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High Silica Bauxite Processing

Economic Processing of High Silica Bauxites – Existing and Potential Processes

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Table of Contents

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1. Introduction

1.1 Scope

This document will critically review existing and potential processes for the economic processing of high silica bauxites. High silica bauxites are usually considered to be those with reactive silica contents[1] in excess of ~8% by weight of the bauxite. “Economic processing” is meant to imply production of alumina at a cost comparable to that from low silica bauxite by a conventional Bayer process.

This review is limited to bauxites as feedstocks for the processes. Bauxites are those ores in which the valuable (extractable) aluminium is in the form of hydroxides or oxy-hydroxides of aluminium (i.e. gibbsite, boehmite and diaspore). In addition the review will be restricted to alkali leaching of bauxites – which includes all forms of Bayer process variations. The review will not address alumina production from non-bauxitic materials such as clays, shales, nephelines or fly ash. It will also not consider alumina production using non-alkaline processes such as those using mineral acids, reduction, or bacterial processes. These have been adequately reviewed (until the mid 1980’s) by O’Connor (O'Connor 1988).

There is an assumption that the reader is familiar with the basics of the Bayer process, and North American liquor terminology. In brief, the Free Caustic content of a liquor is defined as g/L of sodium hydroxide, Caustic (or Total Caustic) is defined as Free Caustic plus sodium aluminate, and Soda is defined as Caustic plus sodium carbonate - all expressed as g/L of equivalent sodium carbonate. Aluminium in solution is expressed as g/L Al_2O_3.

1.2 Bauxite types

Bauxites are usually considered to be of two major types; (1) “lateritic” (sometimes called equatorial) and (2) “karst” bauxites. Both are weathered products from underlying parent rock; lateritic bauxites derive from primary aluminosilicate rocks whereas karst bauxites from interbedded carbonate and aluminosilicate rocks.

Lateritic bauxites, formed in equatorial climates comprise ~90% of the world’s exploitable bauxite reserves (Freyssinet, Butt et al. 2005). The weathering process has resulted in a typical profile in which the valuable aluminous material lies atop of an aluminosilicate base (often clay) and has formed from it through the leaching of silica. Bardossey and Aleva (Bardossy and Aleva 1990) have described 6 types of lateritic bauxites, differentiated mainly by the age of the deposit and the different weathering conditions it was exposed to. The main silicate mineral is kaolinite which is often associated with goethite as the iron mineral. Aluminous minerals are predominately gibbsite and to a lesser extent boehmite.

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[1] Reactive silica is defined later in this document.

Karst bauxites have a different typical mineralogical composition which stems from the presence of carbonates in the parent rock and different weathering conditions to those for lateritic bauxites. Silicate minerals are again dominated by kaolinite, but may include more difficult to process minerals such as chamosite. Aluminous minerals are more likely to be boehmite and diaspore, with the changes to the mineralogy compared to lateritic bauxites sometimes attributed to different oxidative conditions experienced during weathering (Bardossy 1982). Karst bauxites are largely found in Eastern Europe and Northern Asia.

The different mineral composition of these two main bauxite types has influenced the way they are processed. In general lateritic bauxites are easier to digest than karst bauxites and are treated by Bayer process variations using less severe conditions of caustic concentration, temperature and/or holding times. The difference in the "processibility" of these two bauxite types will also influence the strategies for developing viable processes for treating high silica versions of these ores.

The following table describes the approximate compositional differences between lateritic and karst bauxites. It is not intended to be definitive.

Table 1 Approximate mineralogical compositions of lateritic and karst bauxites

Element	Lateritic	Karst
Al_2O_3	Gibbsite, Boehmite	Boehmite, Diaspore
SiO_2	Kaolinite, Quartz	Kaolinite, Quartz, Chamosite, Illite
Fe_2O_3	Goethite, Hematite	Hematite, Goethite Maghemite, Magnetite
TiO_2	Anatase, Rutile	Anatase, Rutile, Ilmenite
CaO	Calcite, Apatite	Calcite, Apatite, Crandallite

A classification of bauxites, particularly from the point of view of Bayer processing has been given by Hill and Robson (Hill and Robson 1981).

1.3 Current world bauxite reserves

Table 2, sourced from 2008 US Geological Survey "Mineral Commodities Summaries", gives world bauxite production and reserves by country. The table gives 2006 and 2007 production figures (sorted from highest to lowest 2007 production) and two indicators of bauxite reserves.

According to the USGS report (Bray 2008) the "Reserve Base" is the part of the resource that meets minimum physical and chemical criteria related to grade, quality thickness and depth, and includes those resources that are currently economic, marginally economic and some that are current sub-economic. By contrast the "Reserve" is a sub-class of this definition, restricted to the part that is economically recoverable with current technologies.

Table 2 World bauxite production and reserves (Bray 2008).

Country	Production		Reserve (10^6 T)	Reserve base (10^6 T)
	2006 (10^6 T)	2007 (10^6 T)		
Australia	62.30	64.00	5,800	7,900
China	21.00	32.00	700	2,300
Brazil	21.00	24.00	1,900*	2,500*
Guinea	14.50	14.00	7,400	8,700
Jamaica	14.90	14.00	2,000	2,500
India	12.70	13.00	770	1,400
Russia	6.60	6.00	200	250
Venezuela	5.50	5.50	320	350
Suriname	4.92	5.00	580	600
Kazakhstan	4.80	4.90	360	450
Guyana	1.40	2.00	700	900
United States	-	-	20	40
Other countries	5.46	6.80	3,400	4,000
World Total	**178.00**	**190.00**	**25,000**	**32,000**

N.B. sorted by 2007 production. * suspected to not include the "new" Paragominas deposit which could easily double this reserve, T=metric ton.

Alternative figures from the most recent Roskill report (Roskill 2008) are slightly different, but cannot be reproduced due to copyright issues. In particular they indicate lower Chinese and higher Guinea production for 2007, with a world total production for 2007 of ~209 MT. Gu (Gu 2008) puts the Chinese reserve at 540 MT and the Chinese bauxite production at ~40 MT for 2007. Vietnam is not listed by the Bray report, probably because the deposits there are only now being evaluated, but this will undoubtedly be a significant source of bauxite in the future.

The Bray report estimates world bauxite *resources* totalling 55–75 billion tons. Resource is defined as the concentration of bauxite such that economic extraction is *potentially* feasible. Resources presumably include non-identified reserves, as well as holdings that are considered non-economic with present technology. The report gives the breakdown of world reserves by region and these are reproduced in Table 3.

Table 3 World bauxite resources by region (total world estimate 55-75 billion tons).

World region	% of world bauxite resource
Africa	33
Oceania	24
South America and Caribbean	22
Asia	15
Others	6

Resources that are currently not part of the demonstrated reserves or reserve bases are almost certainly dominated by bauxites that contain high levels of reactive silica. The 55–66% of world resources that are not currently described as being within the economic reserve indicates the potential for new processes to exploit these holdings and bring them into the realm of economic reserves.

1.4 The Bayer process

The Bayer process is the principal method for production of alumina from bauxite worldwide. The modern version of the process (developed in the 1880's) still maintains the key steps of dissolution of alumina-rich minerals into hot caustic solution, separation of the insoluble phases, followed by gibbsite precipitation and calcination of the gibbsite to alumina (Al_2O_3). A good summary of the process and some variants is given by Misra (Misra 1986). A schematic is shown in Figure 1. Operations with a red background represent those involving either the bauxite or mud, and thus represent the so-called "red-side" of the Bayer process. Operations with a white background relate to processes in the absence of these solid materials, and represent the so-called white-side operations (eg precipitation, evaporation).

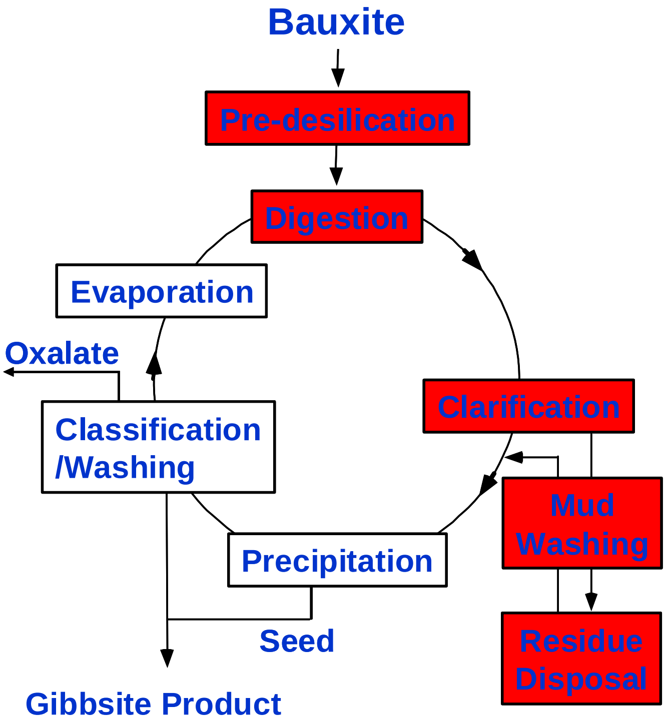

Figure 1 Schematic of the basic Bayer process (Calcination of gibbsite to alumina not shown).

Bauxite is first reduced through crushing and grinding (usually in a portion of "spent" liquor) at ~60°C. Silicate minerals, principally kaolinite, start to dissolve in the spent liquor.

$$3Al_2Si_2O_5(OH)_4 + 18NaOH \rightarrow 6Na_2SiO_3 + 6NaAl(OH)_4 + 3H_2O \qquad \text{eq.1}$$

In many modern operations there is a slurry storage or "pre-desilication" stage in which slurry is kept at high volume-fraction at near atmospheric boiling for several hours to encourage the re-precipitation of the solubilised silica to DSP (desilication products).

$$6Na_2SiO_3 + 6NaAl(OH)_4 + Na_2X \rightarrow Na_6[Al_6Si_6O_{24}].Na_2X + 12NaOH + 6H_2O \quad \text{eq.2}$$

The above equation represents the formation of Bayer sodalite (in which X represents a variety of inorganic anions, most commonly sulphate, carbonate, chloride, aluminate and hydroxide.

Slurry storage usually transforms ~80–90% of the reactive silica into DSP, with the remainder being converted in digestion. Digestion conditions are tailored to the aluminous phase distribution of the bauxite, such that if gibbsite is the only source of recoverable alumina, the digestion is performed at temperatures 140–155°C. Digestion times are often determined, not by the kinetics of gibbsite dissolution, but by the kinetics of residual DSP formation, and more importantly, the reduction of the soluble silica in solution. Bauxites containing non-trivial boehmite concentrations are mostly digested at temperatures 220–270°C. Again, time in digestion is often not dictated by alumina dissolution kinetics, but kept to a minimum to avoid excessive dissolution of quartz which provides additional reactive silica.

Since DSP is usually discarded with the red mud residue, the two equations above demonstrate the loss of sodium hydroxide from the liquor (at least 1 mole NaOH per mole of reactive silica)[1]. This loss of soda from the liquor is the source of the economic penalty and is linear with the reactive silica content of the bauxite. Bauxites with reactive silica contents greater than ~8% by weight (A/S=6.25) are usually considered to be uneconomic.

Bauxite is charged to digestion to achieve a specific alumina supersaturation. The level is chosen to ensure that the supersaturated liquor is stable through the flash train and subsequent clarification stages.

After clarification the liquor is sent to precipitation (gibbsite crystallisation) and the insoluble components (usually referred to as red mud) are sent to a counter-current washing system. The counter-current washing system returns liquor to the circuit but does not provide conditions suitable to recover the so-called “fixed soda” from the DSP.

It is worth noting here that refineries which currently process bauxites with relatively high levels of reactive silica also carry the legacy of high fixed soda in their residue areas. This may have residue disposal and/or environmental consequences.

1.5 Structure of DSP

The Bayer sodalite described in the previous section is only one of several mineral phases that precipitate silica from solution and can therefore be termed “desilication products”[2]. The others that can form include cancrinite (formed at digestion temperatures of ~220°C and above) and also silica substituted tri-calcium aluminates (hydrogarnets) which are the consequence of the dissolution of lime compounds, either from the bauxite itself or from lime added to control liquor impurities (e.g. phosphate).

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[1] In addition, if quartz supplies part of the reactive silica, then alumina is also lost from the liquor.

[2] There are many other forms of “desilication product” that occur during pyrometallurgical processing of bauxite or residue. These are discussed in the relevant potential processes.

The structure of Bayer sodalite is given in Figure 2.

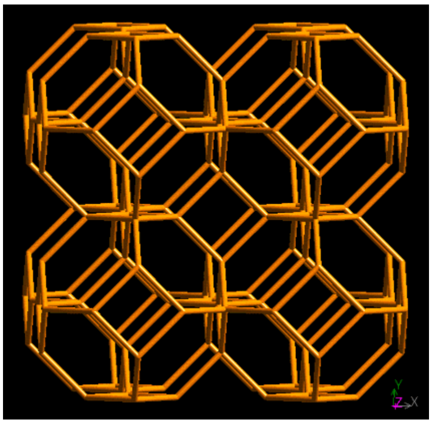

Figure 2 Bayer sodalite schematic showing cubic structure. Full occupancy is achieved with a monovalent ion in each cage, or a divalent ion in every other cage.

The aluminosilicate cage structure has a net three negative charge which is balanced by three sodium ions. At full occupancy Bayer sodalite has a monovalent anion (and associated sodium) in each cage, or a divalent anion in every other cage (see stoichiometry in equation 2). Soda can be recovered from this structure only if the sodalite cage structure is broken down, or if the included ions can be removed through the openings of the sodalite cage structure (Smith, Wingate et al. 2008).

At high digestion temperatures cancrinite, another cage structured aluminosilicate can form from sodalite. Cancrinite has the same cage stoichiometry as sodalite, but has a different structure Figure 3.

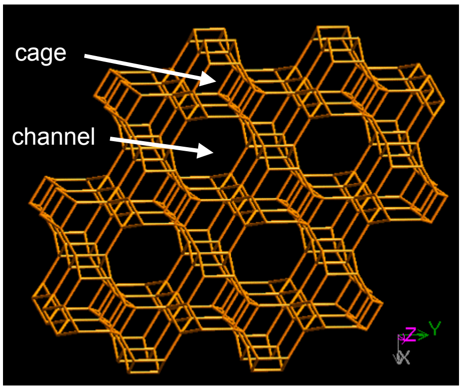

Figure 3 Structure of cancrinite (hexagonal). Cancrinite has two possible sites for included ions, either in cages which are smaller than those in sodalite, or in channels which are wider than the sodalite cage dimensions.

Cancrinite has two possible locations for included ions, either in the cage structures (which are smaller than those in sodalite) or the larger linear channels that form part of the hexagonal structure. The size and location of the channels mean that the preferred inclusion for cancrinite is calcium carbonate ($Na_6[AlSiO4]_6.2CaCO_3$). Thus cancrinite has 25% less sodium than sodalite and the added bonus of favouring a non-useful anion.

Other compounds that can be considered desilication products (which are particularly relevant to options for processing high silica bauxites) are the hydrogarnet series of minerals. These are silica substituted grossulars of the general formula

$Ca_3Al_2(SiO_4)_n(OH)_{12-4n}$. Natural minerals exist for integer n values, 0 (hydrogrossular or tri-calcium aluminate, TCA), 1 (katoite), 2 (hibbschite) and 3 (grossular). Isomorphous substitution of Si^{4+} for $4H^+$ gives rise to a range of solid solution compounds under Bayer conditions, ranging from $0.6>n>0$ (Whittington 1996b).

1.6 Strategies for caustic loss minimisation

In a Bayer type process, reactive silica will dissolve in the caustic aluminate solution and re-precipitate as a variety of (mostly) sodium aluminium silicates which are then discarded as part of the red mud residue. The opportunities to reduce the soda lost to the system therefore fall into three broad strategies:

1. Reduce the input of reactive silica to the process. This could take the form of beneficiation which may be preceded by a pre-treatment to allow separation of silica from the bauxite, or some other form of pre-treatment that effectively renders the silica unreactive during the subsequent Bayer digestion.
2. Modify the process to produce a lower soda residue. This could be by reducing the fraction of reactive silica transforming to DSP, or by the formation of alternative DSPs with lower soda content.
3. Recover soda from DSP. This would constitute a process developed to return to the Bayer liquor stream valuable caustic derived from the re-processing of either residue or a concentrate high in DSP produced from the residue.

Depending on what technology is being considered/developed in these three strategies, then (1) and (3) could be considered to be “add-ons” to the Bayer process (either at the front or back of the process) whereas (2) would constitute a change to the Bayer process itself. However there are undoubtedly some options which would blur this distinction.

The remainder of this document will concentrate on potential technologies (either previously considered or previously used commercially). They will be grouped under the broad strategies described above. For each technology, a brief description of the principle will be given, together with a status or state of development, and an evaluation of the techno-economic and (where appropriate) ecological hurdles to implementation.

2. Potential Technologies – Strategy One – Reduce Reactive Silica Input

2.1 Screening / washing

Principle:
Screening and washing is effective in reducing silica in the bauxite feed material if the silica is preferentially concentrated in the smaller particles size fractions or fines. Bauxite is “wet screened” on inclined or vibrating screens. The wet screening rejects pisolites lower than a certain size, and, at the same time, washes the fine material (adhering to the larger pisolites) which is also high in silica concentration.

Status:
Weipa bauxite mined by Rio Tinto in Queensland Australia is pisolitic, with the silica level (both kaolinitic and quartz) decreasing with increasing pisolite size. The beneficiation plant operated by Rio Tinto “wet” screens at a specific pisolite size and the undersize (tailings) are rejected. A schematic of the operations is given in Figure 4 (Roberts and Dunne 1980). Although the schematic is dated the essentials are thought to be unchanged. In particular it shows a cut-off size of ~1.7 mm (Weipa ore) and ~0.4 mm (Andoom).

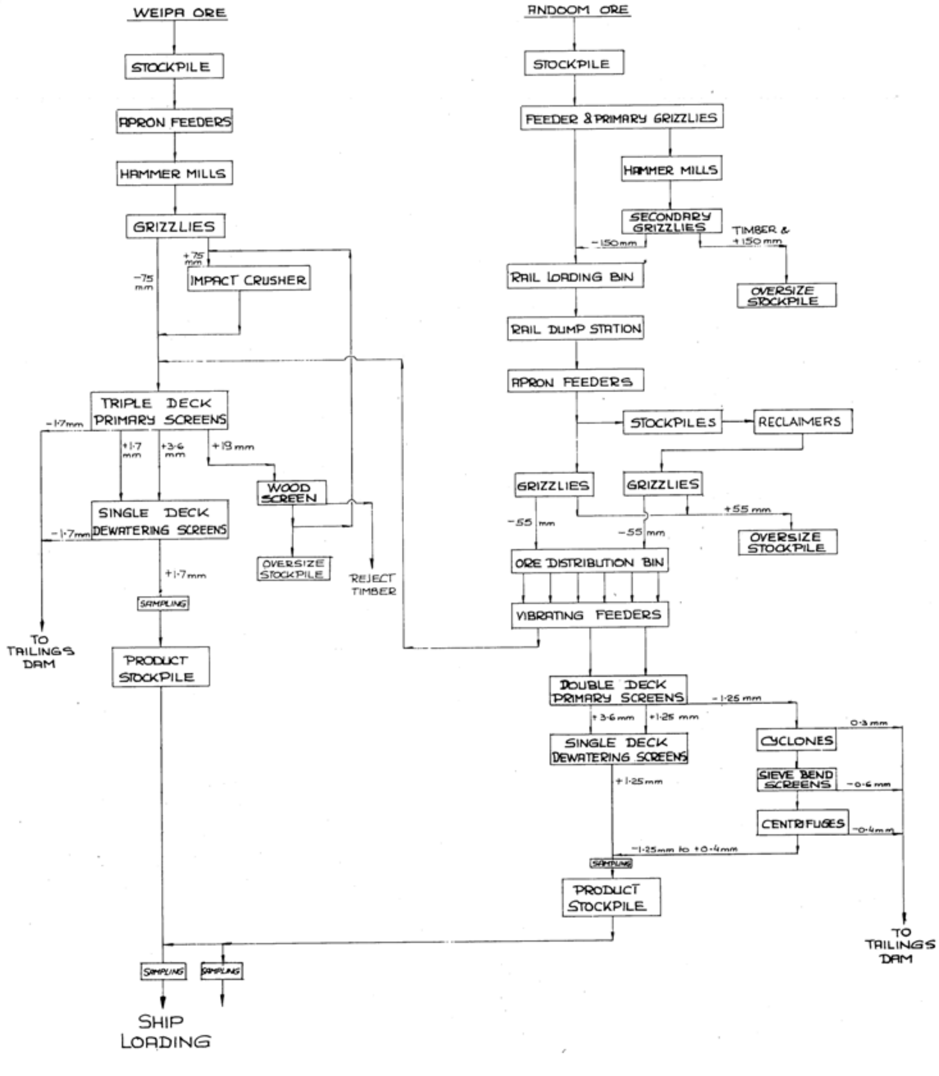

Figure 4 Schematic of Weipa and Andoom beneficiation operations at Weipa (From Roberts and Dunne, 1980)

Sometimes washing and screening will target quartz only. Rousseaux et al. (Rousseaux, Verschuur et al. 2006) examined the use of drum washing (and subsequent cyclones) to remove quartz known to be in Pijiguaos bauxite in the size range 0.1–3.0 µm. Amer (Amer and Abdel-Aal 1996) separated ~82% of quartz from an Egyptian bauxite by simply pulverising and screening at 63 µm.

Hurdles to implementation:
The application of this technology will depend heavily on the micro-mineralogy of the bauxite. In the case of the pisolitic bauxite, kaolinitic silica is sometimes more prevalent in the outer layers of the pisolite, and thus the silica concentration increases with increasing surface area and thus decreasing size. Owada (Owada, Okajima et al. 2005) examined the possibility of "surface grinding" to remove a kaolin rich outer layer in Gove pisolitic bauxite. When quartz is the target, then the effectiveness of beneficiation depends on the size distribution of that mineral and also its *liberation* – i.e. the degree to which the quartz can be separated from the valuable aluminous minerals.

At Weipa, the rejection of the undersize pisolites results in the return of this material to the minesite, essentially unchanged. If pre-processing is needed to liberate the target minerals (i.e. grinding before screening), then this is likely to be done as a slurry, and the rejected material might constitute a tailings disposal issue. In all cases, it is assumed that water is available to aid the screening process. Dry screening may be used in arid mining areas, but will be less effective than wet screening.

2.2 Gravity separation

Principle:
Gravity separation of phases in bauxite relies on the density between the valuable alumina minerals (e.g. gibbsite) and the silicate minerals (e.g. kaolinite). It is rarely used because this difference is small. If this technology has been considered, then the effects of density differences have often been magnified by the use of hydrocyclones. A recent paper by Gao (Gao, Li et al. 2008) describes conditions of the operation of the cyclone equipment to optimise alumina recovery and silica content (A/S ratio).

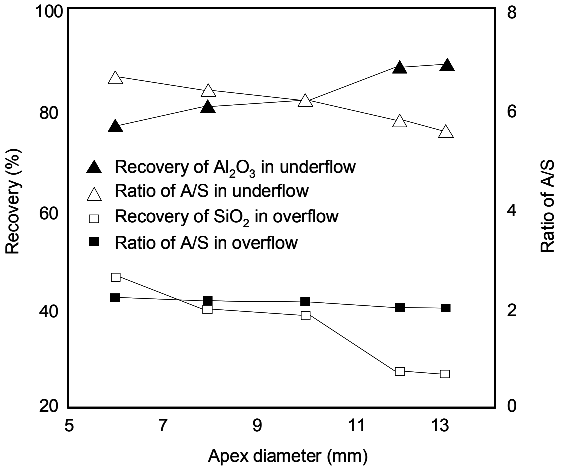

Figure 5 Effect of hydrocyclone geometry on grade and recovery of bauxite (re-drawn from (Gao, Li et al. 2008)).

Gravity separation for beneficiation has been used to target valuable by-products from the reprocessing of Bayer residue. Rao (Rao, Das et al. 1996) examined the possibility of separating titanium minerals (rutile and ilmenite) from Bayer residue sand using standard Wilfley tables. The work was successful partly because of the high density of the titanium minerals which would be heavier than sodalite, goethite and quartz, but lighter than hematite. Picaro (Picaro, Pei et al. 2002) examined the upgrading of DSP and TiO_2 minerals in QAL residue, concluding that a ~40% DSP concentrate could be produced at 89% recovery, but that the richest TiO_2 fraction was ~20-36% at only 7% recovery.

Status:
None of the authors whose work is summarised above have indicated any commercial use of this technology.

Hurdles to implementation:
It is unlikely that gravity separation (or hydrocyclones) could ever be used economically to reduce silica in lateritic bauxites. For these bauxites the alumina and silica minerals are intimately mixed so that adequate liberation is not possible. Sometimes in non-lateritic bauxites (like the diasporic bauxites found in China) the silicate minerals are less intimately mixed. This may explain why Gao has had some success with hydrocyclones.

2.3 Flotation

Principle:
Bauxite can be floated in a suitable medium (usually near neutral aqueous solutions) using proprietary chemicals to absorb on the target minerals to either activate them towards collection/attachment by bubbles or to depress them. In the first variation, valuable minerals preferentially report to the froth phase and are thus separated from silicate minerals which become part of the gangue. In the alternative strategy, the valuable alumina minerals are depressed and therefore report to the tailings (reverse flotation).

Flotation is particularly suited to diasporic ores in which there is sufficient liberation of alumina from silica minerals, and the silicate minerals are of a particle size suitable to flotation ~(10–200 μm).

Status:
After the initial work by the Russians (Andrew, Anishchenko et al. 1973), (Ishchenko, Korus et al. 1974) it has been the Chinese researchers who have developed this area, from the initial work of Li (Li and Chen 1979) to a great body of work in the years 2000 onwards by authors such as Hu (Hu, Ouyang et al. 2008) and Wang (Wang, Hu et al. 2004). A good review is given by Xu (Xu, Plitt et al. 2004) which covers the literature in reverse flotation of diasporic bauxites up until 2004, and more recently Zhong (Zhong, Liu et al. 2008). The western literature perhaps does not reflect the depth of this work. For example it is suspected that a great deal of work has been done by both Chalco and BGRIMM which is less publicised in English and therefore less well known to western researchers. It is also possible that more of their work appears in the patent literature e.g. (Chen and Li 2006).

The industrial implementation of bauxite flotation has been through the Chalco owned Zhongzhou Light Metals Research Institute and associated refinery which has demonstrated this technology with both Shanxi and Henan bauxite (Li, Song et al. 2002).

Hurdles to implementation:
This technology is already being used commercially, and its use is expected to increase for those bauxites which are applicable (mainly diasporic bauxites). A hurdle is expected to be problems with the organic input associated with flotation chemicals especially their effect on downstream processes e.g. digestion (Loginova, Koryukov et al. 1979).

As mentioned before, this technology is not expected to be useful for lateritic bauxites where the silicate and alumina minerals cannot be sufficiently liberated to achieve good upgrading and recoveries. A good explanation of liberation with respect to beneficiation options is given by Solymar (Solymar, Madai et al. 2005).

2.4 Bio-leaching

Principle:
Bacterial strains are mixed with bauxite and a growth medium (usually a glucose or related carbon source) from which certain elements of the minerals are extracted into solution. A key mechanistic question for all mineral bio-beneficiation is whether the solubilisation of elements from minerals involves a form of direct attachment of the bacteria onto the mineral surface, or by the simple chemical action of bacterial metabolites (usually organic acids) on the minerals (Ehrlich 1992).

Status:
Anand (Anand, Modak et al. 1996) examined the leaching of calcium and iron from bauxites, i.e. phases most likely to be solubilised by the action of organic acids. Comparison of the action of the bacteria strain to the leaching produced by the metabolites only (i.e. no bacteria) indicated that the solubilisation was due to both metabolite and direct attachment action. These results were later confirmed by Vasan (Vasan, Modak et al. 2001).

Groudeva and Groudev (Groudeva and Groudev 1983) examined the specific use of "silicate" bacteria to remove silicates from bauxite. The origin of the bacteria was not clear, in that they were said to have been isolated from "soil and rock samples", but the most successful strain was one related to Bacillus circulans. A common problem encountered when trying to "solubilise" silica is the co-leaching of alumina (either from kaolin or from gibbsite) which will suppress the silica solubility in the medium. Bacillus circulans is known to produce "mucilaginous capsules" which evidently can concentrate the alumina and silica dissolved by the bacterial action. Best results were obtained with growing organisms with a glucose food source and fresh medium (i.e. not containing spent nutrient components which can inhibit bacterial action). A continuous flow-through system was tested in which 55% of silica could be removed from the bauxite at ~100 g/L over a period of 5 days.

Hurdles to implementation:
The hurdles to implementation are, most obviously, the time required for pre-treatment. Other considerations are the non specific nature of the dissolution (both aluminium and silicon are dissolved), the requirements for a growth medium, and the separation of the

dissolved silica and the bacteria from the desilicated bauxite. The time issue has been addressed in other bacterial applications by the use of heap leaching technology.

2.5 Magnetic separation

Principle:
Magnetic separation (either wet or dry) is used to produce two product streams, one magnetic (or weakly magnetic) and one non-magnetic. Magnetic separation may or may not be preceded by a pre-treatment designed to enhance the magnetic susceptibility of some minerals (e.g. a reducing roast to encourage the reduction of iron minerals to produce magnetic phases).

Status:
There has been some work on the use of magnetic separation for the reduction of iron contents in bauxites for the production of refractory bauxites (see e.g. (Bhagat, Banerjee et al. 2001) (Rao 1996) (Sadler and Venkataraman 1991)), however there does not appear to be any industrial application of this technology, even in India where the majority of this work has been done. Bartosik (Bartosik, Strnad et al. 1974) indicates that magnetic separation has been used (in conjunction with flotation) to remove both calcite and corundum from bauxite to produce a feed suitable for the Bayer process.

There has been more interest in the use of magnetic separation as part of residue re-use programs, in order to produce an iron based by-product (e.g. (Mishra, Staley et al. 2002)) but again there is no evidence that this has been implemented commercially.

There does not appear to be any work in the literature specifically detailing the use of magnetic separation to remove silica from bauxite.

Hurdles to implementation:
There is some possibility that magnetic separation could be useful for silica reduction on the basis of mineral associations. For instance, if the reactive silica minerals preferentially reported to the magnetic iron fraction by virtue of their associations then an upgrading may be possible. Similarly if boehmite could be separated from quartz, then the possibility may exist of producing a feed lower in reactive silica at higher Bayer digestion temperatures.

2.6 Mechano-chemical treatment of bauxite with lime

Principle:
Mechano-chemical treatment (activation) is a form of ultra-fine grinding in which certain chemical reactions occur that would not in the absence of the grinding. It is thought that the energy required to initiate these chemical reactions is provided by the collisions of the grinding media (perhaps in the form of high localised temperatures) which are then transferred to the reactants.

Status:
The application of mechano-chemical treatment to bauxite was first suggested by Pawlek (Pawlek, Kheiri et al. 1992). They found that ultra-fine ground bauxite promoted high alumina loadings at low temperatures during subsequent digestion, and that the

addition of lime reduced the concentration of dissolved silica exiting digestion. McCormick (McCormick, Picaro et al. 2002) refined this observation and noted that the addition of lime promoted the formation of silica substituted TCA (hydrogarnets) from both kaolinite and quartz, which reduced caustic losses (albeit at high lime charges, >~9% CaO on bauxite). A patent on this technology also exits (Picaro and McCormick 1997).

A recent paper by Fortin and Forté (Fortin and Forté 2007) re-examines the claims of McComick but the authors were unable to reproduce TCA formation using ultra-fine grinding, and thus also did not see any reduction in caustic loss. It is not clear whether this is due to a difference in the methods or materials, or whether there was a fundamental problem with either group's results.

Hurdles to implementation:
The advantage of this technology compared to the "Lime Bayer" technology promoted by Chinese researchers (q.v.) appears to be the formation of hydrogarnets without side reactions. As noted in previous sections, hydrogarnets can be an effective, if inefficient method of reducing caustic losses (typically the molar ratio of Ca:Si in hydrogarnets produced in the Bayer process is 5:1).

Mechano-chemical treatment appears to convert most, if not all silica into hydrogarnets, including some or all of the quartz that would otherwise pass through digestion unreacted. This adds to the inefficiency of the process. These shortfalls combined with the substantial costs associated with ultra-fine grinding of bauxite suggest that this could not be an economical way of reducing caustic losses.

2.7 Roast-leach process

Principle:
When kaolin in bauxite is heated to ~550°C it dehydrates to metakaolinite. Further heating to 980°C causes a sudden "splitting" of the kaolin into 2 or more products. Amorphous silica (SiO_2) is certainly produced. There is some conjecture about the other products: a transition alumina (possibly γ-alumina) and/or and alumino-silicate spinel are produced (Brown, MacKenzie et al. 1985) (Chakraborty and Ghosh 1978) (Santos, Campos et al. 2005). The uncertainty is exacerbated by the fact that both the spinel identified $2Al_2O_3.3SiO_2$ and γ-alumina have similar structures and therefore X-ray diffraction patterns.

After the roast, the bauxite is subjected to a weak alkaline leach that dissolves the amorphous silica (to form a sodium silicate solution). The weakness of the caustic solution ensures that the alumina from the kaolin, and the alumina from the other alumina values (which have also been transformed into transition aluminas by the roasting process) are not dissolved. The "desilicated" bauxite is then fed to a Bayer process variation capable of digesting the transition aluminas produced.

Status:
The process appears to have its origins in Eastern Germany (Schoenfelder and Ginsberg 1960) – which has references to earlier (~1955) East German patents. Some further development occurred in Czechoslovakia (Klan 1959) where it was apparently used commercially for a while.

After a long period, the process has received further attention (Lin, Malts et al. 1998) (Rayzman, Pevzner et al. 2003) (Qiu, Jiang et al. 2004). Rayzman describes the operation of this process on a pilot scale at the facilities of VAMI in St Petersburg. It is not clear whether this process has ever been used commercially within Russia or other former Eastern block countries.

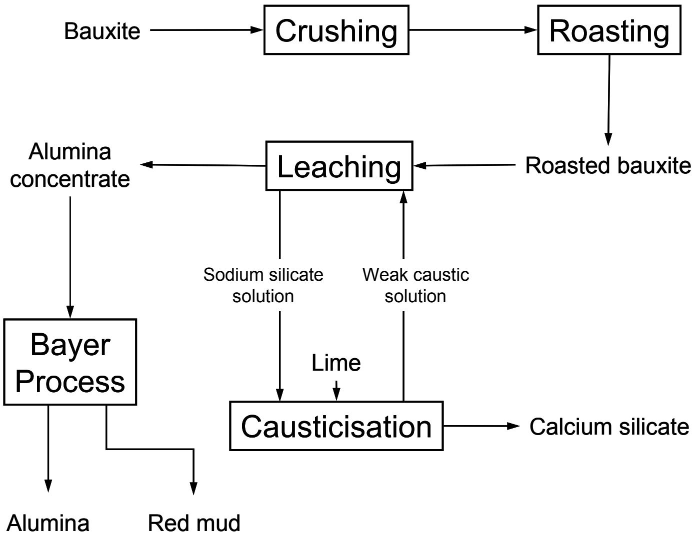

Figure 6 A schematic of the Roast-Leach process (after Rayzman (Rayzman, Pevzner et al. 2003)).

Hurdles to implementation:

Roasting bauxite to ~1000°C is energy intensive and would be difficult to justify economically. However in theory, the process has the potential to reduce soda losses significantly. In addition a portion of the alumina once associated with the kaolin is now potentially available for recovery (boosting the effective “available alumina”). The savings in soda and extra alumina produced need to cover not only the energy of the roast, but the re-activation of the sodium silicate solution – and this has caused much of the problems experienced at VAMI. The silicate solution is limed to produce calcium silicate (a saleable by-product) but this process is compromised by the leaching of small quantities of alumina which reduce its efficiency.

In addition the desilicated bauxite contains transition aluminas instead of the original hydrated (oxy) hydroxides. This necessitates more aggressive Bayer digestion conditions (temperatures over 260°C and retention times exceeding 30 minutes). The suitability of the particular bauxite for this process has to be considered carefully, since if the bauxite contains substantial quartz, the extra DSP formed by additional quartz attack can reduce or even eliminate the caustic saving advantages sought.

In spite of these hurdles there is potential in this approach, especially if a way can be found to offset the additional energy costs.

3. Potential Technologies – Strategy Two - Modify the Process

3.1 Sinter processes

Principle:
In all of the different variations of the sinter process, the common principle is that the raw material is heated, together with another chemical (usually an alkali) to induce a solid state reaction. An alkaline leach is then performed to separate the aluminous material from the insolubles. Of the sinter process variants, two are within the scope of this study – the lime sinter process and the lime-soda sinter process.

In the lime sinter process the additive is a calcium salt (usually calcite – $CaCO_3$). The mixture is heated to above the decomposition temperature of calcite (~825°C) and solid state reactions occur between the lime and the alumina values (gibbsite and boehmite) and also with alumino-silicates (kaolinite). This requires temperatures of ~1150°C or above. The mixture ratios and the sintering conditions are designed to optimise the production of various calcium (aluminium) silicates, which, after cooling, are amenable to leaching with an alkaline solution, either caustic, or more commonly sodium carbonate. Gibbsite is subsequently recovered either by seeding or by carbonation (to regenerate the sodium carbonate for leaching). The equations below describe the primary reactions with silica and with alumina, but many more are also possible, leading to a wide range of products -

$$2CaCO_3 + SiO_2 \rightarrow 2CaO.SiO_2 + 2CO_2$$
$$12CaCO_3 + 7Al_2O_3 \rightarrow 12CaO.7Al_2O_3 + 12CO_2$$

In the lime-soda sinter process the bauxite is heated as before with calcite, but also with a source of soda (usually solid sodium carbonate – soda ash). The relative mixtures of all three components are designed to promote the reaction of the aluminous material with soda to produce sodium aluminate and the reaction of lime with silica to form calcium silicates (Ca:Si 2:1 and 1:1). Soda also reacts with iron minerals to form sodium ferrites[1].

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$
$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$
$$Fe_2O_3 + Na_2CO_3 \rightarrow Na_2O.Fe_2O_3 + CO_2$$
$$4CaCO_3 + Al_2O_3.2SiO_2 \rightarrow 2(CaO)_2.SiO_2 + Al_2O_3 + 4CO_2$$

Again these reactions are not comprehensive, and are given in oxide form for the sake of clarity. Both the (dehydrated) sodium aluminate and the sodium ferrite are soluble in water or weak caustic solution. The sodium ferrite almost immediately reverts to hematite, producing sodium hydroxide which helps stabilise the sodium aluminate.

Status:
The literature on sinter processes is vast. A comprehensive review of many of the process variants is given by O'Connor, including versions designed to process non-

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[1] Sodium may also react with titanium minerals. Also a number of tertiary compounds involving Na_2O, CaO, Al_2O_3 , Fe_2O_3 and TiO_2 will form depending on the mixture ratios and the reaction conditions (Eremin 1974).

bauxitic feedstocks (O'Connor 1988). The specific use of sinter processes for the production of alumina from low quality (high silica) bauxites is given in a series of articles collected in a 1974 issue of Travaux (ICSOBA). In particular the papers by Bartosik (Bartosik, Strnad et al. 1974), Eremin (Eremin and Shmorgunenko 1974) and Tomka (Tomka 1974) are useful. Although these papers represent snapshots of technology that was in use over 30 years ago, the sinter process in the Eastern block countries was then in widespread use, and these papers represent well established process variants.

More recently the efficiency of phase formation (including the avoidance of the undesirable α-alumina is discussed by Lu and Feng (Lu, Fang et al. 2003) and general optimisation of the sinter process by Li et al. (Li, Liu et al. 2004).

The commercial operations still using this (and related) technology are those processing low grade, often diasporic ores in both Eastern Europe (Russia, Ukraine, Turkey) and China. Refineries still using the sinter process include Zhongzhou, Nanting and Shandong in China, Bogoslovsk, Tikhvin and Kammensk in Russia and Dnjepr in the Ukraine.

Hurdles to implementation

The main disadvantage of these processes is energy costs. Whilst typical Bayer refineries, processing high grade lateritic bauxites can expect to produce alumina at ~11–13 GJ/t Al_2O_3, the sinter process energy costs are ~38 GJ/t Al_2O_3 (Arlyuk 1995). New refineries are very unlikely to adopt such technology, and the trend has been to adapt older refineries to more efficient Bayer technology, where this is seen to be appropriate for the bauxite used. In some cases there are limited options for domestic bauxite supplies, and this explains the continued use of sinter and combination processes (see next section) especially in China.

An inherent technical problem with these technologies is the high level of dissolved silica that is generated by the presence of many and diverse calcium (aluminium) silicates, some of which have greater solubilities than the corresponding phases produced in a standard Bayer process (Liu, Li et al. 2003). Product quality concerns (over silica and associated soda) have prompted refinery modifications to include green liquor deep desilication (seeding with TCA) (Bartosik, Strnad et al. 1974) (Li, Liu et al. 2003) which again adds to the cost of production.

3.2 Combination process (Bayer-sinter)

Principle:

The combination process first uses a regular Bayer process to extract alumina values from the high silica bauxite. Soda and alumina losses are allowed to occur in this first stage and report to the residue. The residue is then subjected to a lime-soda sinter, in a similar fashion to that already described. Often the exit leach solution from the second stage provides the starting liquor for the Bayer stage with fresh bauxite.

The advantage of this combination (compared to a single lime-soda sinter) is the energy saving associated with heating a reduced mass of residue compared to the bauxite from which it was produced. Malts (Malts, Shmorgunenko et al. 1984) also claims that the melt conditions for mixtures containing red mud is more advantageous than those for bauxite. In addition, and dependent on the bauxite and process variant used, the combination process can be used to achieve greater alumina loadings in the process liquor (greater liquor productivity) than could be achieved by a single lime-soda sinter process.

Status:
A good overview of the East European versions of the combination process is given in the papers by Prokopov and Malts (Prokopov and Malts 1974) and Reisner (Reisner 1974). The main concern in recent researches is one of energy, and Liu (Liu, Aye et al. 2006) has indicated the steps taken between 1995–2000 at the Zhongzhou refinery to reduce the energy consumption of the combination process by ~7 GJ/t Al_2O_3. The table below (taken from the Liu paper) shows the relative energy intensity requirements of the sinter process, the combined process and straight Bayer.

Table 4 Comparison of energy intensities of alumina refinery variants (from (Liu, Aye et al. 2006)).

Refinery name	Production method	Ore type	Energy Intensity GJ/t Al_2O_3.
Zhengzhou	Combined	Diaspore	34.15
Shanxi	Combined	Diaspore	37.28
Guizhou	Combined	Diaspore	43.31
Zhongzhou	Combined	Diaspore	52.17
Pinguo	Bayer	Gibbsite and diaspore	15.10
Shandong	Sinter	Diaspore	40.50
(un-named) France	Bayer	Diaspore	13.52
Pinjarra (Australia)	Bayer	Gibbsite	11.21
Shennigola (Greece)	Bayer	Diaspore	14.86
Straford* (Germany)	Bayer	Gibbsite	9.60

* This is likely to be the Stade refinery since there is no Straford refinery in Germany.

Other developments in the combination method have examined the optimisation of materials flow (Liu, Yu et al. 2002).

Hurdles to implementation:
Sinter and Bayer-sinter methods are generally considered to be reliable but old technologies. They are still used because, for some bauxites, there are no alternatives (or the Bayer alternative is even more expensive due to the loss of caustic soda). Improvements that have been made during the past ~ten years have been aimed at process optimisation, especially to reduce energy consumption. To be economically competitive with Bayer processing of low silica bauxites, energy consumption would have to be cut by at least 50% and perhaps 65%. This appears unlikely without step change technology development.

3.3 Bauxite activation

Principle:
The Rio Tinto (Comalco) bauxite activation process involves a thermal pre-treatment designed to make the valuable alumina phases (gibbsite and boehmite) amorphous (Bhargava, Allen et al. 2004). The benefit of this process is that subsequent Bayer processing can be done under less severe conditions (especially temperature). This

allows more effective extraction of the boehmitic phases, reduced operating temperatures and costs, and the elimination of most, if not all, organic phases and the problems they bring with them. The heat treatment is relatively low temperature (~500–550°C) for a short time (i.e. flash calcining) and thus the kaolin is unaffected (a portion of the kaolin might start dehydration to meta-kaolinite, but this does not significantly affect its reactivity and desilication characteristics). This there is thus no benefit for caustic loss minimisation from this reaction.

The benefits for high silica bauxite processing come from the reduction of digestion temperature and the consequent reduction (or elimination) of quartz attack that would normally occur under the temperatures commonly used to digest boehmitic bauxite. This process can be advantageously combined with double digestion (see next section) to further enhance the extractability of the alumina bearing minerals, since, according to Hollitt (Hollitt, Kisler et al. 2002) there may be difference in the solubilisation of amorphous alumina from boehmite, compared to amorphous alumina from gibbsite. Comalco (Rio Tinto) has a number of patents over this process (Hollitt, Grocott et al. 2000a), and (Hollitt, Grocott et al. 2000b).

Status:
The bauxite activation process was developed by Comalco at the time when the plans for the future Yarwun refinery (Gladstone, Queensland) were well advanced. It is the author's view that the process was considered for the refinery, but on balance the owners decided on more proven technology[1].

Rio-Tinto continues to develop this technology for possible use in the future.

Hurdles to implementation:
There are many benefits to this technology, which are listed in great detail in the patents and the AQW paper (Hollitt, Kisler et al. 2002). The only benefit directly related to caustic consumption is the reduction in processing temperature and hence quartz attack.

A similar reduction in the high temperature digestion may be achievable using Double Digestion technology only, but a detailed comparison would be required. An additional hurdle surrounds the conditions for the roasting itself. Moisture control (to avoid problems with amorphous alumina rehydration) and alumina mineral transformation during the very small reaction times (order of 10's of seconds) can provide issues of stability.

3.4 Double digestion

Principle:
Double digestion is the application of the principle of counter-current digestion to the Bayer process (Doucet 1993) (Doucet, Hendricks et al. 2002). In this technology the bauxite and liquor streams move in opposite directions. Fresh bauxite is contacted with liquor at ~150°C that has already been through a high temperature "boehmite digestion". The gibbsite from the fresh bauxite dissolves producing a highly loaded liquor. The slurry is separated under high pressure and temperature using a pressure decanter.

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[1] Even though the current technology at the Yarwun refinery does include a number of new aspects, it was considered less radical than bauxite activation.

The liquor is flashed and goes to precipitation, whereas the solids are next contacted with spent liquor at a higher temperature to dissolve the boehmite. After this second digestion the slurry is again separated, with the solids flashed and sent to residue, and the liquor directed to the first digestion.

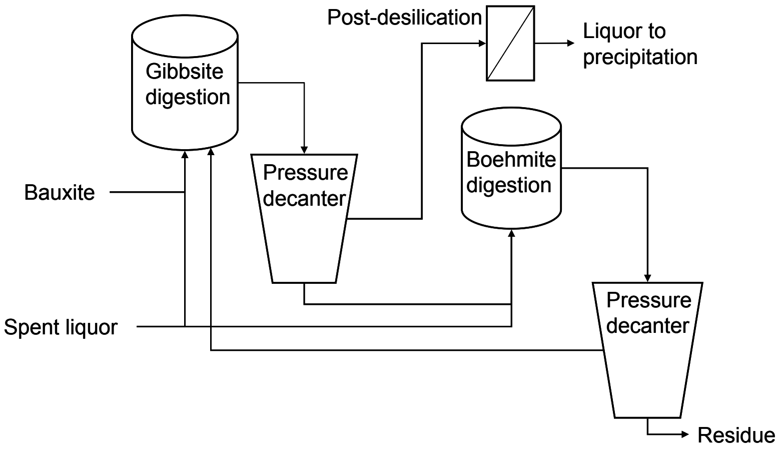

Figure 7 Double Digestion circuit schematic (adapted from Doucet (Doucet 1993)).

As with the bauxite activation technology, the key advantage of this process with respect to caustic loss is the reduced high temperature processing. The saving in soda consumption will clearly depend on the bauxite used, and would be suitable particularly to boehmitic bauxites with high quartz contents.

Status:
Double digestion is proven technology that has been implemented in several refineries. The enabling decanter technology was first developed by Alcan (Iida, Stewart et al. 1994).

It is interesting to note that although double digest technology has proven benefits, there has been a growing trend for new (Greenfield) refineries to opt for the leaner tube digester technology which is more energy efficient and simpler (de Boer, Edwards et al. 2005).

Hurdles to implementation:
As a proven technology, the hurdles to implementation are those related to economics. Retrofitting double digest technology is expensive but has been achieved recently for the Gove refinery in the Northern Territory Australia (Valenti and Ho 2008). Although the primary driver in this case was to recover boehmite that was increasing in their bauxite feeds, the operation of double digestion compared to a single high temperature digest will undoubtedly save some soda.

Two particular drawbacks that have been identified with double digestion are boehmite reversion in the first digestion stage where the alumina loadings in liquor are high, and solid boehmite is present, and the need for green liquor desilication (Lamerant and Ferret 2002). Both of these disadvantages have been targeted in a patent by Rodda (Rodda and Shaw 1996) in which the gibbsite digestion is reduced to 2-5 minutes (to avoid boehmite reversion), followed by solid-liquid separation and green liquor desilication. Interestingly, the Rodda patent describes similar gibbsite digestion temperatures to Sumitomo (see section 3.7) but does not claim any reduction in reactive silica dissolution (this may be as a result of higher caustic concentrations). The two stage post-digestion desilication that follows does result in soda savings through the precipitation of hydrogarnets, but the primary objective of this technology is to reduce silica in liquor and its detrimental downstream effects.

3.5 Low soda DSPs

Principle:

The benchmark for soda content in DSP is that of Bayer sodalite. The formula $Na_6[AlSiO_4]_6.Na_2X.yH_2O$ (where X can be a variety of inorganic anions) indicates a molar Na_2O/SiO_2 of 2/3. Low soda DSPs are therefore defined to be DSPs in which the molar soda to silica ratio is less than 2/3.

In either hydrometallurgical or pyrometallurgical methods of forming DSPs, emphasis has been almost exclusively in producing forms of calcium (aluminium) silicates which may or may not contain some soda. The most desirable end-products in this series are calcium silicates in which the Ca:Si molar ratio is either 1:1 or 2:1. These DSPs contain no soda and represent an efficient consumption of calcium. Although these products are the goal of some thermal processes (sinter, combined process), calcium silicates have rarely been reported to occur in hydrometallurgical processes with Bayer liquor (a notable exception is the hydrothermal lime process, see section below).

The main non-sodalite DSPs produced within the Bayer process are the hydrogarnet series $Ca_3Al_2(SiO_4)_n(OH)_{12-4n}$, and cancrinite $Na_6[AlSiO_4]_6.2CaCO_3.yH_2O$. Whittington (Whittington 1996b) concludes that under hydrothermal formation conditions in Bayer liquors n is restricted to <0.1–0.8. Iron can also substitute in the hydrogarnets, but only at high digestion temperatures (>250°C) (Zoldi, Solymar et al. 1987). Hydrogarnets therefore represent an effective means of reducing soda losses, but are inefficient (compared to calcium silicates) in terms of their lime consumption (Ca:Si ratio). They also constitute a significant loss of alumina from the liquor.

Cancrinites offer the potential of a 25% reduction in soda in DSP (compared to sodalite). However it should be remembered that the calcium carbonate inclusion in cancrinite effectively replaces the Na_2X in sodalite. If X=sulphate or chloride ion (for example) then although cancrinite formation reduces “soda loss”, this soda is not, in fact, useful caustic soda (i.e NaOH or $NaAl(OH)_4$). Cancrinite formation is only observed under high temperature digestion conditions (Whittington 1996a).

Status:

The addition of lime to form hydrogarnets ***specifically*** to reduce soda losses has been pioneered by Chinese researchers (Zhao, Hu et al. 2002) (Gu, Yin et al. 2002). Additions of up to ~16% CaO on bauxite have been used (Zhao, Hu et al. 2002) which can reduce the soda content of the residue to ~2.5 wt% (this small content was considered to be from liquor adhered to residue and not a soda containing mineral phase). “Lime-Bayer” is currently used in several Chinese Bayer refineries including Shanxi and Henan (Gu 2008). Hydrogarnets are very stable under typical Bayer digestion conditions (Ni, Goldman et al. 1979) and thus the process is quite robust.

The description of the iron-hydrogarnets goes back to the pioneering work of Ni (Ni, Bunchuk et al. 1968), but it is the extensive work of Solymar and co-workers from Aluterv that have promoted the use of these “catalytic” additives in high temperature digestions for the reduction of soda losses (Zoldi, Solymar et al. 1987). The technology was first introduced to control iron problems, especially those related to goethite to hematite transformations (Boros, Csillag et al. 1978) but was soon after suggested to offset the alumina losses associated with normal hydrogarnet formation (Solymar, Orban et al. 1983). An important paper that summarises the Hungarian experience with iron hydrogarnets for soda loss minimisation is given by Solymar et al. (Solymar, Steiner et al. 1997). The technology is based on the production of iron hydrogarnets with the general formula (*NB* compare to the hydrogarnet formula in section 1.5).

$$Ca_3[Al,Fe]_2(SiO_4)_{3-x}(4OH)_x$$

Where ideally x=1 or 2. The theory of hydrogarnet formation and stability in these conditions is given in the book by Ni (Ni, Goldman et al. 1979)[1]. Recently the technology has been revisited in a patent (Medvedev, Kiselev et al. 2002) and a paper (Medvedev, Akhmedov et al. 2003). This technology is very attractive, since if the iron hydrogarnet can be produced with x=1 (above) then the Ca:Si molar ratio becomes 1.5:1 compared to the hydrothermal aluminium hydrogarnets (5:1). In addition the iron hydrogarnets represent a smaller loss of aluminium. According to the paper by Medvedev (Medvedev, Akhmedov et al. 2003) five refineries (one in Bosnia, 2 in Russia and 2 in the Ukraine) are using the iron hydrogarnet technology.

Hurdles to implementation:
The economic feasibility of the “Lime Bayer” process depends heavily on the availability and cost of lime compared to caustic soda. Generally lime charges of ~16% CaO on bauxite would not be considered to be economic outside of China. But in that country, where lime is plentiful and cheap, the process does find acceptance, especially when its economics are compared to, say, the combination process.

Cancrinite formation is favoured by high digestion temperatures, long digestion times (suggesting that cancrinite can form from sodalite and/or hydrogarnets) and the presence of lime. Unfortunately some of these conditions also favour quartz attack which generally increases soda loss by increasing DSP production.

There is no known commercial process specifically based on soda savings from cancrinite production. If a way could be found to encourage the formation of cancrinite under the conditions normally used for high temperature digestion (especially to encourage sodalite to cancrinite transformation) then there would be some merit in this approach.

The iron hydrogarnet technology, although very attractive, also requires significant operating costs. In particular, in the Medvedev patent (Medvedev, Kiselev et al. 2002) there appears to be a complex internal cycle to regenerate very low A/C liquor for the mud digestion (a similar requirement appears in the hydrothermal lime process, next section). Also, the mud digestion requires the addition of an active iron source (sodium ferrite) possibly to allow the reaction to occur at lower temperatures than would otherwise be the case. It is not clear from Medvedev’s publications how or where the sodium ferrite is produced.

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[1] This book is in Russian (no translation available) and the author includes it here only from references by other authors.

3.6 Hydrothermal lime treatment

Principle:
This patented process, developed by Comalco in the early eighties[1], digests Bayer residue and lime at ~280°C in very low A/C liquor (low alumina) for ~20 minutes. These conditions lead to the formation of calcium silicates (mostly di-calcium silicate) which are stable in Bayer liquor and efficient at saving caustic. The process is therefore a hydrothermal equivalent of the combination process.

The problems that are immediately apparent with this technology is that the re-digestion requires the Bayer digested slurry to be flashed to atmospheric pressure, deliquored, re-slurried in low A/C liquor and heated up to the second digest temperature. The cost of this step, along with the requirement for a high caustic low A/C stream (which Comalco suggested could made by salting out $NaAl(OH)_4$ from spent liquor) made the process unattractive at the time (see Figure 8).

Status:
The process was patented by Comalco in 1982 (Cresswell and Milne 1982a) and described by Cresswell in the Bayer literature (Cresswell and Milne 1982b) (Cresswell and Milne 1984). There does not appear to be any development or use of the process (at least none published outside Comalco/RioTinto) since this time.

Several years after the Comalco patent, Sagin (Sagin 1988) described a similar hydrothermal process designed to replace residue sintering in the combined process. The advance that Sagin proposed was to design the lime digestion to encourage the formation of the desilication product $Na_2.Ca_2Si_2O_5.(OH)_2$ which, it is claimed, is superior to di-calcium silicate in two important ways – firstly it requires half the lime charge, and secondly it can be easily re-processed to recover soda without returning silica to the process. A similar desilication product has also been mentioned by Rayzman and Fillipovitch in the pyrometallurgical equivalent – “High Alkaline Sintering Method” (Rayzman and Fillipovich 1999).

Hurdles to implementation:
At the time that the Comalco and Sagin processes were developed double digestion was presumably not available (or at least not in commercial use). Double digestion technology could be used to save considerably on energy costs of re-digestion. The problem of how to create a high caustic low A/C stream still remains however, as well as how to integrate this process into a regular Bayer cycle (particularly washing).

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[1] The original idea appears in a paper by Klan (Klan 1971).

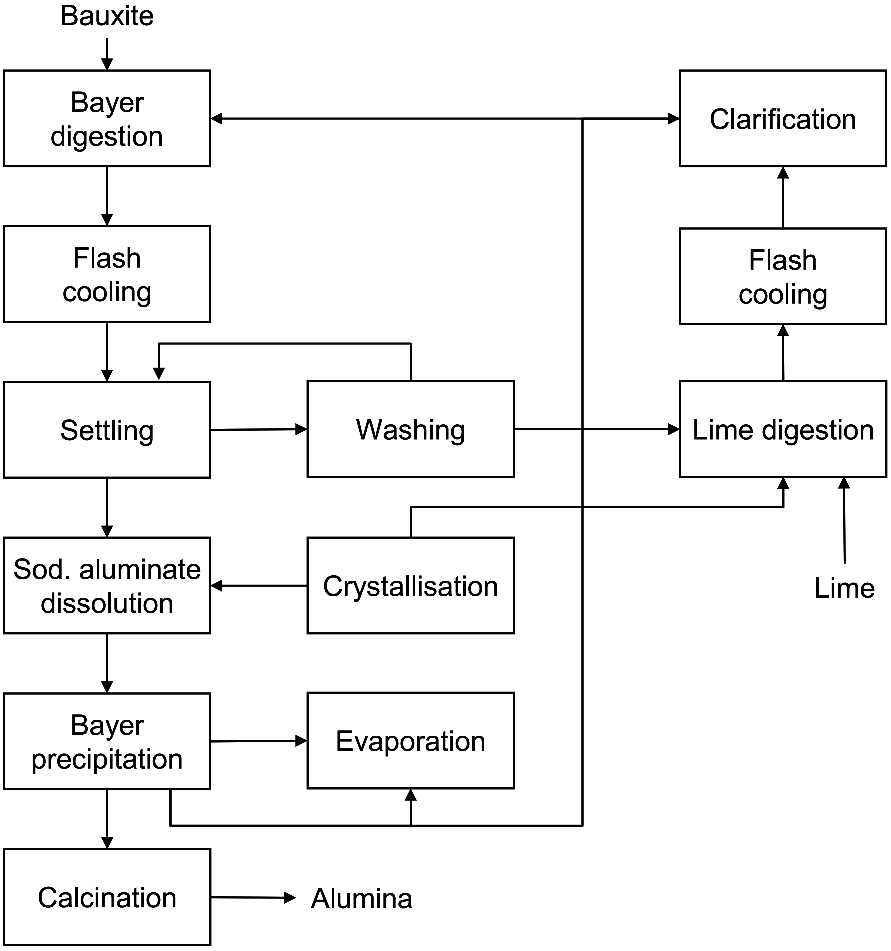

Figure 8 Process flowsheet for Hydrothermal lime treatment of residue and its incorporation into the Bayer cycle (after Cresswell 1984).

3.7 Differential extraction processes

Principle:
The main principle of these processes (for the processing of high silica *gibbsitic* ores) is exploiting the difference in extraction rates of gibbsite and kaolin. In the most recent variation (the Sumitomo process), at low temperature digestion (130^{o}C), gibbsite can be almost totally extracted into Bayer liquor at good loadings (A/C~0.69) in 2–5 minutes. In the same amount of time, only a fraction of reactive silica (kaolin) dissolves and almost none of this has precipitated into DSP (Figure 9).

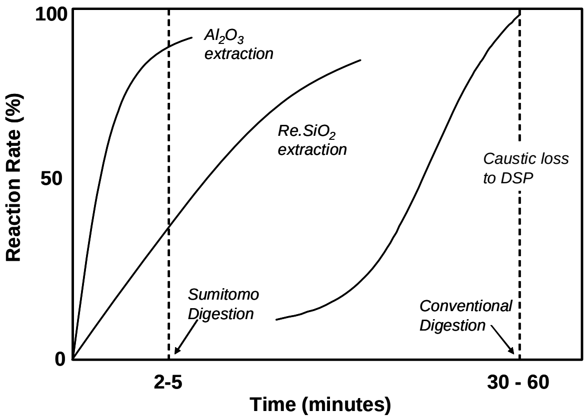

Figure 9 Schematic of the principle of the Sumitomo process (adapted from Harato et al. (Harato, Ishida et al. 1996)).

After this short digestion, the slurry is rapidly solid-liquid separated using a pressure decanter, and the kaolin-containing residue is subjected to high rate washing to prevent further reactive silica transformation to DSP. The pregnant liquor has a high concentration of dissolved silica which necessitates a seeded, post-digestion desilication prior to hydrate precipitation.

When operated under "careful control" the process is claimed to reduce caustic consumption by ~50% compared to a conventional Bayer process (Harato, Ishida et al. 1996).

Status:

The original work in this area was done by Takahashi (Takahashi 1962) who considered the use of two bauxites, one high silica and one low silica. The high silica bauxite is digested under conditions of low temperature (80–105°C i.e. atmospheric digestion) and solid-liquid separated under conditions to maximise the amount of undigested reactive silica in the residue. The liquor from the atmospheric digestion is then used to digest further low silica bauxite in a conventional digestion. The second digestion therefore increases the alumina loading and desilicates the liquor.

Other variations are by Grubbs (Grubbs 1986) and Iwase (Iwase and Murase 1988). They found that when bauxite is ground and separated into fine and coarse fractions, the fine fraction is richer in silica and poorer in alumina than the coarse fraction. The principle of Takahashi can then be applied to a single bauxite, separated into two fractions.

Improvements to this concept (principally in the area of solid-liquid separation) were provided by Oku (Oku and Suzuki 1973), Iwase (Iwase 1987), where the slurry was flash-cooled before separation and by Harato (Harato, Ishida et al. 1993) where a pressure decanter was used. The Sumitomo variation (Harato, Ishida et al. 1993) was operated continuously from 1994–2000 at the Ehime refinery, but was discontinued when the company strategy changed, and the refinery was used to produce specialty alumina.

Fulford (Fulford, Chinloy et al. 1991) also patented a version of this process using double digestion technology in which it is claimed the second digestion stage in the double digester can be used as the post-digestion desilicator. Fulford does not claim soda savings, but it is clear that the application of this technology to a Sumitomo type process would be advantageous.

Banvolgyi (Banvolgyi and Siklosi 1998) proposed another variation in that gibbsite is charged to very high Al_2O_3 loadings (close to the solubility of the gibbsite) at which the free hydroxide concentration in the liquor is very low. This free hydroxide concentration is the driver for not only gibbsite dissolution but also kaolin dissolution, and hence low free hydroxide concentrations further retard kaolin dissolution. The high A/C (alumina loadings) produced by this variation would normally cause problems with alumina reversion during solid-liquid separation and even though the digestion time is not so critical as with the Sumitomo version, Banvolgyi recommends pressure decantation be conducted at or near digestion temperature. The process is patented (Banvolgyi, Zoldi et al. 1992) and the theory behind the process has been described (Banvolgyi 1992).

Hurdles to implementation:
The Sumitomo process is restricted to gibbsitic bauxite ores because of the low digestion temperatures. There are a number of potential problems with all versions of this process including the operation of the pressure decanters, especially the effectiveness of flocculants, the operation of the high rate washers, and the effectiveness of the post-digestion desilication, especially aspects of seeding (Harato, Ishida et al. 1996). However, developments in these operations over the period since this technology was introduced are likely to provide at least partial solutions. Of particular importance would be the combination of modern double digest technology with the Sumitomo variation.

The Sumitomo process remains the only commercially used hydrothermally-based Bayer process variation specifically designed to reduce caustic consumption. As such it would be one of the process options with the highest potential.

4. Potential Technologies – Strategy Three - Soda Recovery Processes

4.1 Lime sinter of DSP

Principle:

There are several variations of the Bayer process in which a DSP concentrate is formed from the precipitation of DSP from a silica saturated liquor, either before or after digestion. The DSP concentrate can then be re-processed to recover caustic. Reprocessing of the DSP can be by the use of any sinter process of known technology (e.g. the lime-soda sinter). In this respect the process is similar to the combination process, but it is differentiated from it by the use of a DSP concentrate in the sinter stage rather than sintering the whole residue solids.

Status:

In the various processes already described in the sections on differential extraction and double digestion, post-digestion desilications will provide a "pure" DSP concentrate. Some of this will be returned to seed the desilication, but it also provides a source of DSP concentrate for re-processing.

In a process patented by Comalco (Hollitt, Crisp et al. 1998) the whole of the spent liquor stream is used to treat the raw bauxite with the aim of completely dissolving the reactive silica. The solids charge is designed to ensure that the resulting level of silica in liquor is not high enough to trigger the precipitation of DSP at the particular temperature of the dissolution (~100^oC). After dissolution, the slurry is solid-liquid separated. The high silica liquor is seeded with DSP and desilicated, producing a DSP concentrate which is separated. The liquor is recombined with the silica leached bauxite and sent to regular Bayer processing. There is no evidence of any commercial application of the Comalco technology.

The Comalco patent appears to have a number of antecedents, in which the silica is extracted into spent liquor before digestion – all are Japanese. A selection are: (Kanehara, Morishige et al. 1983) (Kokoi, Sakamoto et al. 1993) and (Tanjo, Yudate et al. 1994). The objective in all of these works appears to be the production of Bayer residue low in soda (and silica) and higher in iron for re-use in the cement industry. In most cases there is no indication of the use of the DSP concentrate to recover soda.

Hurdles to implementation:

The benefit of this process compared to the combination process would be the energy savings associated with re-processing a 100% active concentrate rather than a total solids residue. However the extra capital and operating costs associated with the production of the concentrate would not be expected to be economically favourable when compared to the conventional Bayer process with soda losses included.

These economics are significantly influenced by the economics of the sinter, the products of the sinter, and how easily a concentrated caustic stream can be produced and returned to the Bayer process. A paper by Rayzman (Rayzman and Fillipovich 1999) summarises a particular VAMI technology designed to reduce sinter costs by using coal in the sintering process of high iron bauxites. However this relatively dirty fuel source brings its own environmental problems.

4.2 Weak acid leaching of DSP

Principle:

Weak acids can be used to leach or dissolve soda from sodalite DSP. CO_2 reaction with sodalite can leach the caged soda from DSP (caged soda represents 25% of the total sodalite soda). The equation for this process for hydroxide inclusion (hydroxy-sodalite) has been given by Cooling et al. (Cooling, Hay et al. 2002) -

$$Na_6[AlSiO_4]_6.2NaOH + 2CO_2 \leftrightarrow Na_6[AlSiO_4]_6 + 2NaHCO_3$$

The mobility of the soda is significantly dependent on the included anion, and since Bayer sodalite from high silica refineries is more likely to contain aluminate and carbonate, this leaching may not be as efficient as with hydroxy-sodalite (Smith, Wingate et al. 2008). It is not known whether H^+ in carbonic acid could ion-exchange for sodium which is part of the cage structure itself.

Treatment with a stronger (sulphurous) acid can dissolve the DSP itself liberating silica into the acid solution. Amorphous silica can be precipitated from the leach solution, which is then causticised with lime to produce a caustic stream (recycled to the refinery) and solid calcium sulphite (which is calcined to regenerate CaO and SO_2). The process has been patented by Comalco (Cresswell, Grayson et al. 1986) (Cresswell 1992).

Status:

Carbonation of residue has been developed over a number of years by Alcoa in Australia, primarily to ameliorate the residue (both chemically and physically) to improve red mud disposal practices. The release of soda from sodalite by this process is considered to be part of the neutralisation process and its recovery is not a priority.

There is little in the literature on the dissolution of DSP with sulphurous acid, but the use of residue to scrub SO_2 from stack gases has received attention (Yamada, Fukunaga et al. 1979) (Yamada and Harato 1982) (Leoni and Penco 2002). The reactions produce both sodium sulphite and sodium bisulphite which are rapidly oxidised to sodium sulphate. It is unclear what happens to the silica phase, although a spinel phase is most likely. In a soda recovery process the challenge would be to separate the sodium sulphate and causticise it to recover caustic value.

Hurdles to implementation:

It is unlikely that a soda recovery process based on carbonic acid leaching could be viable. The maximum recovery of soda is ~25% and the leaching is unlikely to produce a caustic stream that is concentrated enough to return to the refinery.

Recovery of soda by sulphurous acid leaching however targets all of the DSP soda although 100% recovery is never achieved (Yamada and Harato 1982). Causticisation by lime and the calcination of $CaSO_3$ would be significant process costs. Despite these shortcomings, this process has potential.

4.3 Complex causticisation (mud causticisation)

Principle:

Complex causticisation was a term coined in the 1980's by Hungarian researchers to describe a two stage hydrothermal soda recovery process using lime (Baksa, Vallo et al. 1986) (Baksa, Boros et al. 1984). In the first stage lime is added to a residue slurry at ~95^{o}C. The lime reacts firstly with alumina in solution to form hydrogarnets (or TCA depending on the amount of silica in solution). Thereafter the lime attacks solid Bayer sodalite, liberating soda, alumina and silica. Lime combines with the released alumina to form more hydrogarnet, and, when the alumina is exhausted, lime reacts with silica in liquor to form (amorphous) calcium silicates. Soda, once associated with the sodalite, is liberated as useful caustic. To minimise the lime reacting with liquor alumina, this process is usually performed on last washer underflow where liquor strength is low. However this also means that the caustic produced from the breakdown of the sodalite is also of low strength, and needs significant evaporation to be useful.

The solids from the first stage are re-slurried in a concentrated solution of sodium carbonate. The high carbonate concentration causes the breakdown of hydrogarnets to form calcite ($CaCO_3$) liberating sodium aluminate which can also be returned to the process. Apparently the amorphous calcium silicate produced in the first stage is stable through the second stage and does not revert to sodalite. An optimisation of this second stage has been described by Liu (Liu, Zhang et al. 2004).

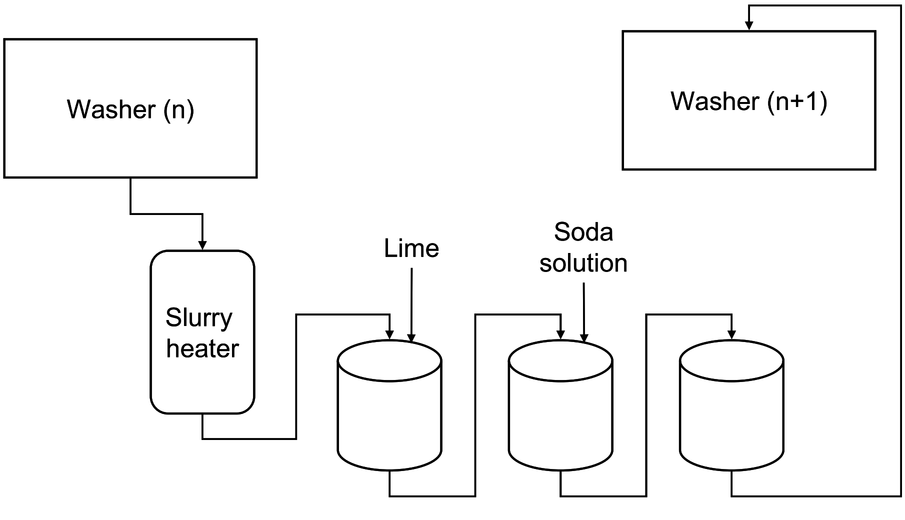

Figure 10 Schematic of the complex causticisation of red mud residue - adapted from Baksa (Baksa, Vallo et al. 1986).

Status:

According to "Alumina refineries and producers of the world", this process has been used commercially in the Hungarian refinery at Ajka from the mid 80's until at least 1998 (Aluminium-Verlag 2007). There is no information on whether other installations use this process.

Hurdles to implementation

There are several hurdles to implementation with this process. The first is high lime consumption, in that significant lime is used to scavenge alumina in solution before the DSP can be broken up, and this detracts from lime efficiency. Additionally the recovery of caustic from the first stage depends heavily on the efficiency of washing and thus the integration of the process into the back-end of the Bayer process is critical.

Another potential problem is that the second stage needs a reasonably concentrated stream of sodium carbonate. Local trona (sodium carbonate ore) has been suggested by the inventors for this purpose, but of course this is not available to all refineries. The production of such a stream from within the Bayer process itself is not seen as economical.

4.4 Mechano-chemical treatment of residue

Principle:
The recovery process is based on the principle of ultra-fine grinding of residue. The mechanism of soda recovery is not clear, but as with similar grinding of the bauxite (section 2.6) it is thought to be the energy of the collisions (ore with ore or ore with grinding media) that produces phase changes that would not normally occur without the grinding.

Picaro (Picaro 2000) claims that the ultra-fine milling of red mud residue (with or without additives such as lime) can result in caustic recovery from DSP. Alumina is also recovered but it is not clear whether this comes from DSP or from unextracted or re-precipitated alumina values. Recoveries of ~40% of the soda from DSP are claimed without additives, and up to 70% recovery for residue milling with lime.

The mechanism for soda recovery is not clear and has not been disclosed. Since XRD patterns of the sodalite become less well defined after milling, the speculation in the patent was that the soda is leached through a partial breakdown / amorphitisation of the sodalite structure.

Status:
There does appear to be any disclosed further work since the patent.

Hurdles to implementation:
The process does not appear to be tested under rigorous conditions. This needs to be done and the soda recoveries confirmed. There is a concern that if silica is released into solution that might trigger the re-formation of DSP which would be counter-productive, and so the fate of the silica is important to determine.

The cost of ultra-fine grinding must be weighed up with the benefit of soda recovery. In this respect, the beneficiation of residue to produce a DSP concentrate (or the production of pure DSP, see section 4.1) or the use of new grinding technology may be advantageous.

5. Summary and Conclusions

5.1 Strategy One options

Options in this strategy are concerned with beneficiation of reactive silica or bauxite pre-treatments. They are, by their nature, largely dependent on the mineralogy, liberations and associations of the minerals in the bauxite ore. As such, they will find specific applications for particular bauxites; for example the washing and screening of Weipa pisolites and the flotation of kaolin from diasporic ores in China.

There is no beneficiation process that will be suitable for bauxites in general. However, the particle size distribution for quartz in bauxite is almost always coarser than for the alumina and alumino-silicate minerals such as gibbsite and kaolin. Therefore, removal of quartz from bauxite (by flotation or another beneficiation technique) could be a general strategy to reduce reactive silica input for boehmitic bauxites.

Two pre-treatment options that are relatively independent of mineralogical associations are the mechano-chemical treatment of bauxites, and the roast-leach pre-treatment. Both these options need to be examined in more detail, especially with respect to cost and the economics of the soda saved.

5.2 Strategy Two options

Options within this strategy are less bauxite dependent than those in strategy one.

Both sinter and combination processes are robust, reliable technologies that have been used extensively to process high silica ores for many years in the former Eastern Block and in China. Although they have been the subject of much research with respect to reducing their energy consumption, it is clear that they can never be reduced to the level to compete with standard Bayer processing of high quality ores.

Both bauxite activation and double digestion (although different process variations) have the same objective with respect to high silica bauxite processing, i.e. they both allow the digestion of bauxite at temperatures sufficiently lower than normal for boehmitic ores, to reduce the degree of quartz attack (and therefore soda loss). These are variations which are known to work, and are currently available. Although bauxite activation has other benefits (e.g. organics destruction) it would not provide any extra benefit with respect to soda loss, and therefore would not be as attractive as double digestion. It should be pointed out that although these process variations can clearly save soda, their cost/benefit needs to be established.

Low soda DSPs potentially offer the most exciting prospect with respect to soda saving. However sodalite and cancrinite (for the sodium alumino-silicates) and hydrogarnets (for the calcium aluminium silicates) appear to be overwhelmingly the most stable desilication products. It is likely that in the unpublished literature of the alumina companies and other research organisations has examined different alumino-silicate mineral structures, and other DSP cations to encourage DSP phases other than those mentioned above. However since there is no disclosed advances in this field, it is also likely that these phases are not stable enough under Bayer processing conditions to be useful. If this is the case, then the opportunities for low soda DSPs appear to be restricted to cancrinite and (iron) hydrogarnets.

Hydrothermal lime treatment (the hydrothermal version of the combination process) shows great potential, in that the conditions needed to produce calcium silicates (some of the most efficient desilication products) are not far from those used in the Bayer process. The temperatures needed (~280°C) may have been unusual when the process was being developed, but are reasonable now (the new Rio Tinto refinery at Yarwun uses tube digestion at ~270°C). In addition, double digestion technology (and pressure decantors) could make the second (lime) digestion reasonably energy efficient. A remaining problem would the supply of a high caustic, low alumina stream for this digestion.

The Sumitomo (and related) processes provide an excellent option for the processing of high silica gibbsitic bauxites. The hurdles to the use of such a process, including engineering problems associated with the operation of high-rate washers, pressure decantors are likely to have diminished with improvements in technology and control strategies over the last 10 years.

5.3 Strategy Three options

Options in this category are also less dependent on bauxite, and have the added benefit of being somewhat separate from the workings of the Bayer process itself. As such, some could be treated as "swing processes", i.e. used only at times that justified their use (e.g. when caustic prices are high), or for other operational reasons detailed below.

There appears to be little scope to justify the concept of a pre-digestion desilication stage on the economics of soda recovery by lime sinter alone. However this process results in a Bayer residue almost free of non-quartz silica and soda which would have some environmental benefits (legacy and potential future licence to operate issues).

Recovery of soda from the use of weak acids such as the aqueous forms of CO_2 and SO_2 with residue are possible but, in common with the lime sinter of DSP processes, are likely to have bigger benefits from the reduction of residue alkalinity. Of the two, the SO_2 process is the most likely to be useful in terms of returning soda to the process.

The chemistry of the complex causticisation process (mud causticisation) process has never been adequately explained (especially the fate of the silica in the second stage). However it is unlikely that the lime efficiency in this process could be elevated to a point of being economical without a step change in the technology (especially the recovery of alumina in the second stage with normal Bayer process streams). The technology is appealing though, especially since it is independent of both the bauxite and the process itself (it would essentially be a "bolt-on" rear end process applicable to most operations). It is possible that the economics could change if this process was combined with another to produce a DSP concentrate.

Ultra-fine grinding of the mud would need more evaluation to be dismissed, but at present there is no clear indication of the fate of the other DSP components (especially silica) if and when soda is recovered. The stability of the changed desilication product (after soda removal) is critical in determining the robustness of any soda recovery process.

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Aluminium-Verlag (2007). Alumina refineries and producers of the world, Aluminium-Verlag, Dussseldorf.

Amer, A. M. and E. A. Abdel-Aal (1996). "Mineralogical studies and hydrometallurgical processing of Egyptian bauxite." Transactions of the Indian Institute of Metals **49**(1-2): 25-28.

Anand, P., J. M. Modak, et al. (1996). "Bio-beneficaition of bauxite using bacillus polymyxa - calcium and iron removal." International Journal Mineral Processing **48**(1-2): 51-60.

Andrew, P. I., N. M. Anishchenko, et al. (1973). "Mechanism of the anionic flotation of chamosite and gibbsite." Tsvet. Metall. **116 (6)**: 16-20.

Arlyuk, B. (1995). "Comparative Evaluation of Efficiency of Using Bauxite and Nepheline Ores for Production of Alumina". Light Metals, The Minerals, Metals & Materials Society, 420 Commonwealth Dr , Warrendale, Pennsylvania 15086, USA**:** 121-131.

Baksa, G., J. Boros, et al. (1984). "Process for the Reduction of the Sodium Hydroxide losses of the Bayer-type alumina production." Patent US4486393

Baksa, G., F. Vallo, et al. (1986). "Complex Causticization: An Effective Means for the Reduction of NaOH Losses in an Alumina". Light Metals, New Orleans, LA, USA, Metallurgical Soc of AIME, Warrendale, PA, USA.

Banvolgyi, G. (1992). "Reactions of gibbsite and kaolinite in the Bayer liquor: a comprehensive kinetic model and an improvement of the low temperature digestion." 7th International Congress for Study of Bauxites, Alumina and Aluminium.: 1-16.

Banvolgyi, G. and P. Siklosi (1998). "The improved low temperature digestion (ILTD) process: an economic and environmentally sustainable way of processing gibbsite bauxites". Light Metals. San Antonio, Texas, The Minerals, Metals & Materials Society, 420 Commonwealth Dr , Warrendale, Pennsylvania 15086, USA**:** 45-53.

Banvolgyi, G., J. Zoldi, et al. (1990). "Prodn. of alumina from gibbsite bauxite - by digestion in caustic- aluminate liquor to produce liq. phase with controlled reactive hydroxyl ion content" Patent AU8943731-A. ; CA2000832-A (27 Apr 1990); BR8905475-A (29 May 1990); ES2019173-A (01 Jun 1991); US5122349-A (16 Jun 1992); CA2000832-C (11 May 1993)

Bardossy, G. (1982). Karst bauxites. Amsterdam, Elsevier.

Bardossy, G. and G. J. J. Aleva (1990). Lateritic Bauxites. Amsterdam, Elsevier.

Bartosik, L., K. Strnad, et al. (1974). "Technical and economic problems in the processing of low grade bauxites for the production of aluminium oxide." Travaux ICSOBA(12): 175-194.

Bhagat, R. P., B. Banerjee, et al. (2001). "Beneficiation tests on an Indian bauxite incorporating magnetic separation." Transactions of the Institution of Mining and Metallurgy Section C-Mineral Processing and Extractive Metallurgy **110**: C165-C168.

Bhargava, S., M. Allen, et al. (2004). "Thermal activation of bauxite." Chemistry in Australia **71**: 6-8.

Boros, J., Z. Csillag, et al. (1978). "Catalyst for bauxite digestion - for the conversion of goethite to haematite." Patent DE2754289-A; JP53071700-A; FR2373489-A; HU15955-T; BR7800124-A; SU691073-A; US4226838-A; JP81013651-B; GB1597006-A; CA1114173-A; RO76285-A; DE2754289-C; IT1087523-B

Bray, E. L. (2008). Mineral Commodity Summaries, US Geological Survey.

Brown, I. W. M., K. J. D. MacKenzie, et al. (1985). "Outstanding problems in the kaolinite-mullite reaction sequence by ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance; II, high-temperature transformations of metakaolinite." Journal of the American Ceramic Society **68**(6): 298-301.

Chakraborty, A. K. and D. K. Ghosh (1978). "Re-examination of kaolinite-to-mullite reaction series." Journal of the American Ceramic Society **61**(3-4): 170-173.

Chen, X. and W. Li (2006). "Parallel floatation process of desiliconization for bauxite" Patent CN1869258-A

Cooling, D., P. S. Hay, et al. (2002). "Carbonation of bauxite residue". Sixth International Alumina Quality Workshop. Brisbane, Qld**:** 185-190.

Cresswell, P. J. (1992). "Chemical processing of bauxite tailings". International Bauxite Tailings Workshop, Perth.

Cresswell, P. J., I. L. Grayson, et al. "Values recovery from bayer process red mud - to obtain directly recyclable sodium aluminate soln" Patent DE3545388-A; FR2575149-A; AU8551016-A; US4668485-A; DE3545388-C; IT1188213-B

Cresswell, P. J. and D. J. Milne. "Alumina and soda recovery esp. from red mud - by digestion in presence of lime" Patent AU8288102-A; US4483830-A AU8288102-A 17 Mar 1983 198317.

Cresswell, P. J. and D. J. Milne (1982b). "A Hydrothermal Process for Recovery of Soda and Alumina From Red Mud." Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 227-238.

Cresswell, P. J. and D. J. Milne (1984). "Hydrothermal recovery of soda and alumina from red mud". Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 211-221.

de Boer, D. J., M. Edwards, et al. (2005). "Design, start-up and operational aspects of the new digestion process at Comalco alumina refinery, Gladstone, Queensland". Seventh International Alumina Quality Workshop. Perth, W.A.**:** 32-36.

Doucet, J. (1993). "Double digestion: Technology that leads towards quality and efficiency". Third International Alumina Quality Workshop. Hunter Valley, NSW**:** 93-101.

Doucet, J., C. Hendricks, et al. (2002). "Pressure decantation technology: the Kaiser Gramercy experience". Sixth International Alumina Quality Workshop. Brisbane, Qld**:** 94-99.

Ehrlich, H. L. (1992). "Metal extraction and ore discovery". Encyclopedia of Microbiology, Academic Press. **3:** 75-80.

Eremin, N. I. and N. S. Shmorgunenko (1974). "Some theoretical and practical questions of low-grade bauxite processing by the sinter process and the in-series combined Bayer-sinter process." Travaux ICSOBA(12): 213-222.

Fortin, S. and G. Forté (2007). "Mechano-activated bauxite behaviour". Light Metals. Orlando, Florida, Minerals, Metals and Materials Soc (TMS), Warrendale, PA, USA**:** 87-92.

Freyssinet, P. H., C. R. M. Butt, et al. (2005). Ore forming processes related to lateritic weathering. Colorado, SEG.

Fulford, G. D., D. R. Chinloy, et al. (1990). "Bayer alumina prodn. with has enhanced red mud sepn. stage - carried out at temp. above slurry liq. phase atmospheric boiling temp." Patent EP382383-A2; EP382383-A (16 Aug 1990); AU9048782-A (09 Aug 1990); BR9000421-A (15 Jan 1991); US4994244-A (19 Feb 1991); CN1045254- A (12 Sep 1990); EP382383-A3 (04 Mar 1992); CA1330865-C (26 Jul 1994); EP382383-B1 (08 May 1996); ES2086368-T3 (01 Jul 1996); IE81147-B (03 May 2000)

Gao, S., X. Li, et al. (2008). "Beneficiation of low-grade diasporic bauxite with hydrocyclone." Transactions of Nonferrous Metals Society of China **18**(2): 444-448.

Groudeva, V. I. and S. N. Groudev (1983). "Bauxite dressing by means of *Bacillus circulans*." Travaux (ICSOBA) **13**(18): 257-263.

Grubbs, D. K. (1986). " Parallel purification of alumina with physical pretreatment - Alumina Extraction From Low Grade Ores." Patent US4614641

Gu, S. (2008). "Chinese Alumina Industry - Development, Prospect and Challenge in the Future". Eighth Alumina Quality Workshop Darwin, N.T.

Gu, S., Z. Yin, et al. (2002). "Intensifying method of Bayer digestion process of diasporic bauxite in China". Light Metals Seattle, WA, USA, Metals and Materials Society/AIME Warrendale, PA**:** 83-88.

Harato, T., T. Ishida, et al. (1996). "The development of a new Bayer process that reduces the desilication loss of soda by 50 % compared to the conventional process". Fourth International Alumina Quality Workshop, Darwin, N. T.

Harato, T., T. Ishida, et al. (1993). "Process for producing aluminium hydroxide from alumina-containing ore" Patent EP564659-A; WO9309062-A; WO9309062-A1; JP5193931-A; AU9227992-A; EP564659-A1; BR9205404-A; AU658235-B; EP564659-A4; US5545384-A; EP564659-B1; DE69228865-E; CA2099279-C; JP3438240-B2

Hill, V. G. and R. J. Robson (1981). "The Classification of Bauxites from the Bayer Plant Standpoint." Light Metals: 15-27.

Hollitt, M., S. Grocott, et al. (2000). "Treatment of an alumina process feedstock includes controlling the contact time of the solid alumina feedstock during heating" Patent WO200010919-A. ; WO200010919-A1 (02 Mar 2000); AU9954977-A (14 Mar 2000);

AU727363-B (14 Dec 2000); EP1109740-A1 (27 Jun 2001); CN1324328- A (28 Nov 2001); JP2002523326-W (30 Jul 2002); US6616902-B1 (09 Sep 2003)

Hollitt, M., J. P. Kisler, et al. (2002). "The Comalco bauxite activation process". Sixth Alumina Quality Workshop. Brisbane**:** 115-122.

Hollitt, M. J., A. J. Crisp, et al. (1998). "Removal of silica from Bayer process bauxite feedstock - by contacting with caustic liquor then separating the silica bearing liquor from the solids" Patent WO9822390-A. ; EP950020-A; WO9822390-A1 (28 May 1998); AU9749357-A (10 Jun 1998); EP950020-A1 (20 Oct 1999); AU716537-B (24 Feb 2000); CN1242756-A (26 Jan 2000); JP2001503727-W (21 Mar 2001); US6309615-B1 (30 Oct 2001)

Hollitt, M. J., S. Grocott, et al. (2001). "Treating alumina process feedstock by heating via direct contact with combustion gas, cooling, and controlling the contact time to ensure tri- and monohydrate alumina decomposition" Patent WO200018685-A. ; WO200018685-A1 (06 Apr 2000); AU9963206-A (17 Apr 2000); AU725611-B (12 Oct 2000); EP1135333-A1 (26 Sep 2001); CN1320102- A (31 Oct 2001); JP2002525261-W (13 Aug 2002); US6582670-B1 (24 Jun 2003)

Hu, Y. H., K. Ouyang, et al. (2008). "Flotation of kaolinite and diaspore with hexadecyl dimethyl benzyl ammonium chloride." Journal of Central South University of Technology **15**(3): 378-381.

Iida, F., F. Stewart, et al. "Pressure decanter for solid separation from a liq. slurry - with an incoming pressurised liquid more efficiently separated without depressurisation" Patent EP696225-A; WO9426383-A; WO9426383-A1; AU9466427-A; US5407561-A; FI9505329-A; BR9406391-A; EP696225-A1; EP696225-B1; DE69401206-E; ES2096468-T3; AU681657-B; CN1122581-A; HU76198-T; HU215983-B; CA2160346-C; KR329711-B; CN1051244-C

Ishchenko, V. V., V. M. Korus, et al. (1974). "Flotation of silica from bauxite." Tsvet Metall. **17**(3): 7-11.

Iwase, H. and A. Murase (1988). "Alumina extn. in Bayer process without sol. silica extn. - includes classifying bauxite in fine and coarse granules, treating in sodium aluminate, sepg. residue etc" Patent JP63190709-A; JP93001212-B

Iwase, M. (1987). "Prodn. of aluminium hydroxide from bauxite - by extracting alumina with soda aluminate, using tubular reactor, flashing resultant mixt., quickly cooling etc" Patent JP62230613-A

Kanehara, M., H. Morishige, et al. (6 May 1983). "Modification method of red mud" Patent JP S62-230613-A

Klan, P. (1959). "Removal of silicon oxide from roasted bauxites by caustic soda" Patent PV 5373-59

Kokoi, H., A. Sakamoto, et al. (9 Jul 1993). "Production method of red mud containing low soda" Patent JP H05-170434-A

Lamerant, J.-M. and Y. Ferret (2002). "Boehmitic reversion in a double digestion process on a bauxite containing trihydrate and monohydrate". Light Metals Seattle, WA, USA, Metals and Materials Society/AIME**:** 181-184.

Leoni, F. and C. Penco (2002). "Bauxite residue desulphurisation system (BRDS) at Eurallumina". Sixth International Alumina Quality Workshop**:** 162-167.

Li, W., P. Song, et al. (2002). "A new process technology of bauxite concentration-tube digestion for alumina production". Light Metals Seattle, WA, USA, Metals and Materials Society/AIME Warrendale, PA**:** 95-100.

Li, X. B., X. Liu, et al. (2003). "Study and application of intensified sintering process for alumina production." Chinese Journal of Non-ferrous metals **14**(6): 1031-1036.

Li, X. B., X. M. Liu, et al. (2004). "Study and application of intensified sintering process for alumina production." Chinese Journal of Nonferrous Metals **14**(6): 1031-1036.

Li, Y. and D. Chen (1979). "Beneficiation of diaspore-kaolinite bearing bauxite by flotation." Jinshu Xuebao/Acta Metallurgica Sinica **15**(3): 319-322.

Lin, I. J., N. Malts, et al. (1998). "The complex chemical treatment of alumina-silica-containing materials." Journal of Materials Synthesis and Processing (USA) **6**(1): 27-35.

Liu, G., X. Li, et al. (2003). "Stability of calcium silicate in basic solution." Transactions of Nonferrous Metals Society of China **13**(5): 1235-1238.

Liu, G., Y. Zhang, et al. (2004). "Alumina recovery from sodium hydrate alumino-silicate." Chinese Journal of Nonferrous Metals **14**(3): 499-503.

Liu, L.-R., Q.-B. Yu, et al. (2002). "Influence of material flow in alumina manufacturing process with Bayer-sinter combination method on its energy intensity." Dongbei Daxue Xuebao/Journal of Northeastern University **23**(10): 944-947.

Liu, L., L. Aye, et al. (2006). "Analysis of the overall energy intensity of alumina refinery process using unit process energy intensity and product ratio method." Energy **31**(8-9): 1167-1176.

Loginova, I. V., V. N. Koryukov, et al. (1979). "Effect of some flotation reagents on the digestion of bauxites." Soviet non-ferrous metals research **7**: 634-637.

Lu, S., R. L. Fang, et al. (2003). "Study on the extraction of aluminium oxide from low grade bauxite ore by an environmentally friendly method." Chemical Industry Engineering Progress **22**(3): 391-394.

Malts, N. S., N. S. Shmorgunenko, et al. (1984). "Production of alumina by combination Bayer-sintering method". Bauxite, Los Angeles, CA, USA, Soc of Mining Engineers of AIME, New York, NY, USA.

McCormick, P. G., T. Picaro, et al. (2002). "Mechanochemical treatment of high silica bauxite with lime." Minerals Engineering **15**(4): 211-214.

Medvedev, V. V., S. N. Akhmedov, et al. (2003). "Hydrogarnet technology of processing the bauxite raw material as up-to-date alternative to Bayer-sintering technique." Tsvetnye Metally(11): 58-62.

Medvedev, V. V., A. I. Kiselev, et al. (2002). "Method for hydrochemical processing of aluminosilicate feedstock" Patent RU2193525-C1

Mishra, B., A. Staley, et al. (2002). "Recovery of value-added products from red mud." Minerals & Metallurgical Processing **19**(2): 87-94.

Misra, C. (1986). Industrial Alumina Chemicals. Washington, American Chemical Society.

Ni, L. P., L. V. Bunchuk, et al. (1968). "A study of hydrogarnets formed in the Al_2O_3-CaO-Fe_2O_3-Na_2O-SiO_2-H_2O system." Russian Journal of Inorganic chemistry **13**(11): 1585-1587.

Ni, L. P., M. M. Goldman, et al. (1979). Processing of iron-rich bauxites, Moscow Metallurgica.

O'Connor, D. J. (1988). Alumina Extraction from Non-Bauxitic Materials. Dusseldorf, Aluminium-Verlag.

Oku, T. and A. Suzuki (1973). "Sepn of aluminates - from slurries,in prodn of alumina" Patent JP73037678-B1; GB1307316-A; US3716617-A; JP73037678-B

Owada, S., D. Okajima, et al. (2005). "Two approaches for reducing wasted 'red mud': possibility of upgrading bauxite and 'red mud'". Seventh International Alumina Quality Workshop. Perth: 205-209.

Pawlek, F., M. J. Kheiri, et al. (1992). "The leaching behaviour of bauxite during mechano-chemical treatment". Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA: 91-95.

Picaro, T. "Red mud processing" Patent EP880467-A; WO9729992-A; WO9729992-A1; AU9715853-A; EP880467-A1; BR9707549-A; AU719126-B

Picaro, T. and P. G. McCormick. "Bauxite treatment" Patent EP880468-A; WO9729993-A; WO9729993-A1; AU9715854-A; EP880468-A1; BR9707543-A; AU719117-B

Picaro, T., B. Pei, et al. (2002). "Separation and mineralogical analysis of Bayer red mud." Developments in Chemical Engineering and Mineral Processing **10**(5-6): 475-489.

Prokopov, I. V. and N. S. Malts (1974). "Industrial realisation and perspectives of further development for low grade bauxite processing." Travaux ICSOBA(12): 237-244.

Qiu, G. Z., T. Jiang, et al. (2004). "Activation and removal of silicon in kaolinite by thermochemical process." Scandinavian Journal of Metallurgy **33**(2): 121-128.

Rao, M. B. S., B. Das, et al. (1996). "Beneficiation of titanium minerals from sand rejects of an alumina refinery plant by Gravity separation." Powder Handling and Processing **8**(4): 351-353.

Rao, R. B. (1996). "Novel approach for the beneficiation of ferruginous bauxite by microwave heating." Minerals and Metallurgical Processing **13**(3): 103-106.

Rayzman, V. L. and I. K. Fillipovich (1999). "Integrating coal combustion and red mud sintering at an alumina refinery." JOM-Journal of the Minerals Metals & Materials Society **51**(8): 16-18.

Rayzman, V. L., I. Z. Pevzner, et al. (2003). "Extracting silica and alumina from low grade bauxite." JOM-Journal of the Minerals Metals & Materials Society **55**(8): 47-50.

Reisner, K. H. (1974). "Studies on the reactive behaviour of Bayer red mud in sintering with lime and soda." Travaux ICSOBA(12): 299-312.

Roberts, R. H. and J. F. Dunne (1980). "Bauxite Mining and Beneficiation by Comalco Ltd. at Weipa, Qld." Mining and Metallurgical Practices in Australia J. T. Woodcock. Parkville Victoria, Australian Institute and Mining and Metallurgy**:** 368-371.

Rodda, D. P. and R. W. Shaw. "Extraction of alumina from bauxite by double digestion - including fast low temp. digestion of gibbsite fraction, solid/liq. sepn., digestion of boehmite fraction and two-stage post-desilication" Patent EP777628-A; WO9606043-A; WO9606043-A1; AU9532481-A; EP777628-A1; BR9508761-A; KR97705519-A

Roskill (2008). The Economics of Bauxite and Alumina, Roskill Information Services.

Rousseaux, J.-M., H. Verschuur, et al. (2006). "Beneficiation of High Quartz Content Bauxite from Los Pijiguaos". Light Metals Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 47-52.

Sadler, L. Y. and C. Venkataraman (1991). "A process for the enhanced removal of iron from bauxite ores." International Journal of Mineral Processing **31**(3-4): 233-246.

Sagin, V. C. (1988). New hydro-chemical processing of combined treatment of alumino-silicates and high silica bauxites, Moscow Metallurgica.

Santos, H. D., T. W. Campos, et al. (2005). "Thermal phase sequences in gibbsite/kaolinite clay: electron microscopy studies." Ceramics International **31**(8): 1077-1084.

Schoenfelder, H. and H. Ginsberg (June 7 1960). "Method for reducing the silica content of alumina-containing materials of the clay type" Patent US2,939,764

Smith, P., C. Wingate, et al. (2008). "Mobility of included soda in sodalite". Eighth International Alumina Quality Workshop. Darwin N.T.**:** 27-30.

Solymar, K., F. Madai, et al. (2005). "Effect of Bauxite Microstructure on Beneficiation and Processing". Light Metals. San Francisco, CA, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 47-52.

Solymar, K., M. Orban, et al. (1983). "Methods for Reducing NaOH Losses in the Hungarian Alumina Plants." Travaux ICSOBA **13**(18): 377-390.

Solymar, K., J. Steiner, et al. (1997). "Technical peculiarities and viability of hydrothermal treatment of red mud". Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 49-54.

Takahashi, T. (14 Jul 1962). "Method to use high silica bauxite by extracting alumina from high silica bauxite" Patent JP37-008257-B

Tanjo, M., O. Yudate, et al. (21 Jun 1994). "Process for producing iron-making material composition comprising bauxite dissolution residue" Patent JP H6-172876-A WO 93/20251.

Tomka, L. (1974). "Technology of aluminium oxide production from low modulus bauxites by the sintering method." Travaux (ICSOBA)(12): 195-211.

Valenti, R. and P. Ho (2008). "Rio Tinto Alcan Gove G3 experience on pre-assembled modules". Eighth International Alumina Quality Workshop Darwin, N.T.**:** 1-5.

Vasan, S. S., J. M. Modak, et al. (2001). "Some recent advances in the bioprocessing of bauxite." International Journal of Mineral Processing **62**(1-4): 173-186.

Wang, Y., Y. Hu, et al. (2004). "Reverse flotation for removal of silicates from diasporic-bauxite." Minerals Engineering **17**(1): 63-68.

Whittington, B. I. (1996a). "The chemistry of CaO and $Ca(OH)_2$ relating to the Bayer process." Hydrometallurgy **43**: 13-35.

Whittington, B. I. (1996b). "Quantification and characterisation of hydrogarnet and cancrinite present in desilication product (DSP) by powder X-ray diffraction". Fourth International Alumina Quality Workshop. Darwin, N.T.**:** 413-422.

Xu, Z., V. Plitt, et al. (2004). "Recent advances in reverse flotation of diasporic ores - A Chinese experience." Minerals Engineering **17**(9-10): 1007-1015.

Yamada, K., T. Fukunaga, et al. (1979). "Process of sulfur dioxide removal from waste gas by red mud." Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 69-79.

Yamada, K. and T. Harato (1982). "SO2 removal from waste gas by red mud slurry - pilot plant test and results of plant operation " Kagaku Kogaku Robunshu **8**(1): 32--38.

Zhao, H., H. Hu, et al. (2002). "Digestion of diasporic bauxite with mass ratio of Al2O3/SiO2 no greater than 7 by Bayer process with an excessive addition of lime". Light Metals. Seattle, WA, Minerals, Metals and Materials Society (Warrendale, Pennsylvania)**:** 101-104.

Zhong, H., G. Liu, et al. (2008). "Flotation separation of diaspore from kaolinite, pyrophyllite and illite using three cationic collectors." Minerals Engineering **21**(12-14): 1055-1061.

Zoldi, J., K. Solymar, et al. (1987). "Iron hydrogarnets in the Bayer process". Light Metals, Minerals, Metals and Materials Society (TMS), 184 Thorn Hill Road, Warrendale, PA, USA**:** 105-111.