product quality can be caused, as demonstrated by the results of a plant trial in which a “humate removal” chemical, poly-diallyldimethylammonium chloride (poly-DADMAC), was added to the plant liquor (Power and Tichbon, 1990). Dosing poly-DADMAC was found to be effective in removing high-molecular weight organic compounds (loosely referred to as “humates”—see Part 1 of this review for a discussion of this term in the Bayer context (Power and Loh, 2010)) from the liquor, and after about six weeks the level of “humates” was estimated to have been reduced by about 30%. At this point, sodium oxalate solids began to appear throughout the precipitation circuit, which led to a series of undesirable effects. First, the elutriation behaviour of the solids in the precipitators was affected as fine oxalate needles co-precipitated with gibbsite triggered production of finer product and the formation of three-dimensional matrices which caused a flotation effect and severely disrupted the seed balance of the plant. Co-precipitation also occurred on the walls of tanks and pipes resulting in a dramatic increase in the rate of scale formation and consequent loss of equipment utilisation. Product quality was also affected by an increase in soda impurity and fines content, and a reduction in particle strength. Removal of dosing allowed the “humate” concentration to return to previous levels and normal plant operation to be re-established.

The material associated with the flotation phenomenon has become known as “non-setting hydrate”, or “NSH”. NSH is caused by the formation of complex three-dimensional networks of gibbsite and sodium oxalate crystals which form flocculated masses which settle very slowly with little compaction, and which are readily entrained by flowing liquor. The NSH can be seen as a layer which forms on top of settled gibbsite if a bottled sample of precipitator slurry taken from a plant or from a laboratory precipitation test is left to stand, as shown in Fig. 18(A). Fig. 18(B) is an electron microscope image showing the structure of the NSH, in which gibbsite crystals can be seen to be incorporated into a three-dimensional web of oxalate crystals. The photographs in Figs. 18 to 20 were extracted (with the permission of the publisher) from a detailed study by Reyhani et al. (2000) of oxalate/gibbsite co-precipitation.

Careful study of the complex interactions between sodium oxalate and gibbsite solids during crystallization has revealed that the surfaces of each solid may provide nucleation sites for the other. Also, organic substances can have significant effects in either promoting or inhibiting such interactions. These effects can have a dramatic influence on the shapes and particle size distributions of the product solids (Reyhani et al., 1999, 2000), as well as on the crystallization yields achieved. Kingsley and Wilcox (1986) reported that oxalate adsors to the surfaces of gibbsite to a small extent only, but nevertheless may cause a measurable decrease in gibbsite precipitation yield due to preferential adsorption at gibbsite growth sites. Nikolic et al. (2004) also report a decrease in gibbsite growth rate due to oxalate adsorption. Reyhani et al. (2000) have shown that gibbsite particles are not preferred nuclei for oxalate crystallization. While some oxalate nucleation was observed on gibbsite in pure sodium aluminate solutions, it appeared to occur only at a small number of sites. Growth was found to not be epitaxial and therefore the oxalate crystals were attached only weakly to the gibbsite. An example of competition between gibbsite and oxalate growth units for growth sites on the gibbsite surface can be inferred from the SEM image shown.

1 Aluminium tri-hydroxide, or gibbsite, is commonly referred to in the industry as “hydrate” (an abbreviation of “alumina tri-hydrate”).
in Fig. 19, in which an (acicular) oxalate crystal appears to disrupt the normal growth of a (hexagonal) gibbsite crystal.

On the other hand, sodium oxalate needles appear to have sites which are favourable for gibbsite nucleation. This results in the formation of multiple single crystals of gibbsite nucleated at kink sites on the oxalate surfaces (Reyhani et al., 1999), which can lead to the generation of a large population of very fine gibbsite crystals attached to oxalate in the plant environment, as shown in Fig. 3 of Power and Tichbon (1990). It has been observed that oxalate nucleates preferentially on the end [002] faces of acicular oxalate crystals, which led to the suggestion that the preference for kink sites may be enhanced because they reveal [002] faces, possibly indicating some degree of epitaxy (Reyhani et al., 1999). Fig. 20(A) shows the initial stages of nucleation of gibbsite on oxalate, and after 24 h the oxalate needles are completely encased in gibbsite (Fig. 20(B)). In this way, the presence of oxalate needles stimulates the formation of gibbsite nuclei, and at the same time inhibits them from agglomerating. This combination of effects provides at least a partial explanation of the well-known phenomenon of fines generation in the presence of solid-phase oxalate in the Bayer process (Brown and Cole, 1980; Lever, 1983; Reyhani et al., 1999; The and Bush, 1987; Vergheese, 1988), which as noted above can have major negative implications for refinery operation and product quality (Chartouni, 1989; Lever, 1983; Minai et al., 1978; Power and Tichbon, 1990; Yamada et al., 1973).

### 7.3. Indirect effects: sodium oxalate control

In addition to the direct effects that oxalate crystallization can have on the operation and economics of the Bayer process, the control of oxalate to mitigate those effects introduces other constraints which in turn may carry significant costs. If the concentration of sodium oxalate in the precipitation section of a refinery is allowed to build up to the COC, spontaneous oxalate crystallization will occur, with the consequences described above. Short-term management of such an event requires actions such as reducing the overall concentration (TA) of the liquor and water-washing the recycled gibbsite seed (The and Bush, 1987). These actions are expensive in raw materials as they require the addition of extra water for dilution and energy for subsequent evaporation. They also tend to increase soluble liquor losses and hence the need for additional caustic soda. Finally, lowering the TA reduces precipitation yield which is a major cost to the operation.
Maintaining the concentration of oxalate in the liquor stream to below the COC requires balancing the oxalate output with the oxalate input. In the processing of bauxites of low organic carbon content, this can often be achieved through the normal soluble losses. However for bauxites of moderate to high organic carbon content, maintaining a suitable liquor TA generally requires the continuous removal of sodium oxalate, which necessitates the installation and operation of significant capital equipment. The costs of oxalate removal must be balanced against the benefits in order to determine the optimum removal rate and plant operating conditions, in particular liquor TA and precipitation temperature profile. Optimising oxalate removal requires knowledge of both the thermodynamics and rates of the crystallization of sodium oxalate as a function of key process variables, in particular seed rate, TA and temperature (Beckham and Grocott, 1993; McKinnon et al., 1999). Increased operating flexibility may be possible through the use of chemical additives designed to increase the COC in the precipitation area specifically, while not interfering with oxalate removal elsewhere in the process (Farquharson et al., 1995).

8. Soda in product

Sodium is the main impurity by weight in smelter grade alumina, with typical concentrations in the range of 0.25 to 0.50 % Na₂O (soda), which is in the order of ten times the amount of the next largest impurities, silica and iron (Syltevik et al., 1996). Although sodium is a major component of the electrolyte bath (sodium aluminium fluoride), the soda content of the alumina is critical to the economic performance of the smelter through its effect on the sodium/aluminium balance (Syltevik et al., 1996). It is also detrimental to fluoride adsorption in the dry scrubbing process (Coyne et al., 1989).

Early theories suggesting that soda may be incorporated in precipitated gibbsite through the inclusion of liquor in voids (Misra and White, 1971; Ohkawa et al., 1985; Sato and Kazama, 1971) have largely been disproven, and it is now generally accepted that the soda in alumina is predominantly due to chemical incorporation of sodium in the growing gibbsite lattice (Vernon et al., 2005).

The soda content of alumina has been found to depend on the square of the supersaturation during gibbsite precipitation (Sang, 1988). Armstrong (1993); Armstrong et al. (1996) confirmed the quadratic dependence on supersaturation, and also quantified dependencies on temperature and the TOC for the Queensland Alumina (QAL) plant, as follows:

$$\frac{dS}{dA} = a \times \left( \frac{A}{T/C} - \frac{A}{T/C_\infty} \right)^2 \tag{9}$$

where:

- $dS/dA$ incremental mass of soda incorporated/incremental mass of alumina precipitated
- $A/T/C$ A/TC ratio at time $t$
- $A/T/C_\infty$ equilibrium A/C ratio
- $a$ 0.000598 + T - 0.00036 + 0.019568 * TOC/TC

The coefficients for the “a” term demonstrate that TOC has the second greatest influence (after supersaturation). Eq. (9) has the same form as the equation for gibbsite growth rate (Vernon et al., 2002), which implies that soda incorporation is a linear function of growth rate.

The first attempt to explain soda incorporation on the basis of a precipitation mechanism appears to be the suggestion by Grocott and Rosenberg (1988) that the sodium ions which are released from sodium aluminate at the growing surface must diffuse away from the surface to avoid being trapped by the growth front. It was further hypothesised that the presence of adsorbed organic molecules could interfere with the escape of sodium ions, facilitating their incorporation into the growing crystal. Vernon et al. (2005) have investigated the mechanism of soda incorporation using a statistical thermodynamic model which assumes that sodium ions are trapped at surface defects, along the lines of the theory developed by Hall (1953) for semiconductor growth in the solid state, and which has been shown...
to be applicable to growth from solution (Tsuchiyama et al., 1981). According to this model, soda incorporation is low until a critical growth rate is reached, after which soda incorporation increases rapidly and then flattens off towards a plateau value, as shown for a range of temperatures by the S-shaped curves in Fig. 21, which demonstrates an excellent fit of the model to experimental data (Vernon et al., 2005). The range of supersaturation generally encountered in practice in the Bayer process is shown in the ellipse, which is consistent with the observation that the relationship between soda incorporation and gibbsite growth rate is generally found to be linear in practice. This model is based on the assumption that the rate of generation of surface defects increases with supersaturation, which in the current content may be interpreted as an increase of the degree of birth-and-spread versus spiral growth. This assumption has been qualitatively verified by using SEM imaging to observe the appearance of surface nuclei as a function of supersaturation, as illustrated in Fig. 22.

A number of studies have established a link between organic compounds in solution and the incorporation of soda into precipitated gibbsite (Armstrong et al., 1996; Clerin and Cristol, 1998; Grocott and Rosenberg, 1988; van Bronswijk et al., 1999; Watling et al., 1996). Grocott and Rosenberg (1988) demonstrated a linear relationship between incorporated soda and the fraction of Bayer plant liquor in synthetic liquor/plant liquor mixtures. They also demonstrated a correlation between the strength of adsorption of organic molecules to gibbsite and the degree to which they enhanced soda incorporation. Hence, compounds with multiple hydroxyl groups were found to be the most potent promoters of soda incorporation.

Armstrong extended the range of compounds studied and concluded that compounds with adjacent hydroxy groups on an aromatic carboxylic backbone could enhance soda incorporation by up to 100% during the growth phase of gibbsite precipitation (Armstrong, 1993). He also noted that the same compounds generally tended to decrease the gibbsite growth rate, so the increase in soda incorporation was not a result of increased overall growth rate. This implies that the first factor, “a”, in Eq. (9) is reduced by the presence of these organic molecules.

This point was investigated by Vernon et al. (2005) using tartrate as a model organic compound known to adsorb to gibbsite surfaces, inhibit precipitation and increase soda incorporation (Armstrong, 1993). As shown in Fig. 23, tartrate has a dramatic effect on soda incorporation, particularly in the range of growth rates encountered in Bayer process practice. It was observed that the presence of tartrate resulted in significant roughening of the gibbsite surface due to a large increase in the number of secondary nuclei produced. This was interpreted as an increase in secondary nucleation due to poisoning of growth sites by adsorbed tartrate, which effectively increased localised crystallization rates. Increased soda incorporation is therefore consistent with an increase in specific reaction rate (i.e. rate per unit of area represented by active growth sites) even though the overall reaction rate is diminished by the presence of tartrate.

In addition to the incorporation of soda by trapping at gibbsite growth sites, soda in product can be significantly increased by the presence of co-precipitated sodium oxalate (Brown and Cole, 1980; Power and Tichbon, 1990; Sang, 1988).

9. Organic process additives

A wide range of chemical additives is used to enhance the efficiency of the Bayer process. The most significant in terms of both amounts used and
process impact are the flocculants, clarifiers and filtration aids that are now used universally in various aspects of solid/liquid separation. Indeed, the introduction of additives was crucial to the development of the low cost, energy-efficient alumina refineries of today. The first use of an organic chemical additive appears to be the addition of starch as a filter aid for the pressure (“Kelly”) filters that were used to separate the bauxite residue from the green liquor after digestion (Hudson, 1988). Under the wartime conditions of the 1940s, refineries in the USA were required to process lower grade bauxite. This meant much higher residue loads and drove the main Kelly filters to be replaced by settling tanks for bulk residue separation, with filtration reserved for “polishing”, i.e. for removing residual fine material from the clarifier overflow liquor. This change increased the need for starch, which was then used as a flocculant, clarifier and filtration aid. The development of cheaper, more efficient flocculants in the 1960s and 70s led to the gradual replacement of starch (Pearse and Sartowski, 1984). This change was accelerated by the realisation that starch degradation products were detrimental to precipitation (The, 1980), although it was reported as late as 1996 that for one particular refinery the organic carbon input from starch was 1.0 kg/tonne of alumina produced, which was 18% of the total organic carbon input, while the carbon input from flocculant was only 0.009 kg/tonne (Solymár et al., 1996). It has also been suggested that the use of synthetic flocculants in place of starch results in a greater proportion of the higher molecular weight “humic” compounds being removed by adsorption onto mud particles because the synthetic flocculants are effective at much lower surface coverage than starch, which leaves active sites available for the adsorption (Pearse and Sartowski, 1984).

9.1. Flocculants

The first synthetic flocculants to be introduced to the alumina industry were polyacrylate/polyacrylamide co-polymers, the molecular weights and functionalities of which could be optimised to suit particular bauxites and process conditions, in particular the liquor concentration (Hudson, 1987; Pearse and Sartowski, 1984). At least two different formulations are generally used, one for the high concentration green liquor settler, and others for the lower concentration liquors in the mud washing circuit. Plants in Jamaica were among the first to adopt synthetic flocculant technology, due to the poor settling qualities of the residue from Jamaican bauxites (Kahane et al., 2008). A new generation of flocculants based on hydroxamated polyacrylamide polymers (HxPAM) was developed in the 1980s. They delivered improved performance over a range of parameters, including improved thickener underflow densities and overflow liquor clarieties at lower dose rates, and increasing the flow rates through the polishing filters (Ryles and Avotins, 1996). For example, the change to HxPAM flocculants was credited as a significant enabler in achieving a 65% improvement in production rate without major capital costs at the Worsley refinery (Kahane and McRae, 1996). However, the higher unit costs of these new flocculants and ongoing improvements in polyacrylate/polyacrylamide technology slowed their adoption.

Liquid flocculants are generally supplied in diluted form to aid dosing and dispersion. The solvent oils enter the liquor circuit and make a minor contribution to the overall impurity input, but virtually all of the flocculant added to the mud settlers and washers reports to the bauxite residue where its impact is minimal (Pearse and Sartowski, 1984). Any negative side-effects effects to the main refinery process are usually attributable to incorrect application rather than inherent effect on the liquor. For example, over-dosing or inadequate mixing of flocculants can lead to excessive solids carryover in clarifier overflow liquors and binding of polishing filters (Pearse and Sartowski, 1984), overloading of clarifier rakes, and/or increased scale formation rates in tanks and pipes. Proper dosing and vessel design are essential in order to minimise the usage and maximise the effectiveness of flocculants (Kahane et al., 2008).

9.2. Dewatering aids

The use of organic dewatering aids to improve the filtration of gibbsite product prior to calcination has significant advantages in reducing the energy requirement for calcination, the volume of wash water required to remove liquor from the filter cake, and the amount of residual soda in the cake (Mura, 1998; Pearse and Sartowski, 1984; Singh et al., 1999; Wainwright, 1985). Dewatering aids are surfactants which work by reducing surface tension by adsorption at the air/liquid interface, and/or by reducing the solid/liquid contact angle by adsorption at the solid/liquid
interface. Surface tension reduction is achieved by the use of anionic surfactants such as sodium dodecyl sulphate (SDS), whereas cationic surfactants such as cetyl trimethyl ammonium bromide (CTAB) are used to reduce the contact angle. Non-ionic surfactants such as coco alcohol ethoxylates can affect both surface tension and contact angle, the relative effects being a function of structure, in particular the number of ethoxylate groups in the molecule (Puttock et al., 1984). The presence of high molecular weight compounds from the Bayer liquor adsorbed to the gibbsite can have a significant effect on the adsorption of dewatering aids, by enhancing the adsorption of anionic surfactants and decreasing the adsorption of cationic surfactants (Hind et al., 1999; Wainwright et al., 1986). Overall, it appears that anionic surfactants are the most important constituents of a successful dewatering aid (Singh et al., 1999; Wainwright et al., 1986), although a variety of formulations have been proposed to optimise performance. For example, the addition of a small amount of cationic surfactant to an anionic surfactant has been claimed to have significant benefits (Puttock, 1985).

In addition to their distinct process benefits, there may be negative effects associated with the use of dewatering aids. For example: ammonium-based cationic surfactants can hydrolyse to the corresponding amines in alkaline solution (Singh et al., 1999), which could be responsible for amine odours in the filtration area; the anionic surfactants may contain sulphonates (Osgerby and Osgerby, 1987; Puttock et al., 1984) which may contribute to sulphur dioxide or mercaptan emissions when calcined; and residual surfactant retained in the wash water may enter the main liquor stream where it could conceivably affect precipitation yield, foaming or oxalate filtration in other areas of the refinery.

9.3. Scale promotion and inhibition

The formation of scale on the surfaces of tanks, pipes and other process equipment is a major concern in the operation of alumina refineries. Some examples of the effects of oxalate and gibbsite scales are given above. Scale formation can be promoted by the presence of some organic compounds. For example, presence of gibbsite precipitation inhibitors can result in a tendency towards plate-like crystals, which in turn can lead to an increased gibbsite scale formation on pipes and vessel walls (Watling, 2000).

One of the most widespread and difficult scales in alumina plants is sodium aluminosilicate (desilication product, or DSP) scale, which typically forms on hot surfaces, particularly in heat exchanger tubes, digesters and flash vessels for example. Various chemical additives have been tested with the aim of inhibiting scale formation, generally through preferential adsorption of a polymer (Addai-Mensah et al., 2001). Most of these studies have met with limited success, however a proprietary formulation which does appear to be capable of preventing scale formation has recently been developed (Spitzer et al., 2005).

It is claimed that the additive acts by interfering with the growth of embryonic crystals in a catalytic fashion, so that it is effective at very low dose rates, and that extensive testing has revealed no detrimental side effects.

9.4. Miscellaneous additives

A variety of chemicals is added to the liquor which may impact yield by changing the particle size distribution of the solids in precipitation, and many of which contain surfactants and oils. These may be chemicals added deliberately to influence gibbsite particle size or shape (“crystal growth modifiers” (“CGMs”), see Section 5 above) or to increase oxalate stability, or which enter the liquor as a result of, for example: addition for a different purpose such as improving dewatering of solids in filtration; unintentional leakage such as of lubrication oils from process machinery; or contamination of reagents such as vegetable oils in bulk caustic soda due to inadequate cleanup between cargos. A number of process chemicals, such as liquid flocculants, contain oils as carriers (diluents) of the active component. Because Bayer process liquors are generally almost fully recirculated, any chemical which continuously enters the liquor stream has the potential to build up to unexpectedly high concentrations which may have significant effects on process efficiency and/or product quality. Recognition of this has led alumina producers to institute controls on the addition of chemicals to the process, including comprehensive impact testing prior to approval of any chemical for use. Process chemicals may contain ten or more individual components in formulations which are intended to target one particular aspect of the operation, such as dewatering aids applied to filtration. Such formulations are generally proprietary and may contain components with the potential for unexpected, and possibly severe, side effects elsewhere. As a result, effective use of process chemicals requires a good level of co-operation between supplier and customer, and rigorous testing of formulations before approving them for use in an alumina plant (Graham and Davies, 1990).

10. Volatile emissions

It has long been recognised that the digestion of bauxite is generally associated with odour emissions which are due to the formation of volatile organic compounds (VOCs) in the reaction of organic compounds with the alkaline Bayer liquor (Forster and Grocott, 1996). In a study at the Queensland Alumina plant, the non-condensable fraction of the digestion vapours (which account for approximately 2% of the total gaseous emissions from digestion, the remaining 98% being water vapour) were shown to account for 82% of the odour emissions associated with the plant (Graham et al., 2002). The proportion of the VOCs that could contribute to digestion odour formed only 0.3% of the mass of gases emitted (nearly 90% was hydrogen and 0.9% was methane, the remainder being mostly nitrogen, carbon oxides and oxygen) (Graham et al., 2002). Nevertheless, odour has become a key issue for some alumina plants (Coffey, 2002; Coffey and Donoghue, 2006; Coffey and Ioppolo-Armanios, 2004; Forster et al., 2005; Galbally, 2004, 2008), and is an emerging issue overall.

The generation of VOCs and hydrogen can be understood by reference to the base-catalysed redox reactions of organic compounds in digestion given in Part 1 of this review series (Power and Loh, 2010). Further insight into the mechanisms of hydrogen production has been provided by the recent work of Costine et al. (2010, 2011a, 2011b, 2012). The oxidation of complex organic compounds by water leads to hydrogen as the major reduction product, but can also lead to the generation of methane, propane and other volatile hydrocarbons as well as alcohols, aldehydes and ketones, as reduction products (Loh et al., 2010b). Consistent with this, methanol, acetaldehyde, formaldehyde, acetone and methyl-ethyl ketone have all been identified in the vapours from bauxite slurry storage (desilication) tanks, digesters and/or evaporators (Galbally, 2004, 2008; Galbally et al., 2012).

In addition, it is reasonable to suppose that precursor compounds containing nitrogen and sulphur groups would lead to the formation of ammonia, amines and mercaptans as reduction products, which, though present in trace amounts only, would undoubtedly contribute to the odours that characterise bauxite digestion.

Acknowledgements

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Appendix. Specific effects on precipitation of gibbsite of organic compounds generally found in Bayer process liquors

The compounds included here are those identified in Part 1 of this review series as being generally present in Bayer process liquors (Power and Loh, 2010). It is noted that not all authors agree on the nature of the specific effects in some cases; where there are disagreements the assessments shown in this table are an attempt to represent the consensus view. The references cited should be consulted for further information. It should also be noted that only compounds reported in the open literature as present in Bayer process liquors are included here, so this list excludes many of the compounds mentioned in this review which could present and potentially have effects at low concentrations.

Key:
- HAO = hydrate-active organic
- Yield = precipitation yield effect
- PSD = particle size distribution effect
- Soda = product soda effect
- N = no; Y = yes; L = lowers; R = raises

### Compounds

#### 1. Aliphatic acid anions

<table>
<thead>
<tr>
<th>Compounds</th>
<th>HAO</th>
<th>Yield</th>
<th>PSD</th>
<th>Soda</th>
<th>References</th>
</tr>
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<tr>
<td>Formate</td>
<td>N</td>
<td>L</td>
<td>N</td>
<td>N</td>
<td>Ang and West (1992); Brown et al. (1986); Verghese (1988)</td>
</tr>
<tr>
<td>Acetate</td>
<td>N</td>
<td>L</td>
<td>N</td>
<td>N</td>
<td>Ang and West (1992); Beckham et al. (2005); Brown et al. (1986); Verghese (1988); Wellington and Valcin (2007)</td>
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<tr>
<td>Propanoate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Butanoate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>No references found to specific effects.</td>
</tr>
<tr>
<td>Valerate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>Palmitate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>Stearate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>No references found to specific effects.</td>
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<tr>
<td>Oxalate</td>
<td>N</td>
<td>L</td>
<td>Y</td>
<td>Y</td>
<td>Brown et al. (1986); Brown and Cole (1980); Calato and Tran (1992); Kingsley and Wilcox (1986); Lever (1978); Lever (2004); Nikolic et al. (1999); Smeulders et al. (2001); The (1980); The and Bush (1987); Tucker et al. (1986)</td>
</tr>
<tr>
<td>Malonate</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td></td>
<td>Power (1991)</td>
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<tr>
<td>Succinate</td>
<td>N</td>
<td>N</td>
<td>–</td>
<td>Y</td>
<td>Brown et al. (1986); Grocott and Rosenberg (1988)</td>
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<tr>
<td>Glutarate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Adipate</td>
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<td>–</td>
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#### 2. Aromatic acid anions

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#### References


