

The surface chemistry of Bayer process solids: a review

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Abstract

The Bayer process is used for refining bauxite to smelting grade alumina (Al_2O_3), the precursor to aluminium. The process was developed and patented by Karl Josef Bayer 110 years ago, and has become the cornerstone of the aluminium production industry worldwide. Production of alumina reached 46.8 megatonnes (Mt) worldwide by the end of 1997, with Australia the worlds largest producer of bauxite and refiner of alumina with just under 30% of world production. Although the refining process is well established and the basic theories underpinning it are well defined, the fundamental chemistry of the Bayer process is not well understood. Of particular interest to industrial and academic researchers alike, is the chemistry of the Bayer process solids—aluminium trihydroxide, ‘red mud’ and sodium oxalate. The surface chemistry of these solids is of great industrial importance as the refining industry experiences significant restrictions due to limitations imposed on the process by surface chemical reactions. Of scientific interest is the conceptual advancement of our knowledge and understanding of the nature of surfaces under extreme (non-ideal) conditions. A review of the current literature relating to these important Bayer process solids is thus presented. While not exhaustive, the review is thorough and aims to familiarise the reader with current levels of understanding regarding the nature of Bayer process solids surfaces under Bayer process conditions, and the significant roles these solids play in the overall efficiency of the refining process. It is hoped that this review will provide a useful starting point for researchers new to the area of Bayer process research, whilst also stimulating further fundamental research in this economically and scientifically significant area. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Australian aluminium industry was born in 1955 when a State/Commonwealth joint venture

began producing alumina and aluminium at Bell Bay in Tasmania. The venture was the result of the desire of Governments of the day to end Australia’s dependence on overseas supplies of aluminium, while also acquiring the skills and technology to produce this valuable commodity. The initial capacity of the plant was a (relatively) meagre 12 kilotonnes (kt) per year, with all the bauxite used imported.

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Today, the Australian aluminium smelting and alumina refining industries contribute AUD\$2.2 billion and AUD\$2.5 billion, respectively to Australia's export income. Current forecasts suggest this contribution is likely to increase to a total of AUD\$5.7 billion by the end of 1998 [1]. Regrettably, the refining industry experiences significant restrictions due to limitations imposed on the process by surface chemical reactions. Currently, these reactions either directly or indirectly cost the Australian alumina refining industry at least AUD\$150 million per year in lost production. Development of an understanding of the chemical nature of these reactions is vital if Australian refiners are to remain competitive on the world stage. Planned capacity expansions in China, India and Vietnam, combined with a continuing push for increased capacity utilisation at existing refineries, demand this of Australian refiners.

Australia is the world's largest producer of bauxite and refiner of alumina. In 1988, it was estimated that Australia had bauxite stocks of over half a billion tonnes [2], with the major reserves located in the Darling Ranges (Western Australia), Gove (Northern Territory) and Weipa (Queensland) areas (Fig. 1). Currently, Australia mines 43 megatonnes (Mt) of bauxite per annum, producing 13.3 Mt of alumina, or just under 30% of annual world production [1]. Given this large production tonnage, Australia produces a relatively small amount of aluminium per annum (1.4 Mt, or just over 5% of annual world production; [1]). Most indicators suggest aluminium production will gradually increase with time, however the (relatively) high cost of electrical power in Australia will always be somewhat of a limiting factor in this respect.

Many bauxite ores are of poor quality (<40% available alumina; [3]) and have a relatively high organic content. Bauxites having 60% available alumina are relatively rare (*pure* gibbsite— $\text{Al}(\text{OH})_3$ —has only 65.4% available alumina), and ores having 50% available alumina are considered high quality by most alumina refiners. Unfortunately, many Australian ores are at the lower end of the scale, with Darling Range bauxite being particularly low in available alumina content (30–35%) and having high silica and iron

oxide content [4]. The high organic content of Australian ores (total organic carbon—TOC \approx 0.15–0.30 (w/w)%) is of great concern because of the surface-active nature of many of the organic compounds that find their way into the Bayer process. These surface-active compounds are major factors in the limiting surface chemical reactions mentioned previously and, as such, are the subject of ongoing investigation at a number of academic and/or industry supported research centres.

2. Aluminium and alumina—a global perspective

Aluminium is electrochemically produced from alumina using the Hall–Héroult process. Alumina is in turn produced from the ore bauxite using the Bayer process. Aluminium's properties are well documented, and include its light weight, low melting point, corrosion resistance, good thermal and electrical conductivity, and high reflectivity. In addition, the physical properties of aluminium can be enhanced through alloying, mechanical working and heat treatment. Aluminium is thus extensively used worldwide in a wide range of light, high tensile strength, alloys (which may also contain manganese, nickel, copper, zinc and other metals). These alloys are in turn used in the aeroplane and maritime fabrication industries, machinery manufacture, and in the casting of lightweight components for myriad other applications (cooking and eating utensils for example). The range of properties offered by aluminium alloys, combined with its inherent light weight, have resulted in the widespread use of aluminium on a global scale. Most alumina produced is used for the production of aluminium, however alumina does have several other uses, the majority of which take advantage of its chemical inertness and/or large surface area. Alumina is, for example, used in chromatography and catalysis, in the formation of refractory materials, and as a dehydrating agent.

Alumina and aluminium are valuable commodities worldwide. One has only to look around oneself, be it at home, at work, or at play, and one will invariably find aluminium of some form.

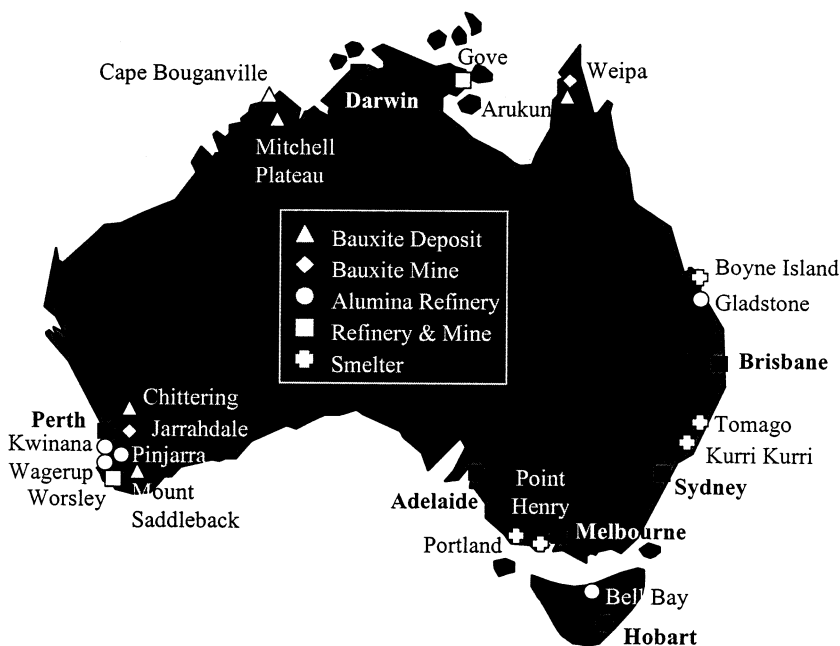


Fig. 1. Location of bauxite deposits, bauxite mines, alumina refineries and aluminium smelters within Australia.

Apparent world consumption of primary aluminium is estimated to have increased in 1997 to ≈ 21.2 Mt, with consumption forecast to increase further to 21.7 Mt in 1998. World production of primary aluminium is thus expected to increase to 22.2 Mt in 1998, after a similar increase in 1997. Not surprisingly, world alumina production is anticipated to follow suit, with production to reach 46.8 Mt by end 1997. Aluminium and alumina prices are also expected to increase in 1998 (after recent falls in both) as demand increases with stronger world economic growth, with prices set to reach US\$1871 and US\$227 per tonne, respectively [1].

3. The Bayer process

In 1888, Karl Josef Bayer developed and patented a process, which has become the cornerstone of the aluminium production industry worldwide. The Bayer process, as it has become known, is used for refining bauxite (named after Les Baux, the district in France where the ore was first mined) to smelting grade alumina, the precursor to alu-

minium. Typically, depending upon the quality of the ore, between 1.9 and 3.6 tonnes of bauxite is required to produce 1 tonne of alumina.

The Bayer process involves the digestion of crushed bauxite in concentrated sodium hydroxide (caustic) solution at temperatures up to 270°C. Under these conditions, the majority of the aluminium containing species in the ore are dissolved (1), leaving an insoluble residue (called *red mud* in the alumina refining industry) composed primarily of iron oxides, quartz, sodium aluminosilicates, calcium carbonate/aluminate and titanium dioxide (generally present at trace levels), which is removed by settling/filtration. After solids separation, aluminium trihydroxide (gibbsite; $\text{Al}(\text{OH})_3$) is precipitated. This is achieved by cooling the solution and seeding with gibbsite, essentially reversing the initial dissolution process (2). The gibbsite is then removed and washed prior to calcination, where the gibbsite is converted to alumina (3). The extraction process depends almost entirely upon chemical processes occurring at the solid/aqueous interface, as do many of the important industrial and physical processes used throughout the world today, and can be summarised as follows:

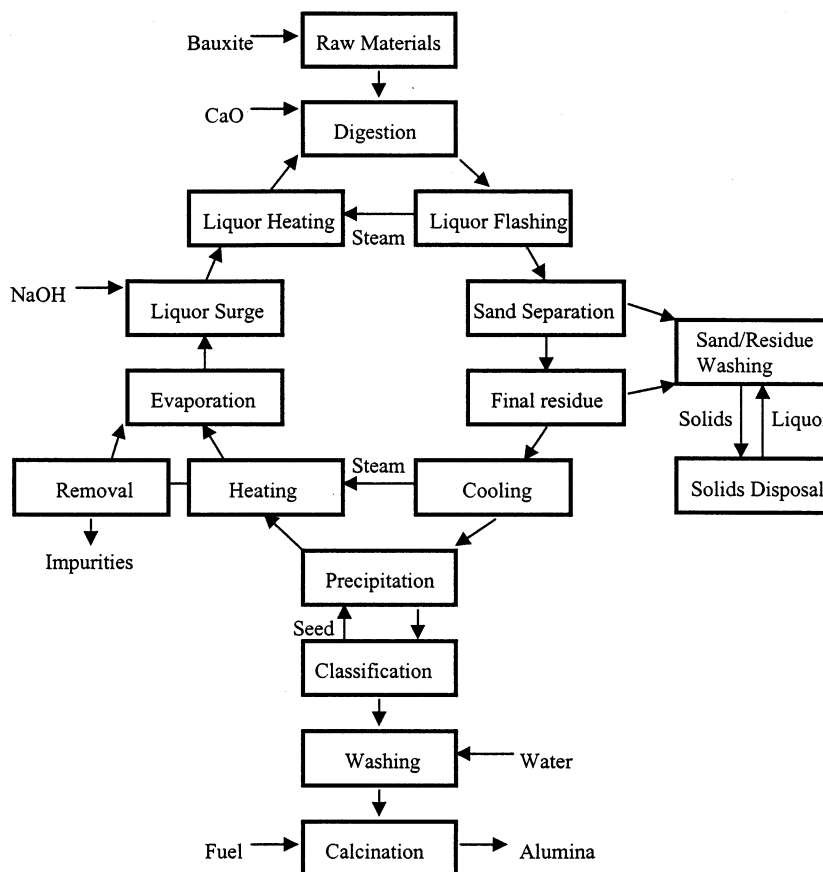
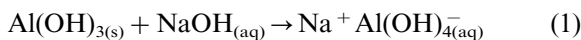
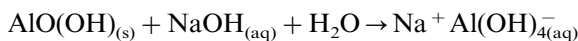


Fig. 2. Schematic representation of the Bayer process depicting its cyclic nature.

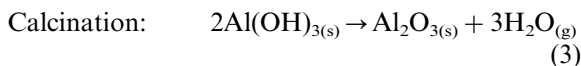
Extraction:



and,



Precipitation:



Bayer process liquors are extremely alkaline ($\text{pH} > 14$), of high ionic strength (6–7 M $[\text{Na}^+]$), and contain a wide variety of organic compounds including polybasic acids, polyhydroxy acids, alcohols and phenols, humic and fulvic acids, and other carbohydrates [5]. These organic com-

pounds are derived largely from decomposed vegetation and roots, give some Bayer liquors their characteristic deep brown-red colour and distinctive odour and, more often than not, complicate chemical analysis. Under the alkaline oxidative conditions existing in the Bayer process, these complex organic compounds are broken down to more simple compounds such as the sodium salts of succinic, acetic and oxalic acids. Predominant among these salts is sodium oxalate.

As the Bayer process is a cyclic one (Fig. 2), any organic matter entering the process stream accumulates with each cycle of the process, with steady state determined by process input and output streams. The major organic exits are generally through the red mud circuit, with the product gibbsite, and via any organics removal processes

in operation (oxalate removal, liquor burning or wet oxidation for example). The major negative effect of this organic matter on the Bayer process is during the gibbsite precipitation stage. If not controlled, the oxalate in Bayer liquor builds up to a certain level of supersaturation, before crystallising in an acicular (fine, needle-like) form. These fine sodium oxalate needles nucleate gibbsite and inhibit its agglomeration, resulting in fine, undesirable gibbsite particles less than ideal for calcining. For some alumina refiners, it is estimated that a reduction of only 0.1 g l^{-1} in the exit concentration of sodium oxalate in the oxalate removal circuit would result in significantly increased plant performance.

3.1. The Australian Bayer process

As mentioned above, the main steps of the Bayer process involve digestion, clarification, precipitation and calcination. While the last two steps are relatively similar the world over, the digestion step is largely dependent upon the form of the aluminium present in the bauxite and varies considerably throughout the world. The three main aluminium minerals present in bauxite are gibbsite (aluminium trihydroxide), boehmite and diasporite (aluminium oxyhydroxides), with most ores containing gibbsite and boehmite. European bauxites are composed almost entirely of the monohydrate forms (Greek bauxite is largely diasporic), with ores from the rest of the world composed primarily of gibbsite and a small amount of boehmite and/or diasporite. Eastern European and Chinese bauxites generally contain boehmite and diasporite, while bauxites from Surinam, India and the United States are predominantly composed of gibbsite [3].

The relative degree of hydration of the mineral is an important economic factor in its processing, with more extreme digestion conditions required for ores containing boehmite and diasporite, as opposed to those containing predominantly gibbsite. Australian ores, with the exception of those mined in the Weipa area, are predominantly composed of gibbsite—Darling Range bauxites contain almost none of the

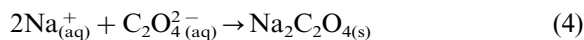
monohydrate form—and consequently require relatively mild digestion temperatures and caustic concentrations. These are typically of the order of 145°C and $4\text{--}5 \text{ M NaOH}$, respectively, compared to $170\text{--}265^\circ\text{C}$ and up to 7 M for ores containing the oxyhydroxide forms [3].

Thus, while Australian alumina refiners are forced to contend with bauxites of generally poor quality (exhibiting low alumina content and high organic content), they are advantaged by the fact that they can extract bauxitic alumina using relatively mild conditions. The comparatively poor nature of Australian bauxite deposits is thus offset somewhat by the less cost intensive extraction procedures required, and is one reason for Australia's ongoing competitiveness on the world stage.

4. Bayer Process solids

Two main chemical reactions limit the productivity and efficiency of alumina refineries in Australia and the rest of the world. These reactions are the precipitation of gibbsite (2) and the crystallisation of sodium oxalate (4). Additionally, the flocculation of fine red mud is an expensive and sometimes limiting operation in the overall refining process.

Oxalate crystallisation:



The aforementioned chemical reactions and the flocculation of red mud are *surface reactions*. As such, their rate can be controlled by the chemistry of the surfaces of the solids and by the presence of surface-active impurities present in the process stream. At present, the surface chemistry of these Bayer process solids is not well understood. Very little is known at all, in fact. The main reason for this limited knowledge is that, until recently, few suitable analytical techniques have been available to examine the surfaces of these solids and the compounds that adsorb onto them. In particular, no in situ techniques have been available.

Not surprisingly, of the three Bayer process solids described, gibbsite seems to have received the greatest research attention from a Bayer process point of view. Investigations pertaining to the nucleation, growth, agglomeration and precipitation of gibbsite have (again, not surprisingly) been particularly prevalent. Research involving red mud has also been reported, with the investigations having a distinct environmental theme. Considering the significant role it plays in the Bayer process, very little has been reported on sodium oxalate.

4.1. Gibbsite (aluminium trihydroxide— $Al(OH)_3$)

The Bayer process is based upon the precipitation of crystalline gibbsite from caustic aluminate solutions. As such, observations pertaining to the nucleation, growth, agglomeration and precipitation of gibbsite under Bayer process conditions are extremely relevant in the context of Bayer process efficiency and productivity.

4.1.1. Structure and morphology of gibbsite

Gibbsite is the most common form of aluminium containing species produced in the Bayer process, and is arguably the most important material present. Gibbsite contains cubic close packed hydroxide ions within layers of edge-shared $Al(OH)_3$ units [6]. These layers of $Al(OH)_3$ are the most prominent feature of gibbsite, giving it a sandwich-like appearance when viewed along the b -axis. The space group of gibbsite is monoclinic or triclinic, with the lower symmetry space groups a result of the distortion of the higher symmetry close packing arrangement of the hydroxide ions.

The 001 crystal face forms the majority of the gibbsite surface [7], and can be observed in the hexagonally shaped face of the thick plates commonly found in the Bayer process. The 001 face is coplanar with the distinctive layers of gibbsite, with its predominance attributed to strong intralayer ($Al-OH$) bonding and comparatively weak inter-layer hydrogen bonding. The edge faces of gibbsite crystals are the 100 and 110 planes which trace voids in the crystal lattice and pass through regions containing only hydroxide groups.

Investigations concerning the structure and morphology of aluminium trihydroxide precipitated from pure, synthetic caustic aluminate liquors have also been reported. Lee et al. [8] found gibbsite formation to be favoured at higher temperatures ($\sim 70^\circ C$), with bayerite (an $Al(OH)_3$ polymorph) formed predominantly at room temperature. Addai-Mensah [9] also found gibbsite to be the main product from isothermal batch precipitation at similar temperatures (65, 75 and $80^\circ C$), with a small amount of bayerite formed during the early stages of precipitation (no evidence of an additional phase such as amorphous aluminium trihydroxide was found). Gibbsite seeded liquors were found to produce gibbsite only in both studies [8,9]. In situ studies by Counter et al. [10] reported the dissolution of gibbsite at atmospheric pressure to result in gibbsite only. However, after 16 h at $160^\circ C$, identical solutions yielded a crystalline product of gibbsite and bayerite. Solutions prepared from aluminium behaved identically to those prepared from gibbsite with the additional heating. The authors proposed that solutions prepared at atmospheric pressure were self-seeding, providing gibbsite-like templates for nucleation of the single crystalline phase, and also that the different methods/materials used for synthetic liquor preparation could account for variances in physical properties determined by different researchers.

Interestingly, Lee et al. [8] found the nature of alkali metal ion to be significant, with hexagonal plates resulting from sodium aluminate solutions, and hexagonal prisms resulting from potassium aluminate solutions. These results suggest that the alkali metal ion plays an important role in the crystallisation mechanism.

4.1.2. Nucleation, growth, agglomeration and precipitation

In caustic aluminate solutions, nucleation is generally observed within 30 min of seed addition [11]. This induction period is seen to decrease with increasing seed charge and temperature, with no precipitate formed without seed addition even after several days at room temperature, suggesting a heterogeneous breeding type nucleation. It has been suggested that broken seed fragments

provide the main source of new crystals, however this alone does not account for the effect of temperature on the generation of fine seed particles at lower temperatures. Hydrogen bonding between the aluminate ions, imparting a quasi-crystalline structure to the solution, has also been proposed as a mechanism of nucleation [11]. Secondary nucleation, nucleation occurring only in the presence of seed crystals, can occur with and without dendritic growth and appears to be a two-dimensional surface nucleation phenomenon. Both forms of nucleation can be dramatically affected by the presence of impurities which alter the characteristics of the adsorbed layer, however this phenomenon is not well understood [12]. In an attempt to further elucidate gibbsite nucleation mechanisms, semi-empirical quantum mechanical molecular modelling analysis of the heats of formation of a wide range of aluminium species has recently been performed [13]. The authors were able to propose a new crystallisation mechanism involving the freeing of bound (chelated) water molecules, suggesting a possible route for the change from 4-fold hydroxyl coordination in the aluminate ion to 6-fold hydroxyl coordination in gibbsite.

The quantitative aspects of new crystal formation have been examined, with models relating saturation number, initial supersaturation, induction time, seed surface area and liquor impurities developed. In general, induction time has been shown to decrease with increase in initial supersaturation, temperature and seed surface area. At sufficiently high surface areas, no measurable induction period could be obtained and little or no secondary nucleation was observed [14,15]. Extremely slow rates of precipitation have been observed during the induction period, confirming the existence of precipitation during this time. Strong evidence is also presented linking the end of the induction period to the onset of secondary nucleation [16]. Other models have been proposed in order to define the basic mechanisms of nucleation, growth, agglomeration and breakdown. Linear growth rate, rate of deposition, rate of nucleation and rate of agglomeration have been identified as being amongst the most important rate processes. The mechanisms

presented are claimed to be the most accepted, as applicable to industrial crystallisation from solution [17]. Models for predicting Bayer process productivity under industrial conditions, and suited to both batch and process situations, have also been described. Both empirical [18,19] and theoretical [20,21] models have been presented.

Agglomeration is an important stage of the Bayer process in which the initial size of the gibbsite particles increases. Agglomeration rate has been shown to increase with increasing seed charge up to a certain point and, thereafter, a decreased rate is observed. Increased stirring rates also have a negative effect, while increased supersaturation results in increased rates of agglomeration [22].

4.1.3. Effect of impurities on gibbsite precipitation

The detrimental effects of organic impurities on the precipitation of gibbsite from Bayer and Bayer-like liquors are well documented (see for example [3]). These impurities have been shown to result in high gibbsite impurity content, liquor and gibbsite colouration, caustic losses (due to formation of organic sodium salts), and increased solution viscosity and density [23]. Various organic compounds have been investigated, with glucoisosaccharinate [24], gluconate [25,26] tartrate [25], and mannitol [23,25] shown to be responsible for decreased gibbsite precipitation yield. Rossiter et al. [26] were able to demonstrate that gibbsite growth rate suppression by gluconate was attributable to reduction in available surface area, and not a change in surface activity. Polyols have also been found to inhibit gibbsite crystallisation from synthetic Bayer liquors, with the strongest inhibitors shown to complex aluminate species in Bayer liquor [27]. Similar organic compounds, sharing the common characteristics of relatively acidic, adjacent hydroxyl groups, have been shown to increase soda (Na_2O) concentration in the gibbsite product [28]. One group of workers was able to develop a mathematical model which allowed them to predict the precipitation yield of any liquor, given its chemical composition and precipitation conditions [29].

In a study investigating the dewatering of gibbsite, significant levels of anionic and cationic surfactant adsorption were observed from aqueous solution [30]. Cationic surfactant (cetyltrimethylammonium bromide) was found to exhibit much higher levels of adsorption than anionic surfactant (sodium lauryl sulfate), and the presence of adsorbed humic material was found to enhance adsorption of both surfactant types. Recent unpublished work by the authors supports this finding, with various alkyltrimethylammonium bromides found to adsorb to the surface of gibbsite under Bayer-like conditions (high ionic strength, high pH).

The solubility of gibbsite is also effected by the presence of common Bayer liquor impurities. The sodium salts of carbonate, sulfate, chloride and Bayer organics have all been found to raise the solubility of gibbsite during precipitation, with the organic impurities found to have the greatest effect, followed by chloride, carbonate and sulfate [31].

As previously mentioned, sodium oxalate has also been shown to have deleterious effects on the gibbsite precipitation process. The most commonly reported effect on the precipitation process is the generation of fine gibbsite particles (fines), due to the presence of oxalate (see for example [32]). Oxalate can also affect gibbsite particle size classification, agglomeration efficiency, smelting procedures, soda concentration and scale growth rates. Below the critical oxalate concentration (i.e. below its stability limit—the solution is supersaturated), soluble oxalate has also been found to decrease gibbsite precipitation yield [33].

The consequence of high process oxalate concentrations is a poor product yield combined with low product purity and poor handling properties. The net result is a less valuable product and reduced profit margin, particularly in areas where the organic content of the bauxite ore is high.

4.2. Red mud

Red mud is produced during the digestion of bauxite with sodium hydroxide. It generally exits the process stream as a highly alkaline slurry (pH 10–12.5) at ≈ 15 –30% solids [34], from where it

is pumped away for appropriate disposal. Red mud is composed primarily of fine particles of silica, aluminium, iron, calcium and titanium oxides and hydroxides (along with other minor components), with the iron impurities responsible for the brick red colour of the mud [35]. Red mud thus has a complex chemical composition (largely dependent on the bauxite source) and, due to its high calcium ($\text{CaCO}_3/3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide content, is relatively toxic and can pose a serious pollution hazard. In addition to this, the amount produced as a result of the refining process is significant.

Red mud is thus of interest to researchers for a number of reasons and has been the subject of many detailed investigations. Of particular interest has been the influence of red mud on the refining process, red mud disposal methods and their influence on the environment, and the application of this abundant waste product in other, unrelated areas.

4.2.1. Behaviour of iron minerals during digestion and clarification

Separation of bauxite residue (red mud) from the process stream of Bayer refineries is a critical step in the refining process. It is affected by processing conditions, as well as the quality of the bauxite [36]. The most common iron minerals in red mud are goethite ($\alpha\text{-FeOOH}$) and haematite ($\alpha\text{-Fe}_2\text{O}_3$). The properties of these minerals, and the chemical interactions they undergo during the refining process, are of great significance to alumina refiners as these compounds can have dramatic effects on post digestion/clarification process steps.

Bauxites rich in goethite have been associated with Bayer process clarification problems. The fine particle size (0.02–2 μm ; [36]) and unique surface properties of goethite impart an adverse effect upon the settling behaviour of red mud. These small particles pose significant problems during clarification because of their inherently slow settling rates. Dissolved iron may precipitate in the form of fine particles ($<1 \mu\text{m}$; [36]) or be transported into subsequent process steps, ultimately contaminating the final gibbsite product. Iron contamination at this stage imparts an unde-

sirable colour to the gibbsite (an important factor in applications where the colour of the gibbsite is of issue), and also affects the quality of the aluminium metal end product [36].

The separation of residual solids from process solutions is generally accomplished (during clarification) by gravity settling, decantation and filtration. The settling process relies upon the aggregation of small particles, with the process often enhanced by the addition of various flocculation agents (polyacrylamides and polyacrylates have been shown to be effective flocculants at high pH [37]). The effectiveness of these flocculants is determined by their interaction with the surface(s) of the particles found in solution, this being largely dependent on the properties of the iron mineral(s) present [36].

Basu et al. [36], have investigated the chemical interactions of iron minerals during Bayer digestion and clarification, and found the clarification behaviour and chemical reactions of iron minerals with Bayer liquor components to have a significant influence on process efficiency and product quality. Investigations of model systems showed the equilibrium solubility of iron in sodium aluminate solutions to increase with temperature and concentration of free soda (Na_2O). Solubility was also affected by the presence of liquor impurities, especially humates. Under clarification conditions, dissolved iron was found to reprecipitate as an iron hydroxide gel. Overall, the clarification properties of the iron minerals were found to depend on the type of iron mineral present, flocculant properties, process parameters and the nature of liquor contaminants present.

4.2.2. Disposal of red mud

For every tonne of alumina produced, between 1 and 2 tonnes (dry wt.) of red mud residues are produced [38]. This residue is highly alkaline, of relatively high surface area ($13\text{--}22\text{ m}^2\text{ g}^{-1}$), contains a number of chemical and mineralogical species [35] and, if not adequately contained, can impact dramatically on the environment. The disposal of this residue thus constitutes a significant proportion of the overall production cost of alumina, and is an area of ongoing concern to alumina refiners worldwide.

Conventional disposal methods have revolved around the construction of clay-lined dams or dykes, into which the red mud slurry is simply pumped and allowed to dry naturally. The design and construction of such residue impoundments has varied considerably over the years [39], with disposal practices generally dependent upon the nature of the immediate environment. The operation of conventional disposal areas was simple and inexpensive, however the potential impact on the surrounding groundwater and environment, and difficulties associated with surface rehabilitation, forced significant changes in disposal practices [38]. Doubly sealed impoundments, incorporating a polymeric membrane as well as clay lining, and drained lakes, having a drainage network incorporated in the lining material, have subsequently seen widespread use. Drained disposal systems have been found to reduce the threat of the residue to the environment, while also increasing storage capacity as a result of better residue consolidation [35]. Dry disposal of bauxite residue, involving enhanced dewatering and evaporative drying, has also been found to further decrease environmental risks and lower overall disposal costs [38].

The disposal of bauxite residues in an environmentally sound manner, and the development of new, site-specific land reclamation and revegetation practices (the capping of used residue disposal areas for example; [40]), is today demanded of alumina refiners worldwide. Thankfully, the world's major refining bodies seem to have responded to the challenge of implementing environmentally sound production practices, and are constantly seeking new and improved methods of residue disposal.

4.2.3. Applications of red mud

A great deal of research has been undertaken with the specific aim of the development of techniques suited to the utilisation of red mud in other, unrelated areas. Red mud is a relatively abundant industrial waste product, the disposal of which is a complicated, cost intensive process. Alumina refiners and researchers have thus devoted significant time and resources to the search for economically viable means of reducing

the volume of waste to be disposed of. Unfortunately, despite this ongoing research, economic uses for bauxite residue are virtually non-existent [35]. The search continues nonetheless.

Successful attempts at recovering alumina and soda from bauxite residues have been made (see for example [41]), however, given the (relatively) high quality of bauxite generally available to refiners, these processes could not be economically justified [35]. The recovery of iron (see for example [37,42,43]), titanium dioxide [44], and other minor elements (vanadium [45] and rare earths [46] for example), has also been attempted, again without commercial success. In general, chemical processes aimed at recovering a constituent of red mud have suffered from inadequate economics and the creation of further disposal problems [35].

The clay-like structure of bauxite residue has been noted by a number of researchers, who have demonstrated that, when fired, red mud becomes a useful ceramic material. The residue can be used in the manufacture of tiles, bricks and insulating materials (see for example [44,47], however the residue must be thoroughly washed and dried prior to use, adding to the cost of the recycling process [35]. Red mud and bauxite have also been used for the production of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ceramic fibres [48]. An important consideration with the use of red mud in building materials is the increased presence (due to the refining process) of naturally occurring radioactive materials.

Industrially, attempts have been made to use bauxite residue as a pH modifier in the heap leaching of gold ores [49], in the removal of sulfur compounds from kerosene oil [50], the hydrogenation of anthracene [51,52], coals and aromatic compounds [53], and as a pigment in anticorrosive marine paints [54].

Attempts have been made to use bauxite residue in agricultural situations. Red mud has been considered for use in acidic soils (because of its alkaline nature), and has subsequently been used as a substitute for agricultural limestone, and an amendment for acidic sand belts. Not surprisingly, bauxite residue has also been used as a treatment for iron deficient soils [35]. Red mud has also been used in sandy soils to increase phosphorous retention [55], to increase nitrogen

and phosphorous removal from sewage effluent [56], and as a flocculant in the treatment of dairy waste water [57]. Toxic heavy metals have been removed from aqueous solution using red mud based adsorbents [34,58], while the reduction in mobility of heavy metals has been achieved through the addition of residue to compost [59].

4.3. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$)

Uncontrolled oxalate crystallisation in the Bayer process is highly undesirable for a number of reasons. Surprisingly then, little fundamental research has been reported on sodium oxalate as regards the significant role it plays in the Bayer process. A volume of literature concerning the role of sodium oxalate in the Bayer process does exist, however the investigations tend to be industry driven, and are mostly empirical in nature. Unfortunately, the majority of research reported involving adsorption of/onto sodium oxalate (or the oxalate anion) has focussed on oxalate the *adsorbate* or *ligand*, not the *adsorbent*. Reported research into solid phase sodium oxalate, other than fundamental structurally and morphologically oriented studies, is (until recently) almost nonexistent.

4.3.1. The structure and morphology of sodium oxalate

The crystal structure of sodium oxalate was first investigated by Hendricks [60] in the late 1930s, with the results inconclusive [61]. The crystal structure of sodium oxalate has since been determined more accurately by Jeffrey and Parry [61], and further refined by Reed and Olmstead [62]. The space group of sodium oxalate is monoclinic, taken as $\text{P2}_1/a$ [61]. The unit cell parameters with reference to the $\text{P2}_1/c$ space group (a - and c -axes interchanged) are $a = 3.449 \text{ \AA}$, $b = 5.243 \text{ \AA}$, $c = 10.375 \text{ \AA}$, and $\beta = 92.66^\circ$ [62]. The oxalate ion is planar within experimental limits (Fig. 3), with each sodium ion surrounded by eight oxygen atoms in a distorted octahedral coordination [61,62]. When grown from aqueous solution, the sodium oxalate crystals grew predominantly as prisms elongated along the a -axis, and exhibited well developed 011 , $0\bar{1}\bar{1}$, $0\bar{1}1$, and

$0\bar{1}\bar{1}$ faces, and poorly developed 100 basal faces. A less common crystal habit was reported to have well developed 010 faces.

Strom et al., using a first-principles application of the Hartman–Perdok crystal growth theory (which defines layers as energetically optimal connected networks or F-slices), have demonstrated the derivation of growth layers (F-slices) using sodium oxalate as a test molecule [63]. Using this method they were able to determine the composition and morphological importance of growth layers with respect to the oxalate molecule. The energetically favoured growth layers were identified, and the theoretical morphology determined. In a second paper [64], the authors were able to construct the structural morphology of sodium oxalate (based upon the application of the aforementioned method, and energy computations of electrostatic and Van der Waals forces), then compare theoretical and experimental oxalate morphologies.

Sodium oxalate crystals grown from aqueous solution were characterised by twinning, while industrially grown crystals were found to be needle-shaped (acicular; [64]). In addition to twinning, growth from pure aqueous solution resulted in a drastic change in the relative morphological importance of the faces. The theoretical morphology was found to be richer than the experimentally obtained morphology, exhibiting many of the properties desirable in an industrial crystallisation situation. The difference between theoretical and experimental morphologies was found to

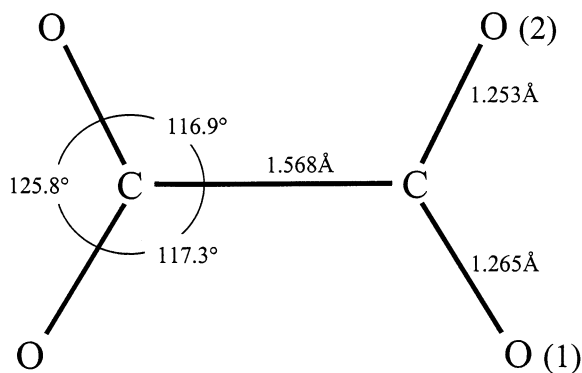


Fig. 3. The planar oxalate ion (adapted from refs. [61,62]).

be dependent on the composition of the mother phase (or liquor), and the overall morphology of the industrially grown crystals bore no resemblance to either the pure solution growth or the theoretical form. Attempts to explain these differences were hampered by a lack of knowledge regarding the exact composition of the mother phase. The authors concluded that knowledge of the structure of inhibiting organic species present in industrial liquors would contribute significantly toward elucidating the mechanisms responsible for the slow kinetics and unfavourable industrial morphology.

4.3.2. Oxalate adsorption studies

As touched upon previously, sodium oxalate the adsorbent has (to the best of the authors knowledge) been the subject of few reported studies. This is most probably attributable to a number of obstacles confronting the researcher interested in adsorption to the oxalate surface. Possibly the most significant of these is the water-soluble nature of oxalate. This, combined with the relatively low surface area of sodium oxalate and the desire to obtain in situ results, has made the task a demanding one. This situation has changed recently however, with a number of papers appearing in the literature.

Using Fourier transform infrared (FTIR) attenuated total reflection (ATR) spectroscopy, one group of workers have recently developed a method for the in situ investigation of the oxalate surface under Bayer-like conditions (pH 12–13; $> 5 \text{ M } [\text{Na}^+]$) [65]. Using this method, they were able to detect the adsorption of a series of adsorbed quaternary ammonium (QA) compounds in a quantitative manner (Fig. 4) [66]. Using this method, dose-response curves were obtained for a series of saturated alkyltrimethylammonium ($R = \text{C}_{12}, \text{C}_{14}, \text{C}_{16}$) bromides (and a synthetic, oxalate stabiliser formulation—N138) adsorbed to the surface of sodium oxalate under the aforementioned extreme conditions (Fig. 5). Results suggested adsorption in the order $\text{C}_{14} > \text{C}_{12} > \text{C}_{16}$ with the N138 formulation falling between the C_{12} and C_{16} compounds, and also suggested that the C_{12} and C_{14} QAs may adsorb to the oxalate surface in a predominantly perpendicular manner,

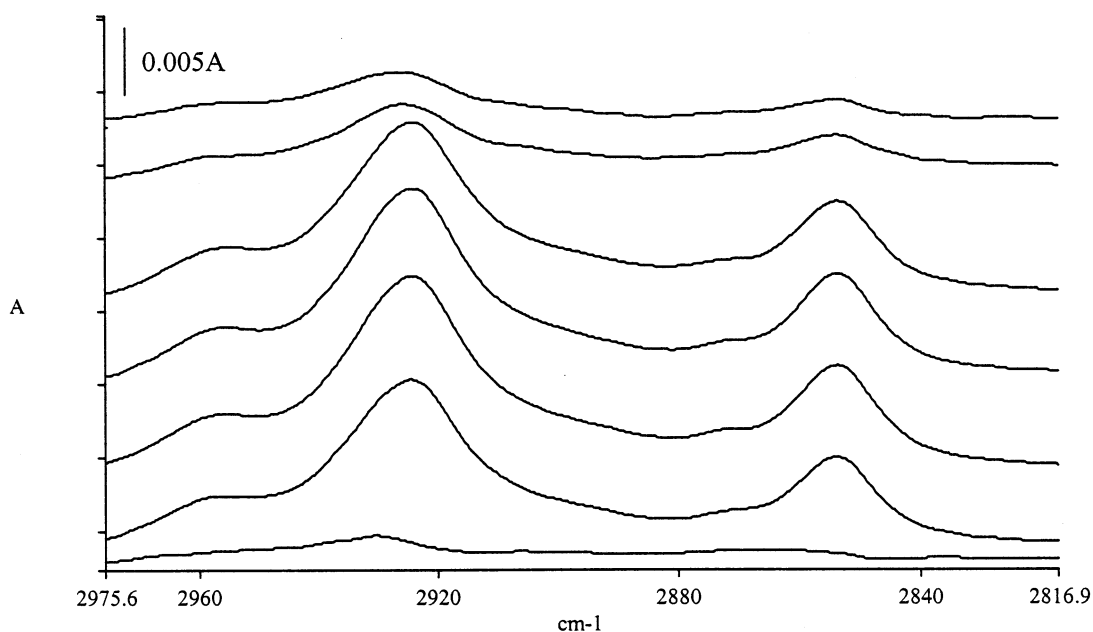


Fig. 4. Representative interfacial spectra of the adsorbed C_{14} QA at 0, 3, 5, 7, 10, 20 and 50 ppm initial QA concentration (bottom to top).

with the amount adsorbed increasing with increasing alkyl chain length. The C_{16} compound on the other hand, may adopt a coil-like structure at the oxalate surface and, as a result, adsorb to a lesser extent than the C_{12} and C_{14} QAs. Decreased adsorption observed at higher QA concentrations was attributed to the formation of large cylindrical or lamellar micelles exhibiting increased stability relative to the adsorbed form of the QA. The formation of these large micellar aggregates was a

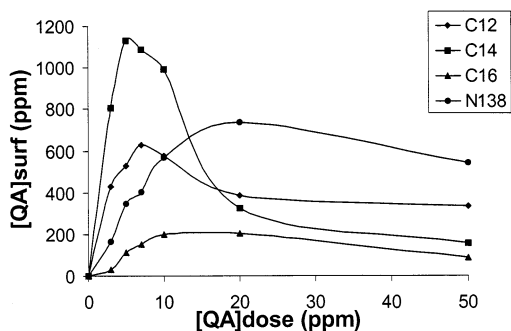


Fig. 5. Dose-response curves for C_{12} , C_{14} and C_{16} QAs, and N138.

result of the high ionic strength of the adsorption matrix.

The same authors were also able to develop a sensitive, specific capillary gas chromatographic (GC) mass spectroscopic (MS) assay for the quantitation of the aforementioned series of QAs in Bayer liquors [5], as well as a more sensitive electrospray MS method for the same compounds [67]. Both methods seem well suited to the measurement of adsorption isotherms for these types of compounds on Bayer process solids.

A number of studies have been reported in which the adsorption of oxalate onto various solid surfaces has been investigated. Cleghorn et al. [68] studied the adsorption of the oxalate anion at the red mud aqueous electrolyte interface, to test the postulate that the removal of oxalate, hydroxide and other species (under Bayer-like conditions) was dependent upon adsorption on the surface of red mud. They investigated the adsorption characteristics of sodium oxalate from aqueous alkaline solutions onto unmodified and treated Jamaican red mud, and some of its pure mineral components. The major

components of red mud exhibited positive adsorption of the oxalate anion, with haematite the most active adsorbent. The adsorption process was found to have a strong inverse dependence on the pH of the aqueous phase, with the experimental data found to best fit the BET adsorption isotherm (this being consistent with the heterogeneity of the surface).

In a series of papers detailing adsorption on hydrous oxides [69–71], oxalate (added as the acid) was one of a number of ligands investigated. The amount of oxalate adsorbed to goethite was found to vary from approximately zero at pH 8 to $\sim 100 \mu\text{mol g}^{-1}$ at $\text{pH} \leq 4$, with the oxalate anion adsorbed in a binuclear manner initially, and forming a monodentate complex as adsorption density increased [69]. On gibbsite [70], oxalate adsorption (at low solution concentrations) was found to occur only on sites exposed on edge faces of the crystals studied. Oxalate adsorbed in a bidentate form, with gibbsite found to adsorb more oxalate than goethite of comparable surface area ($\text{pH} \sim 7$; low solution concentrations). When evaporated onto goethite [71], oxalate was adsorbed via ligand exchange, forming binuclear bridging complexes.

Adsorption of oxalate onto other, non-Bayer solid surfaces has been reported. Shimabayashi et al. [72] found adsorption of the oxalate ion onto hydroxyapatite to be reversible and of Langmuir type over the pH range 7.5–12.0 (30°C). The amount of oxalate adsorbed from sodium oxalate was found to be larger than that from potassium oxalate, due to the size effect of the counter ion, and was found to increase with increasing counter ion concentration. Increasing pH had a negative effect on oxalate adsorption, due to the competing hydroxide ion. Hug and Sulzberger [73] found spectroscopic evidence for the formation of several oxalate surface complexes on titanium dioxide. The vibrational spectra of the adsorbed oxalate suggested several forms of inner spherically bound complexes at lower pH values, this being explained by the formation of protonated and unprotonated surface complexes and the heterogeneity of the titanium dioxide used.

4.3.3. Oxalate in the Bayer process

Uncontrolled crystallisation of sodium oxalate in the Bayer process is highly undesirable for several reasons (as previously mentioned). Oxalate crystals promote heterogeneous nucleation of gibbsite, reducing gibbsite yield [33], and result in fine crystals undesirable for calcining and suitable only for seeding purposes [32]. Oxalate also coprecipitates with gibbsite, producing conglomerates of oxalate needles and gibbsite blocks with a decreased tendency to agglomerate, and high attrition rate [74]. Lastly, during calcination, oxalate decomposes leaving fragile alumina particles with high sodium content, increasing the cost of aluminium production [32]. Overall, high oxalate levels result in a reduced yield of a gibbsite product with low purity and inadequate handling properties.

4.3.4. Oxalate management

It is clearly desirable for alumina refiners to *prevent* oxalate crystallisation during the early stages of gibbsite precipitation. It is similarly desirable for the same refiners to *promote* oxalate crystallisation during any oxalate removal process (or processes). Alumina producers are thus faced with a considerable dilemma: to minimise *and* maximise oxalate crystallisation during the same, cyclic, process. This dilemma has been confronted in a number of ways, with the management rationale generally revolving around oxalate stabilisation during the early stages of gibbsite precipitation, followed by oxalate destabilisation/crystallisation once gibbsite precipitation has been accomplished.

4.3.5. Oxalate removal

A number of methods have been reported for the removal of oxalate (and other organics—the precursors of oxalate) from Bayer process liquors. These have included high pressure/temperature and electrolytic oxidation and use of powerful oxidising agents [75], adsorption of organic/oxalate stabilisers on activated carbons [75,76], alumina, fine gibbsite [75], and ion exchange resins [75,77], liquor calcination [75,78], burning [79], and ozonation [75], and precipitation in fluidised bed and spray trickle columns, from destabilised

and evaporated liquors [75], and using calcium [75,80,81], oxalate seed [75], and alcohol [74]. Oxalate has also been directly destroyed using calcination [82] and microbial decomposition [83], and converted to oxalic acid via ion exchange [84].

Some alumina refiners currently employ a side-stream oxalate removal process where the spent (post-gibbsite precipitation) liquor is evaporated in order to decrease oxalate solubility, and the destabilised liquor is seeded with fine sodium oxalate to induce crystallisation. Unfortunately this method is relatively inefficient, requiring a large amount of oxalate seed to achieve a small amount of crystallisation. Other, similar, processes are used by other Australian refiners forced to cope with high organic content bauxites.

4.3.6. Oxalate stabilisation

As well as the removal of sodium oxalate from Bayer process streams, it is desirable for refiners to stabilise oxalate (with respect to crystallisation) during the early stages of gibbsite precipitation. Any stabilisation processes used however, must not be detrimental to any oxalate removal process in place. Stabilisation of sodium oxalate during oxalate removal would, obviously, work against its removal, and have disastrous consequences on the overall refining process. Any stabilising effects imparted on the oxalate during stabilisation processes must, therefore, be reversible. That is, their effects must be nullified prior to commencement of the next oxalate removal step. The ideal stabiliser would be one that has no negative effects on the refining process and is not degraded or removed during digestion or mud separation [85]. Alternatively, an oxalate stabiliser that was degraded or removed prior to oxalate removal, was relatively cheap (and effective at low concentrations), and could be dosed into the process liquor prior to gibbsite precipitation, would provide a viable stabilisation option.

The humic materials present in Bayer liquor are known to stabilise oxalate with respect to crystallisation. Humic material is known to contain carboxyl, phenolic and alcoholic hydroxyl groups and, in solution, behaves as an anionic polyelectrolyte [85]. It is not surprising then that anionic polyelectrolytes such as polyacrylic acids and

polystyrene sulfonates have been found to act as oxalate stabilisers [85]. Various quaternary ammonium (QA) compounds, having a single long alkyl chain and three shorter chains, have also been shown to exhibit excellent oxalate stabilisation capabilities [86–88]. This class of compounds has been the subject of a thorough study by Alcoa of Australia Ltd. and NALCO Australia Pty Ltd., and has resulted in the development [86–88] and patenting [88] of a commercial synthetic oxalate stabiliser.

This stabiliser provided a significant increase in liquor oxalate stability, was effective over a range of process conditions, and was active in liquors from different refineries. Importantly, the stabilising effect could be neutralised by thermal degradation, with the degradation products inert to oxalate removal and further oxalate stabilisation, and no influence on gibbsite yield/size was observed. Significantly, the reagent was not adsorbed onto the gibbsite surface during precipitation, remaining instead in the liquor or on the oxalate surface [87].

The inhibitory effects of QAs on sodium oxalate crystallisation have recently been investigated using a test specifically designed to measure the impact of various additives on oxalate crystallisation under Bayer process conditions [89]. In real Bayer process liquors, QAs were found to have a dramatic and immediate effect on oxalate crystallisation, reducing oxalate yield by 55–78%, depending upon adsorption time. Similar tests performed in synthetic Bayer liquors were (for a number of reasons) less conclusive than those performed in real Bayer liquors, however the role played by humate in oxalate stabilisation was clearly demonstrated.

5. Conclusions

The specific aim of the research described in this review has been the continued development of understanding of the surface chemistry of Bayer process solids. Continued research into this important area will significantly enhance our understanding of the nature of surfaces and adsorptive processes occurring under Bayer-like conditions,

whilst also contributing to the conceptual advancement of our knowledge and understanding of the nature of surfaces (and adsorption processes occurring thereon) under extreme (non-ideal) conditions. In this respect, it is hoped that this review will stimulate research in this area and encourage further collaboration between scientific and industrial researchers.

The fundamental chemistry of surfaces and adsorptive processes in complex, non-ideal systems has (until recently) not previously been studied and understood to any great extent. As such, the exploration of the basic science of such complex systems will address deficiencies in the current knowledge of this area. Given the number and variety of industrial systems (including the Bayer process) depending upon processes occurring in such complex environments, such research will also provide interesting and useful results applicable to other, significant industrial areas involving extractive/separative processes.

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