

Impurity Removal in the Bayer Process

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Abstract

A wide range of impurities enter the process streams of alumina refineries, most of which originate from the bauxite ore. These impurities, primarily in the form of sodium salts, accumulate in the refinery's liquor streams until a steady state is achieved between the inputs and the various outputs that exist within a typical refinery. Unchecked, these impurities can significantly impact the productivity and/or product quality of the refinery. Not surprisingly, over the 130 year history of the Bayer process, a large number of impurity removal processes have been proposed, and in some cases, implemented. The introduction and operation of these processes has rarely been trouble-free, for reasons of performance, safety or public perception: sometimes all three at once. In this paper, the major impurities present in most Bayer circuits and the various removal mechanisms and strategies that exist to manage them are reviewed, and some of the issues and challenges that have arisen as a result are discussed. The influence that impurities have upon the characteristics of bauxite residue is also described.

Keywords: Organics, oxalate, sulfate, causticisation, bauxite residue

1. Introduction

In the Bayer process, bauxite ore is digested in a highly concentrated caustic soda solution, usually at elevated temperatures and pressures. The process relies upon the lower solubility of the hydroxides of most metals relative to aluminium, but under these conditions it is inevitable that small amounts of a wide range of materials are extracted, typically as the corresponding oxy-hydroxide or hydroxide anions. Due to the cyclic nature of the Bayer process, these anions can accumulate to quite high concentrations in the refinery's liquor stream over time, if not controlled. Apart from possible effects upon digestion behavior or precipitation performance, the formation of these anionic species also represents a loss of caustic soda.

Certain impurities (such as carbonate, oxalate, various organic species and sulfate) are common to most refineries, due to their ubiquitous presence in almost all bauxite deposits, but others can present special problems due to the relative abundance of particular minerals in bauxite from particular regions. While other materials that are added to assist the refining process (such as flocculants) add slightly to the impurity load, they are minor compared to the input with bauxite and rarely accumulate to a level where they cause operational problems.

A comparison of the elemental compositions of bauxite from various locations is shown in Table 1. These data are drawn from various sources, including Lapin et al. [1], Anand et al. [2], Ball and Gilkes [3], Rao and Goyal [4], See and Feret [5] and Wellington [6]. Bauxite composition can of course vary greatly within a region and even a specific deposit, and is further dependent upon the mine plan and cut-off grades, but the data in the table provides an indication of the typical issues that can arise from the processing of bauxite from each of these regions.

Karst bauxites, such as those from Greece and Jamaica, have high inorganic carbon content due to their formation over carbonate minerals such as limestone or dolomite. Western Australian bauxite deposits derive from two quite different parent rock types, but nevertheless underwent similar laterization events. They both contain slightly elevated organic carbon and sulfur contents that, when combined with low extractable alumina content, contribute to high inputs of sulfate, organic salts and oxalate to the refineries that process them.

Guinean, Indian and especially Jamaican bauxites possess a relatively high phosphate content, which can require specific control steps to avoid product contamination. Many Indian bauxite deposits contain high titanium and vanadium content; requiring special removal techniques [7].

Jamaican bauxite is infamous for its high and very fine goethite content, making it difficult to settle during clarification [8], but it also presents special issues with organic carbon, zinc and manganese. See and Feret [9] have suggested these latter elements derive from zinc-substituted lithiophorite ((Al,Li)MnO₂(OH)₂) within the deposit.

Table 1. Composition of various Bauxite deposits.

Species	Guinea	Brazil	Weipa	Greece	Trombetas	W. Australia (1)	W. Australia (2)	India	Jamaica
Al ₂ O ₃ Tot.	49.41	53.4	55.7	56.6	53	37.2	38	48.5	46.8
SiO ₂ Tot.	1.7	4.2	5.8	4.2	5.1	15.5	2.8	2.7	1.98
Fe ₂ O ₃ Tot.	19.06	13.9	11.9	21.9		24.5	35	17	19.2
CaO	0.01		0.01		0.01	0.01	0.01	0.02	1.13
C inorganic	0.06	0.01	0.03	0.41			0.1		0.4
C organic	0.11	0.03	0.23	0.08		0.2	0.2	0.11	0.2
C total	0.17						0.3		0.6
S total	0.032	0.04	0.03		0.06	0.09	0.1	0.05	0.08
P ₂ O ₅	0.14	0.02	0.07		0.01	0.02	0.015	0.13	0.38
TiO ₂	2.94	1.1	2.7	2.8	1.2	2	2.7	5.32	2.25
Na ₂ O	0.01	0.02	0.01		0.02	0.004		0.02	0.03
MnO	0.02	0.01	0.03			0.006	0.003	0.04	0.32
K ₂ O	0.03	0	0.01		0.01	0.06		0.03	0.01
MgO	0.01	0.01	0		0.005	0.006		0.05	0.08
V ₂ O ₅	0.05	0.04	0.06		0.05	0.06	0.05	0.19	0.11
ZnO	0	0	0			0.002	0.003	0.008	0.03
F						0.08	0.06		
LOI	26.7	27	23.2	12.2	27	19.8	21	25.7	26

Guinean bauxite is generally benign with respect to impurity input, although its relatively high goethite content coupled with the need to digest at high temperature to extract the boehmite content can result in problems with iron contamination in the product. Refineries processing this bauxite also tend to produce alumina with elevated gallium content. The comparatively high

haematite content of Weipa's pisolitic bauxite means it does not suffer the same issues with iron, but gallium is well extracted.

These impurities accumulate in the refinery's main liquor streams to a steady state value that is based on the magnitude of the sources (bauxite, additives, recycled lake water) and sinks (dedicated removal processes, intercalation into DSP, exit with product, conversion to other species, and soluble and solid species in the residue). Variations in any of these can cause changes in impurity concentrations that can significantly impact the performance and stability of the refinery.

In some cases, the 'natural' removal processes of the refinery (residue, DSP and product) are sufficient to maintain the impurity content at a low and manageable level. This is often the case with Brazilian bauxite deposits, for example, where the impurity inputs are low and the reactive silica content sufficiently high that dedicated impurity removal processes are either not required, or only operated in campaigns. However, in many cases, it has been necessary for alumina producers to develop specialized removal technologies so as to maintain the productivity and product quality of their refineries at acceptable levels.

For most of these species, the solubility in highly alkaline solutions is very minor and their impacts are rarely felt other than through incorporation into gibbsite and hence the alumina product. Others can have multiple effects, including productivity and product quality – in some cases because managing product quality places limitations on the productivity of the refinery. Sodium itself may be considered a contaminant, and it enters the product in a number of ways, but this is a topic that will not be explored in this paper. For those interested, the topic has been discussed at length by Grocott and Rosenberg [10], Armstrong [11] and Vernon et al. [12], among others.

In light of the above, a vast number of impurity removal processes have been developed over the history of the Bayer process, and it would be impractical to discuss them all. In this paper, some of the technologies that have been developed over the past several decades are explored, focusing on those that have seen commercial success, while also touching on some novel techniques that have not.

1.1. Nomenclature

This paper uses conventional North American nomenclature to describe liquor compositions. Hence the Caustic (C) refers to the sum of the sodium hydroxide and the sodium aluminate concentrations, Soda (S) is the sum of the C plus the sodium carbonate, and both C and S are expressed as the equivalent concentrations of sodium carbonate in g/L. The A concentration is the amount of sodium aluminate in solution, expressed as the equivalent concentration of dissolved alumina (Al_2O_3) in g/L. Total Soda (TS) refers to the sum of the sodium-bearing species in solution, expressed as the equivalent concentration of sodium carbonate in g/L. Where TCA is mentioned, this refers to $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$, commonly written in Bayer notation as $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. DSP (desilication product) refers to sodalite, cancrinite or both.

2. Major Impurities, Their Impacts and Controls

2.1. How Anionic Impurities Affect Productivity

It has been fairly conclusively demonstrated that the major aqueous aluminium species in highly concentrated caustic solutions is the $\text{Al}[\text{OH}]_4^-$ monomer, although the existence of small quantities of a dimer, either $(\text{OH})_3\text{Al}(\text{OH})_2\text{Al}(\text{OH})_3^{2-}$ or $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^{2-}$ have also been deduced. While the dehydrated aluminate monomer AlO_2^- is still often referred to in the

literature by practitioners of the Bayer process, there is no evidence that it actually exists in the range of concentrations encountered in the Bayer process [13].

The solution chemistry of the $\text{Na}^+ / \text{Al}[\text{OH}]_4^- / (\text{OH})^-$ system is greatly affected by the presence of impurities in the form of sodium salts, primarily due to their impact on the ionic strength of the solution. Increasing sodium concentration increases ion pair formation and alters the activities of the aluminate and hydroxyl ions, with the effect of increasing the solubility of aluminium in these solutions. The effect can be readily demonstrated using a suitably derived solubility model such as those described by Rosenberg and Healy [14] or Königsberger et al [15].

While the increase in alumina solubility can be beneficial in the digestion and clarification sections of the refinery circuit (allowing higher A/C's to be achieved and helping reduce auto-precipitation losses), it strongly affects the yield in precipitation, and is often one of the primary limiting factors in the productivity of many alumina refineries. It is not surprising, then, that refineries with a high impurity input with bauxite also tend to have the lowest precipitation yield, as well as the highest TS. These refineries also often tend to have comparatively low alumina losses in the mud settlers and washers, again because of the enhanced alumina solubility (amongst other reasons).

For those species that have low solubility in Bayer liquors, another effect comes into play. In order to manage the potential for these species to crystallize in locations where they can impact on the gibbsite precipitation process, create excessive scale on equipment surfaces, or cause contamination of the alumina, it can sometimes be necessary to reduce the TS concentration to minimize these effects. Alternatively, other reagents must be added to either precipitate the impurity as an insoluble salt, or additives are added to maintain them in solution. In either case, these additives can have side-effects of their own. These will be discussed in the relevant sections below that relate to each of these impurities.

Impurities such as iron, gallium, manganese and phosphorus mainly impact on the quality of the final alumina product, and while their control can result in reduced productivity (for example, lime addition to digestion for iron control can result in reduced extraction if the amount of alumina lost to TCA exceeds the release of aluminium substituted into goethite) [16] the losses are relatively small. Titanium, in the form of anatase or rutile, is a common constituent of many bauxite ores and is known to affect the dissolution rate of boehmite during digestion [17], and to cause sodium or calcium titanate scales [18]. While influential in refineries with high temperature digestion, titanium solubility is low in Bayer liquors and there here have been few reported instances of attempts to control it. Hence, these species will not be discussed further in this paper.

2.2. Carbonate

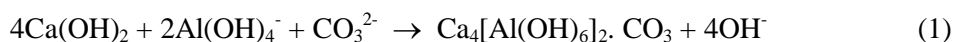
Carbonate is generally the largest impurity input to the refinery. Left unchecked, the refinery's productivity will fall rapidly with every cycle of the liquor through the process as a result of decreasing C concentration, and it is therefore necessary to continuously remove the carbonate and replace it with hydroxyl ions. This can be achieved in a number of ways, of which side-stream causticisation is the most prevalent (the older practice of "inside" causticisation will not be discussed in detail here, as its use is now very uncommon). Removal rates as high as 20-30 kg of Na_2CO_3 per tonne of alumina are not unusual where the bauxite being processed has low extractable alumina and high organic content.

Most carbonate enters the refinery's liquor stream through the degradation of organic species (particularly in digestion), and to a lesser extent through the dissolution of inorganic carbonate

species. Some CO₂ also enters the refinery stream through absorption from the atmosphere, primarily via recycled lake water (if the refinery has a process water catchment lake). The elevated temperatures and high ionic strength of the main Bayer circuit liquors means that dissolution of atmospheric CO₂ via this avenue is quite limited. The mechanisms by which organics degrade to carbonate, oxalate and other organics will be discussed in that section.

Maintaining an acceptable balance of caustic soda to sodium carbonate (the C/S ratio) is typically achieved through a combination of inherent losses (through DSP and liquor losses with bauxite residue) together with a dedicated causticisation circuit. Most of these are side-stream processes, although there are some facilities with relatively low carbonate inputs and high DSP losses that occasionally practice inside causticisation. Other refineries with high DSP losses run their side-stream causticisers in campaigns.

Side-stream causticisation makes use of the familiar reaction of sodium carbonate with calcium hydroxide, but the mechanism by which this takes place is complicated by the presence of the aluminate ion. Several authors have demonstrated [19], [20] that the reaction proceeds first by the rapid formation of a quaternary calcium aluminate species (hydrocalumite, either as the hemi-carbonate or monocarbonate), as shown below:



The hydrocalumite intermediate then goes on to form primarily calcium carbonate or TCA, with the outcome depending strongly upon the reaction conditions.



Combining equations (1) and (2) gives the familiar causticisation reaction, while combining (1) and (3) returns the competing TCA formation reaction.

Conventional side-stream causticisation uses the clarified overflow from one of the mud washers as the carbonate source, and reacts it with milk of lime in a stirred reactor at temperatures of between 90 and 100°C, for up to several hours. Typically, the efficiency of this process is not high, and lime efficiencies (the proportion of lime that actually removes carbonate, expressed as a percentage of the lime added) of 45 – 55% are common. The remaining lime is either converted to TCA, or may remain unreacted within the core of some of the lime particles. For long reaction times, Roach et al. [19] have shown that the achievable C/S in this system can be predicted from the equilibrium between TCA and CaCO₃ in the liquor, as a function of the S concentration. Rosenberg et al. [21] demonstrated that the addition of suitable complexing agents could substantially reduce the rate of TCA formation and allow a new pseudo-equilibrium to be achieved, allowing both higher C/S and lime efficiency to be achieved. The relationship between C/S and S, both with and without a complexing agent (TCA inhibitor), is shown in Figure 1.

Poor causticisation efficiency affects refinery productivity both directly and indirectly, through alumina losses with TCA, and via a lower than optimal C concentration, respectively. Improved causticisation performance can be achieved by increasing the temperature of the causticisation reaction, which dramatically increases the rate of conversion of hydrocalumite to calcium carbonate, minimizing the opportunity for TCA to form, as well as shifting the calcium aluminate / calcium carbonate equilibrium to higher C/S values. High temperature causticisation

processes have been patented by both Worsley [22] and Alcoa [23], and full-scale facilities are being operated by both companies. Alumina losses due to TCA are small in these facilities, due to the very high lime efficiency (>90%).

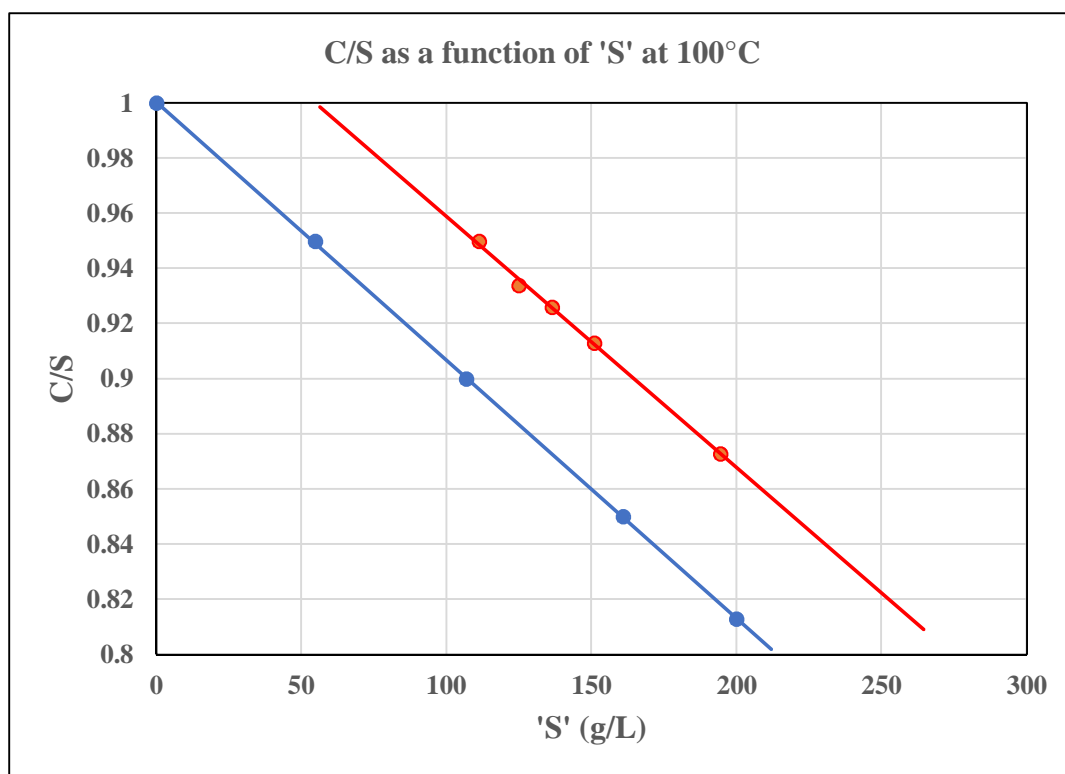


Figure 1. Equilibrium C/S showing the effect of a TCA inhibitor.

● without TCA inhibitor ● with TCA inhibitor

A less common control measure that is applied at a number of sites (mainly where the carbonate input is relatively small) relies on manipulating the ionic strength of the liquor, to effect carbonate precipitation either as anhydrous sodium carbonate, or if there is appreciable sulfate present, as a double salt such as Burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$). These are mostly based on “salting out” in which the liquor to be purified is deep evaporated to a ‘TS’ concentration of typically 450-550 g/L, in a multi-effect falling film evaporator, and the precipitate that forms is separated in a thickener or filter, or both. The removal of oxalate is usually another major objective of this process, so the cake will also contain significant amounts of sodium oxalate and some organics. The organics are typically humates which results in a viscous sticky cake, and can cause filtration problems, with poor cake separation and blocking of the discharge chutes [24].

A related process, referred to as “drowning out” was proposed by Malito and Rogers [25], in which the activity of the anionic species is increased by the addition of a suitable organic solvent, such as methanol or propanol. This method is much less affected by the presence of humates, but has never found commercial acceptance due to operational issues associated with cost (poor solvent recovery), and problems with flammable vapours.

2.3. Sulfate

Sulfate is common in most bauxite ores and can be extracted directly as the anion, for example from kaolin or as iron sulfates such as jarosite, but it also forms from oxidation of sulfide minerals (pyrite or marcasite). The release of the sulfate anion occurs readily from many of these minerals, typically with precipitation of the corresponding hydroxide, with a significant amount being released upon first contact with spent liquor. Some organic species are also rich in sulfur and during the degradation of these organics a range of volatile compounds form that contribute to the characteristic odour of many alumina refineries: Some of the sulfur also ultimately converts into sulfate.

Some sulfate also enters via the lime used in causticisation: A certain amount of sulphate minerals are commonly found in quicklime, either as magnesium sulfate or gypsum, and in the highly alkaline environment of the alumina refinery, much of this is solubilized.

Another source of sulfate that is sometimes overlooked is through the use of cleaning acid. A large alumina refinery can use many thousands of tonnes of Sulfuric acid annually for DSP scale removal. Spent acid is mostly collected and either stored separately or neutralized with lime, but fugitive releases to the refinery's sump systems or process water can result in a 'hidden' source of sulfate to the refinery's liquor streams.

Where the bauxite contains an appreciable amount of zinc, it is necessary to introduce the sulfide anion into the bauxite slurry at some point so as to precipitate the zinc as ZnS. This is done in a number of ways, but the outcome is that a substantial proportion of the sulfide reacts to form various sulfur-containing species including sulfate, sulfite and thiosulfate which accumulate in the liquor stream. This is discussed further in the section relating to Zinc.

For most refineries, the two major removal mechanisms are with entrained liquor in the bauxite residue (with some subsequent return to the refinery via the catchment lake) and through intercalation in desilication product (DSP), where sulfate is the preferred anion. This will be discussed further in the section on Silica removal.

Salting-out evaporation can again be used for sulfate removal, and as described in the previous section, the primary salt that is precipitated is usually Burkeite. However, as mentioned previously, salting-out evaporation suffers from the problem of producing fine crystals that are frequently heavily contaminated with humates and the cake that is produced is highly viscous and difficult to process [26]. Other methods, such as precipitation using Barium have been suggested [27], but most rely on variations to salting-out, such as the drowning-out method of Malito and Rogers [25].

Ostap [28] suggested cooling the solution to be purified to between -10 and -15°C. At this temperature, the decahydrates of sodium sulfate and sodium carbonate can crystallise from solution, without less complication due to co-precipitation of high molecular weight organics. However, the energy requirements of cooling even a small side-stream of hot Bayer liquor to this extent are prohibitively high, and scaling of the equipment is inevitable.

Combining salting-out with an organic removal process, such as liquor-burning, has the advantage of avoiding organic contamination of the precipitate [29], and a process based on this was operated at a commercial scale for many years. However, the presence of other very fine particulates made filtration of the cake difficult, and it was subsequently abandoned.

If there is appreciable fluoride present, the double salt $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$ (corresponding to the mineral kogarkoite) can form. The precipitation of kogarkoite was studied in detail by Wilson et

al. [30], who found that its solubility is lower than burkeite, or anhydrous sodium sulfate, and could thus be expected to precipitate from solution first in a salting out evaporator. Scales of this type have been found on the walls of evaporators at several refineries [30]. The lower solubility of kogarkoite suggests that salting-out may be possible with less deeply evaporated solutions, potentially avoiding severe organic contamination and making the solids easier to settle or filter.

Sulfate and other anions can be intercalated into layered double hydroxides (LDH's). Rosenberg et al. developed a hydrocalumite-based process for the removal of both sodium oxalate and sodium sulfate from Bayer liquors [31] in which the LDH is formed in-situ. The precipitate, which contains the impurity anions, is filtered and the cake discarded. While simple to implement, the process is expensive to operate as it consumes appreciable amounts of both alumina and lime, and to my knowledge has never been applied commercially. O'Hare et al. [32] devised a process based on a lithium-aluminium LDH that avoids the alumina loss issue. By displacing the intercalated anion with carbonate and calcining and re-hydrating the resultant product, the LDH could theoretically be recycled, thereby reducing reagent costs. While never exploited commercially, this remains a viable option for impurity removal from Bayer liquors.

2.4. Organics (other than oxalate)

All bauxite deposits contain organic matter, in varying amounts and states of decomposition. A very large number of papers have been written on the origins and fate of organics in the Bayer process, and anything other than a cursory discussion is beyond the scope of this review paper. Power and Loh [33] have published the most comprehensive recent review on the topic, and is recommended for those seeking further information.

For bauxite deposits that are close to the surface and possess a minimum amount of overburden, the organic matter can have a high proportion of relatively intact plant and animal material, including lignin and cellulose as well as base-soluble high molecular weight polymeric materials such as humic and fulvic acids. Degradation products will also be present, and usually the amount of organic matter will decrease down the lithological profile, while the degree of degradation increases.

Some species, such as lignins and cellulose pass through digestion virtually unaltered, other than some surface hydrolysis reactions, and are removed from the refinery with residue. Others undergo decarboxylation and hydrolysis reactions, creating new soluble sodium salts, as well as insoluble fragments that pass to waste with the residue. Base hydrolysis of the organic species commences in the mill circuit, but most of the degradation reactions occur through digestion, producing CO₂ and oxalate, but also simple organics such as acetate, formate, tartrate etc.

The organic compounds responsible for the characteristic colour of Bayer liquors (which can vary from orange to nearly black, depending upon the relative concentration of the high molecular weight organics), are primarily base extracts of humic and fulvic acids. For simplicity, they will be grouped under the heading of high molecular weight (HMW) organics.

The effects of organics on the Bayer process are widespread, and apart from the effect of high concentrations of organic sodium salts on aluminate solubility, the tendency of many organics to adsorb at the numerous active surfaces of the Bayer process, means that they can greatly affect the rate of reactions (particularly in precipitation). They can also cause morphology changes in the various crystallising species, and increase the incorporation of impurities in product, either by increasing the solubility of contaminants (such as calcium) or by interfering with the diffusion of species away from the growing crystal front [10]. A thorough discussion of the

many issues that can arise from the presence of organics in Bayer liquors can be found in the review by Power et al. [34].

HMW organics are particularly influential on many of the unit operations within the Bayer process, primarily because of their tendency to adsorb strongly on most surfaces. They also represent the major parent species from which simpler organics are produced during repeated cycles of the liquor around the refinery. Removing HMW organics, then, has been a priority for the alumina industry, and a large number of techniques have been proposed over the history of the process.

Many of the processes for removal of HMW organics rely upon the propensity for adsorption mentioned earlier. The use of adsorbents including activated charcoal [35], magnesia [36], dolomite, hydrotalcite [37], TCA, alumina and other caustic-stable materials [38] have been proposed, and used, to some extent. These techniques suffer from some problems in common: The need for high surface areas for effective impurity adsorption often means that the materials are fine and it can be difficult to separate the spent material from the treated liquor, the efficiency is often poor (and hence costly), and the organics that are removed are not necessarily the ones causing the majority of the problems (it is incorrect to think that all HMW's have the same effect). Refineries using this technique often do so in campaigns to address transient surface-chemistry related issues, as it is rarely economic to dose these adsorbents on a continuous basis. Furthermore, these techniques have almost no effect on the bulk of the organics that contribute to elevated liquor ionic strength.

With the advent of caustic-stable poly-sulfone membranes, a number of researchers examined the potential to separate HMW organics from Bayer liquors using nanofiltration. Poor permeate flux rates and rapid fouling led most of these efforts to be abandoned [39]. Recent developments in ceramic membranes may hold promise for this technique, as they allow more effective cleaning regimes.

It is common for a removal process targeting organics to also be directed towards the removal or destruction of sodium oxalate. Where oxalate is the main target, I have addressed them in the section on sodium oxalate. This includes such well-known techniques as the use of liquid anion exchange polymers such as poly-DADMAC.

Where the objective is to remove a broad spectrum of organic species, the choices are relatively few. Most centre on two premises: oxidation, or calcination.

Wet oxidation of Bayer liquors is usually based on the injection of oxygen into one or more of the digester vessels or tubes of a refinery where oxidative cleavage of the organics occurs, ultimately producing a range of "refractory" organics (such as acetate), sodium oxalate and sodium carbonate. Many of the organic compounds present in Bayer liquors will undergo either base-catalysed oxidation by water at elevated temperatures, evolving hydrogen [40]. Base-catalysed cleavage by oxygen also results in the evolution of hydrogen, for many organic species [41]. The risk associated with the presence of both oxygen and hydrogen in a closed system at elevated temperatures is very obvious. At the Stade refinery in Germany, wet oxidation has been used to good effect for many years, by strictly controlling the amount of oxygen to below the explosive limit for an H_2/O_2 mixture. However, it is also essential to avoid any opportunity for gas to accumulate in dead-legs and other voids, a situation which led to the explosion at Stade in 1982, as described by Arnsward [42].

Oxidants other than oxygen have also been proposed, including hydrogen peroxide, ozone [43] and manganese dioxide [44]. In the latter case, while some of the concerns with hydrogen explosions are alleviated, the cost is high and product contamination with manganese is an

issue. The use of a submerged plasma torch has also been proposed [45], but never taken beyond laboratory trials. The combination of hydrogen evolution in the presence of an exposed ignition source would require extraordinary safety control measures.

If a side stream of liquor (typically spent liquor) is evaporated to dryness and calcined, the organic salts are destroyed and converted to sodium carbonate. The sodium carbonate could be re-dissolved and causticized in the usual way, but Yamada and Shibue [46] developed a process, now commonly referred to as Liquor Burning, in which the addition of a molar equivalent of either alumina or gibbsite is added to the mixture prior to calcination to causticize the sodium carbonate in-situ to sodium aluminate. The dry powder that results can then be re-dissolved in spent liquor and returned directly to the refinery. A variant of this, the solid-liquid calcination process [47] enhanced the process by adopting a fluidized bed calciner, and allowed the use of bauxite as the source of alumina. Liquor burning has been successfully applied in Japan and Western Australia, while SLC has been operated in Spain for many years. SLC units were constructed in Gove, Australia, but reportedly were never operated.

Both processes are highly capital and energy intensive, and can be difficult to run consistently. A more serious issue, however, relates to the emission of dusts and odours. While the SLC unit in Spain has apparently been operated without affecting the amenity of nearby communities, the same cannot be said of the three large liquor burning plants operated by Alcoa and Worsley Alumina. Residents in the vicinity of Alcoa's Wagerup refinery began complaining of unpleasant odours and ill-health soon after Alcoa commenced operating its liquor burner at the site, and the dispute that arose over time ultimately drew prominent and strongly adverse national and international attention. The conflict between the company and the nearby community has since been studied by sociologists and business ethics researchers [48].

Biological processes based on microbial degradation of organics have been suggested on several occasions [49]. While none have yet to find commercial application, some recent developments suggest that this technique may be a viable alternative to wet oxidation and liquor burning [50].

Another interesting low energy alternative suggested by Jamieson [51] is to sequester the impurity within a geopolymer. In this concept, rather than remove impurities by purging a portion of the liquor to residue, a control strategy that is common in the industry, a sidestream of liquor is reacted with a reactive silica source such as silica fume or flyash. The solid geopolymer that forms thus theoretically entombs the impurity within its structure. The solid can be cast into geopolymer products, or discarded. The stability of the impurity within the structure was not demonstrated in Jamieson's patent, nevertheless this represents a promising new approach to organic impurity removal.

2.5. Oxalate

Oxalate has special significance in virtually every alumina refinery due to its ubiquitous presence in all Bayer liquor streams and limited solubility. Sodium oxalate tends to precipitate in those sections of the refinery that have the lowest temperature, in particular the precipitation circuit. The impacts of uncontrolled oxalate precipitation are well known and will not be dwelt upon here.

The control of sodium oxalate in the alumina refinery invariably consists of two distinct stages: 1) removal from the main process liquors and 2) disposal or destruction. These two steps rarely occur at the same time, and a vast number of processes and operating practices have been suggested and developed over the history of the Bayer process.

While some oxalate enters the liquor stream as the anion adsorbed onto the various minerals constituting the bauxite ore [52], like carbonate, most oxalate is formed through the oxidative degradation of organic species present in the bauxite. Mechanisms for this and other organic degradation reactions are proposed by Costine et al. [40]

The oxalate cake produced through the side-stream process will also contain an appreciable quantity of high molecular weight organic matter adsorbed at the surface, and these of course are the type of organics most influential in reducing crystallization and affecting morphology. This represents a de-facto targeted organic removal process for oxalate poisons.

2.5.1. Oxalate Removal

Strategies for controlling the concentration of sodium oxalate in the main process streams of the Bayer circuit tend to fall into two main categories, side-stream removal and co-precipitation, and the selection of either of these approaches has a major effect on the subsequent design and operation of the entire refinery.

One well-recognised problem with the crystallization of sodium oxalate in Bayer liquors is the influence of surface-active organics, particularly high molecular weight organics like humates, is that the surface of the oxalate seed crystals becomes poisoned, resulting in a significant reduction in crystallisation rate even when the solutions are still quite supersaturated. The rate can be so slow that the system appears to have reached steady state, and the concentration at which this occurs is referred to as the apparent oxalate solubility. This value is a function of the sodium and oxalate ion activities, but also upon the surface area of oxalate and the humate concentration, betraying the kinetic origin of this apparent solubility.

It is not so well-recognised that with side-stream oxalate removal techniques, evaporation of the feedstock stream can actually result in an increase in the apparent solubility, due to the concomitant increase in surfactant concentration. This results in an oxalate apparent solubility curve such as that shown in Figure 2. This effect was demonstrated in the paper by Atkins and Grocott [53], the implications of which are that a side-stream process will be most effective at the 'S' concentration corresponding to the minimum of the curve, and that further evaporation will actually result in a decrease in oxalate removal capacity. As expected, Atkins and Grocott found that the minimum in the curve was shifted down and to the right as the humate concentration decreased.

Roe and Malito [54] proposed the use of a water- soluble, cationic, polymeric quaternary ammonium compound, poly-DADMAC (poly diallyl dimethyl ammonium chloride) to remove humates by adding it to the feed to the mud settlers or washers, so that the oily resin that forms by reaction with humates can adsorb on the mud particles and hence be discarded with the bauxite residue. This is an expensive process, but for refineries in which the humate input to the refinery is large, it has found continued use. Atkins and Grocott [53] attempted to reduce the cost of the process by means of recycling and regenerating the poly-DADMAC, but were unable to achieve economically acceptable recoveries.

One unfortunate side-effect that arises from use of this material stems from the fact that it is an anion exchange medium, and so the removal of humate is accompanied by the release of chloride anions into solution. Continued use of poly-DADMAC can therefore increase the sodium chloride content of the liquor.

Surfactants can greatly affect oxalate crystal morphology, usually producing very fine needles, networks of needles or even balls. Poor oxalate morphology can itself be the limiting factor in an oxalate removal system, restricting throughput due to problems in filtering or settling the

crystals. The poisoning of oxalate to produce spherical oxalate crystals that can be settled easily from solution and hence improve removal throughput was explored by Keeney and Grocott [55], and also by Morton [56]. The spherulitic oxalate crystals were either formed by adding a surfactant to a Bayer liquor to poison the crystal's edge faces and hence encourage radial growth from a core oxalate nucleus, or were created in a separate system in which an oxalate-rich solution was injected along with the surfactant into a Bayer liquor stream, causing very high local supersaturation and subsequent radial crystal growth. While this scheme was attractive in dealing with the commonly poor filtration characteristics of sodium oxalate needles, they suffered from an inability to maintain purely spherulitic crystal morphology, and a lower oxalate yield than conventional oxalate removal, and were never implemented at full scale.

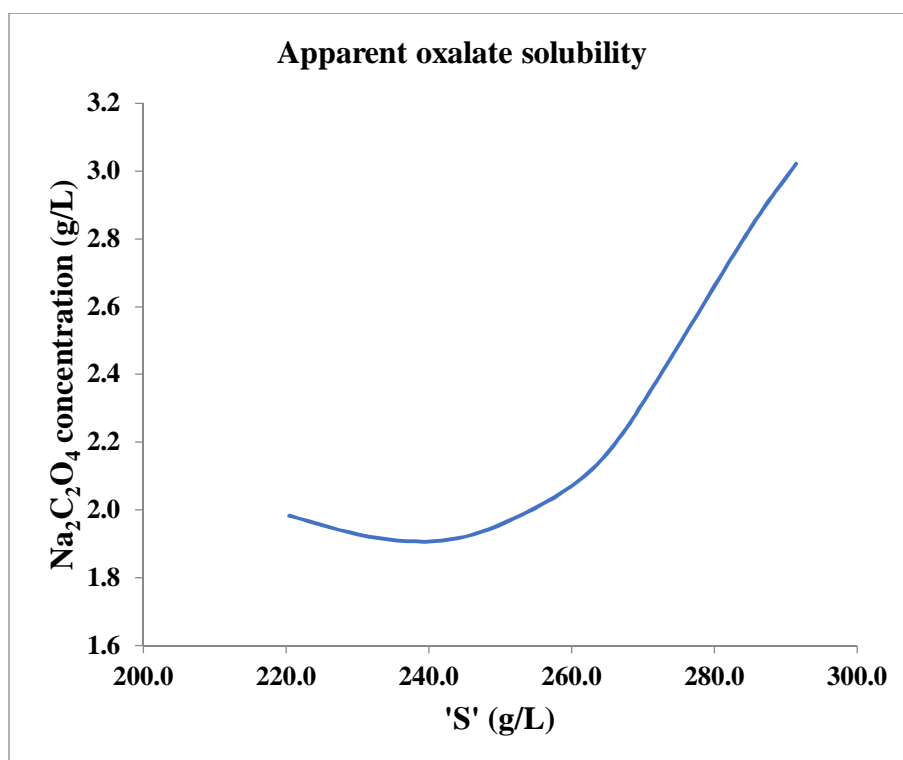


Figure 2. Apparent oxalate solubility as a function of 'S' concentration showing effect of rising humate concentration (re-drawn from Atkins and Grocott [53]).

Williams and Perrotta [38] attempted to minimize the impact of oxalate poisons on the side-stream precipitation of sodium oxalate through the use of various adsorbents, including layered-double hydroxides, magnesia, activated carbon and ESP dust, finding that a combination of the latter two materials were most effective in reducing the apparent oxalate solubility and hence oxalate yield. Like many other techniques using adsorbents, the dose rates are typically of the order of several grams per litre, necessitating the recycle and regeneration of the adsorbent to be economic. Regeneration is often difficult, adding significant complexity, and is usually only partially successful, and such schemes are rarely sustainable long-term.

Another approach to overcoming the oxalate poisoning effect was to induce crystallisation by the application of ultrasonic waves in a pipe reactor [57]. Sonocrystallisation was attempted at Aughinish using specially constructed transducers that initiated crystallisation through local cavitation in the pipe reactors. Bubble collapse creates conditions of high localized temperature and pressure, causing nucleation to occur. During pilot trials, this system allowed a significant reduction in the final oxalate concentration, from 2.5% w/v down to 1.4% w/v. A patent was

filed [58] but lapsed, suggesting that the process suffered problems in scaling up to industrial application.

Salting-out, another common means of removing oxalate from a side-stream, was discussed previously for carbonate. Some aspects of its use for oxalate removal were described by Gnyra and Lever [43], and the complexity and compromises that need to be made in its routine operation were discussed by O’Connell et al. [59]. Alternative precipitation techniques based on chilling of the liquor or “drowning out” were described by Grocott [60]. Energy costs and solvent recovery issues again prevented these techniques seeing commercial application.

In side-stream oxalate removal, sodium oxalate is permitted to co-crystallise with gibbsite under controlled conditions. Oxalate precipitation is avoided in the agglomeration stages due to well-known impacts on product quality and yield [61], and some of the issues that can arise when the process goes awry are discussed by Power and Tichbon [62]. Sodium oxalate is separated from the gibbsite in the seed classification circuit, with most of the oxalate reporting with the fine seed, which is then generally filtered to remove concentrated liquor and the cake washed to dissolve the sodium oxalate. Oxalate morphology and the size distribution of the gibbsite can greatly affect the first filtration step, and may result in excessive amounts of water being required to dissolve the oxalate. The oxalate-rich solution is either sent directly to an oxalate disposal step, as will be discussed next, or recrystallized using a side-stream process.

2.5.2. Oxalate Disposal and Destruction

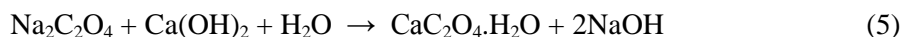
Sodium oxalate is a toxic material and its disposal must be performed in a safe and environmentally sound manner. Disposal of the oxalate with residue, either as an enriched stream or as a solid cake, is not a desirable practice for a number of reasons: 1) It can recrystallize at the surface of the residue due to capillary action and once there can constitute a toxic dust being emanated from the surface of the bauxite residue disposal area (BRDA), and 2) it is soluble and will return to the refinery via the BRDA’s decant and under-drainage systems. Additionally, it is desirable, where possible, to try to recover the sodium hydroxide that is lost from the process during the formation of sodium oxalate.

One common practice is to roast the cake in a rotary kiln, which decomposes the material as follows:



Some sodium oxide can also form through the decomposition of sodium carbonate if the calcination temperature is sufficiently high, but the dominant product is sodium carbonate. This material can be dissolved and causticized separately using slaked lime and returned to the process, or simply discarded with residue. The inevitable presence of organic species often result in a substantial odour (similar to a liquor burner) and together with the escape of alkaline fugitive dusts, these systems have the potential to create health and amenity problems both within the refinery and with surrounding communities and their use has diminished in recent years. An obvious alternative to calcination is to add the oxalate cake to the feed to a liquor burner, in which case the sodium oxalate is causticized by reaction with alumina to sodium aluminate. While this improves the overall efficiency of sodium recovery by the liquor burner, the issues described earlier apply equally in this situation.

Causticisation is a very common approach to converting the oxalate into an insoluble form that is suitable for disposal in a BRDA. Ostensibly, the sodium oxalate reacts with calcium hydroxide to form calcium oxalate monohydrate as follows:



However, the sodium oxalate is usually presented in the form of a solution in the wash liquors from fine seed filtration, and the presence of significant amounts of sodium aluminate and carbonate in the wash liquors results in the majority of the calcium hydroxide being involved in side-reactions to form various calcium aluminate species and calcium carbonate, as was described by Rosenberg [20, 31]. The net result is that the efficiency of lime utilization for oxalate removal can be as low as a few percent.

Recognition of the low efficiency of oxalate causticisation led to the development of a two-stage system [31] in which the aluminate was first removed from the solution by reaction with lime to produce hydrocalumite according to equation (1) described earlier. The hydrocalumite was separated by filtration and sent to the carbonate causticiser, while the clarified oxalate-rich solution was further treated with lime to produce calcium oxalate monohydrate. Lime efficiencies of up to 80% were claimed for this process.

The oxalate-rich wash stream can also be treated using a biological destruction processes, as was originally proposed by Brassinga et al. [63], in which the solution was first acidified to bring the pH to a near-neutral range. This was adapted for alkaline solutions by Morton for either continuous or batch operation [64]. A batch system was operated successfully at the Worsley refinery for many years, but required constant intervention to operate reliably in this mode and was eventually discontinued. Alcoa subsequently developed a continuous biological reactor based on Morton's invention, using a well-proven moving bed bioreactor as is commonly employed in water treatment systems. This system has proven capable of dealing with a large proportion of the sodium oxalate output at several Alcoa sites [65]. The products of biological degradation are sodium bicarbonate and sodium carbonate, and the treated stream is thus suitable for return to the mud washing stream of the refinery where it can be efficiently causticized using the refinery's existing carbonate causticisation circuit.

Photocatalytic oxidation of sodium oxalate in air and pure oxygen, with and without TiO_2 catalyst, has been examined in laboratory studies [66, 67]. The need to acidify to obtain a suitable oxidation potential, and the expense of the catalyst, have prevented the uptake of this approach in the past. Interestingly, Suss et al. [68] found that sodium oxalate cake exposed to sunlight without the use of catalyst degraded by up to 20% over the course of 6 weeks. This is unexpected, given the outcomes of previous photocatalytic studies, and the possibility of microbial action cannot be discounted.

2.6. Chloride

When diaphragm-type cells were the dominant technology for caustic soda production, sodium chloride was a significant impurity input to the refinery. With modern membrane cells, chloride ingress via this source has become negligible. However, most bauxite ores contains a small amount of chloride, typically in the form of halite. Further, if hydrochloric acid is used for cleaning purposes, some of this can also enter the liquor stream via sumps or accidental discharge into the process. As mentioned earlier, refineries that use poly-DADMAC will also receive chloride through anion exchange.

Sodium chloride is a difficult impurity to remove, due to its very high solubility and the scarcity of insoluble chloride species that could be used to precipitate it from solution. No practical methods for its targeted removal have been published in recent literature, and its control is largely through avoidance of extraneous input, removal as entrained liquor in residue and intercalation in DSP.

2.7. Fluoride

Fluoride is common in the earth's crust, and is present in most bauxite ores as a proxy for hydroxide in gibbsite or boehmite, in the various clay components that constitute the reactive silica, or in various other fluoride-containing minerals such as fluor spar [69]. It is inevitably present in most refinery liquor streams, albeit rarely analysed. Exit streams are with residue (as entrained liquor, and some incorporation into DSP and TCA from filter aid or spent causticiser solids), or with product (via incorporation into gibbsite, substituting for the hydroxyl ion – in which case it is probably emitted as HF in the calciner stack gases). For the most part, the amount present in solution is low and will rarely make its presence felt. However, fluoride will readily form double salts with a number of other anions (notably metallic anions such as vanadate and arsenate) [70] and also the sulfate ion [30]. These sodium fluoride double salts have comparatively low solubility and can precipitate from solution at the internal surfaces of evaporators, causing scales and reducing evaporator efficiency [71]. In extreme cases, they can also co-crystallise with gibbsite in the precipitation circuit, resulting in serious product quality issues similar to the familiar oxalate “shower”, in which gibbsite crystals nucleate on the surfaces of the double salt in the high supersaturation stages of precipitation [30].

At the ETI plant in Turkey, fluoride manifested as mainly impure NaF, producing scales in the tanks and pipes downstream of the evaporators [71]. A removal system based on salting out of the NaF cake was implemented, in which evaporator discharge was treated with fresh caustic soda to salt out the NaF, and the precipitate thickened before filtration. In this way, a relatively pure NaF cake was obtained.

At the Worsley refinery in Western Australia, a removal process was developed that was based on the substitution of fluoride for hydroxide in the aluminate ion. By manipulating the reaction conditions to encourage a high degree of fluoride substitution in sodium aluminate, fluoride is preferentially removed by reaction with slaked lime during the formation of TCA [72].

When lime is added in digestion, some fluoride will also be removed as fluorhydroxyapatite and fluorapatite.

2.8. Other Halides

Bromide and Iodide may also be present in bauxite in small quantities but their concentrations rarely rise to significant levels and hence have little impact on the process. Indeed, many refineries will be unaware of their presence in their liquor streams. If they do cause issues, their presence will be felt in emissions from other impurity removal processes, such as liquor burning. In the liquor burner, these halides are evaporated to dryness and are present as their sodium salts. In the liquor burner kiln, or in the subsequent baghouses, they can be oxidized to elemental bromine or iodine and be discharged with the off-gases. In extreme cases, this has resulted in visible coloured plumes. In at least one location this necessitated the installation of a halide gas scrubber, to reduce the halides back to their respective anions.

2.9. Silicates

Every alumina refinery based upon the Bayer process includes some form of desilication facility. The topic of desilication has been extensively reported upon in the literature, and the concepts are very familiar, so they will not be discussed in detail here.

Desilication (also referred to as pre-desilication) is an essential part of the impurity balance of every refinery, as the product of silica removal is itself a removal medium for a range of significant refinery impurities. Inorganic impurities such as sulfate, carbonate and chloride are

trapped within the cages of sodalite, or in both the cages and channels of cancrinite. Sulfate is the favoured anion for inclusion in sodalite, as the structure appears to template around the sulfate anion [73]. For many refineries, especially those with high reactive silica content, DSP represents the primary impurity removal process for these anions, requiring only occasional operation of the carbonate causticisers to maintain a stable liquor composition.

Refineries processing bauxite with very low reactive silica content can suffer increased impurity loads in the liquor stream, and if caustic soda loss is too low, fresh caustic input may be insufficient to maintain efficient equipment cleaning.

Desilication also represents one of the major operating costs of many refineries, as the dissolution of siliceous minerals such as kaolinite and subsequent precipitation of DSP consumes the majority of the caustic soda consumption. The reaction sequence is often written as follows, where the reactive silica component is kaolinite:



where: Na_2X represents the sodium salt of the impurity.

Inspection of equations 6 and 7 reveals that the net alumina loss to the process from DSP formation is usually zero, unless there is appreciable quartz dissolution. However, the high caustic soda consumption has driven many attempts to minimize DSP formation, or to change the stoichiometry of the reaction products to lower sodium content. A comprehensive review of these studies has been published by Smith [74], but in summary, very little success has been met, and pre-desilication remains the main technique for removal of silica from bauxite.

One notable exception is a process developed by Harato et al. [75], which capitalizes on the more rapid dissolution rate of gibbsite relative to kaolin. In this process, the bauxite slurry and liquor are heated separately and then passed to a tube digester for a few minutes, at which point gibbsite dissolution is essentially complete, but kaolin has only partially dissolved. The digested slurry is then rapidly thickened: the separated liquor is passed to a separate desilication vessel, and the slurry, containing the partially reacted kaolin is passed to the mud washing circuit. Since the time available for DSP precipitation in the heaters and digester is short, the pregnant liquor contains high dissolved silica content, necessitating a separate seeded desilication vessel, and subsequent flash system and DSP separator. A reduction in soda loss of more than 50% is claimed to have been achieved in routine operation with this process. However, it should be noted that the alumina extraction efficiency is slightly lower with this system, clarification of the liquor can be problematical, and the process is unsuitable for boehmitic bauxite.

2.10. Zinc

High levels of zinc are common in Jamaican bauxites where it apparently exists primarily as Zn substituted lithiophorite [9]. Zinc is extracted from bauxite as the zincate anion, $\text{Zn}(\text{OH})_4^{2-}$, and is captured within gibbsite during precipitation, affecting product quality.

Almost all zinc control methods are based on the low solubility of ZnS in alkaline solutions. One early method developed by Hrishikesan et al. [76] in 1969 and still in common use involves the addition of sodium sulfide to the digester blow-off slurry, followed by a short period of slurry retention to facilitate adsorption of the ZnS particles on the mud.



A variation on this theme was patented by Magrone [77], in which sodium sulfide was added into the settler feed, and zinc sulfide was added to the settlers to act as seed, thus obviating the need for a separate holding tank. In both the above processes, the zinc sulfide departs with the red mud.

Another process in use today was developed by Bird and Vance [78], in which sodium zincate is first formed and then reacted with sodium sulfide to produce high surface area zinc sulfide crystals, which act as seed. A slight excess of sodium sulfide is maintained in the solution, and the slurry is then injected into the clarifier overflow where it removes the zincate present in the liquor. The solids are removed in the liquor filters and discarded with residue.

The addition of elemental sulfur to bauxite in mill feed is practiced at some Russian refineries. The sulfide anion is formed in digestion, effecting the zinc removal. The advantage of this process is the relative low cost of sulfur, but a variety of oxidized sulfur species also forms and adds to the overall impurity level of the refinery. Suss et al. [79] recently described modifications to the process to minimize the formation of secondary sulfur species.

The only process that does not specifically rely on the formation of zinc sulfide was proposed by Thé [80], in which settler overflow liquor is passed over a bed of haematite, preferably coated with zinc sulfide. In laboratory tests, this achieved reductions in both zinc and copper, without the need to introduce sodium sulfide or elemental sulfur to the system. To my knowledge, this process has never been applied commercially.

2.11. Vanadium

Vanadium is a common constituent of many bauxite ores and it enters the liquor stream during digestion as the vanadate ion, $V_2O_5^{2-}$. Some Indian ores, in particular, are very high in Vanadium content, to the extent that it is necessary to remove it via a salting-out process using spent liquor. It is probable that this process is aided by the presence of fluoride in the liquor stream, as the fluoride-vanadate double salt is much less soluble than vanadate itself. This process is practiced at a number of Indian refineries [7].

For most other refineries, vanadium is removed primarily via incorporation into TCA [81], and via soluble losses with residue. A process based on removal with TCA [72] has been implemented at the Worsley refinery.

3. Impacts of Impurity Removal on Bauxite Residue Characteristics

One of the common factors in nearly all of the impurity removal practices described above is that the by-products of removal find their way into the BRDA, either homogeneously mixed with the bauxite residue, or deposited separately in trenches or dedicated storage areas. With the increasing global imperative to find alternative uses for bauxite and thus minimize bauxite residue storage, these practices require review, and in many cases alternatives must be found.

One of the greatest barriers to utilization of bauxite residue, of course, is the high sodium content. More efficient washing will assist this, but alternative impurity removal processes must be found to retain the impurity balance of many refineries, which rely upon high soluble losses or even practice liquor purging. Similar considerations apply to the dumping of salting-out cake with residue.

The solid alkalinity of bauxite residue derives largely from the presence of DSP and TCA, both of which buffer the residue at high pH even after it has been initially neutralized (this is

sometimes referred to as pH “bounce-back” or “reversion”). In the case of DSP, this also constitutes a mechanism for the slow release of soluble sodium into the residue as the DSP decomposes. While the minimization of DSP has been a goal of the industry for many decades, for residue use it is necessary to either reduce its input or find new ways to destroy it.

Alternatives already exist for TCA. The high efficiency causticisation processes described earlier can greatly reduce TCA content in residue, and other sources, such as filter aid, can be isolated from the residue and potentially re-used. The practice of sodium oxalate causticisation, due to its inefficiency, also contributes to the presence of unstable quaternary calcium aluminate species in residue, along with unreacted lime. Alternatives, such as the recent developments in biological oxalate destruction, hold promise as a means of reducing this.

The presence of zinc sulfide can result in odours (due to biological activity), and contribute to the toxic content of the residue (although it could be argued that this is simply returning the zinc to its source). Similarly, sulfates, when present with an organic source such as oxalate, can be reduced and create odour problems.

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