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High Silica Bauxite Processing

High silica bauxites - detailed process review, process selection and innovation

NON CONFIDENTIAL VERSION

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1. Introduction

1.1 Previous work in ATF-06-4.

A previous report to the APP (Smith 2008) described the worldwide trend of declining bauxite grades and the importance of research into economic ways of processing of high silica bauxites. The major cost penalty associated with processing high silica bauxites is the loss of caustic soda from the recirculating Bayer liquor. This comes about when reactive silica compounds from the bauxite dissolve into the liquor and re-precipitate as soda containing “desilication products” (DSPs) which are generally discarded with the red mud waste.

The report described three strategies for preventing the loss of soda associated with DSP formation - these are:

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.

The report described 7 processes for beneficiating or pre-treating bauxite to reduce the input of reactive silica into the process, 7 processes which modified the normal Bayer operations which reduced reactive silica transformation or resulted in a low soda form of DSP, and 4 soda recovery processes. For each process a description of principle was given with an indication of its use or present status and a brief discussion of technical, economic or ecological hurdles to its implementation. The summary to the report started the process of identifying the most promising options which will be advanced in the following section.

This report is aimed at stimulating discussion on the options for processing high silica bauxites, and in particular to encourage the engagement and participation of industry sponsors in targeted further research.

1.2 Selection of most promising process options

One method to identify the most promising options for further study would be to rank each against strict criteria for technical and economic success. This would require a form of techno-economic evaluation for each of the options identified in the previous report. As a first-pass measure, the authors have chosen another, less rigorous selection process that includes an assessment of processes on the basis of several criteria on which they have made judgements using their own experiences and expertise. These criteria include:

- i. technical viability (is it technically possible and/or technically robust?)
- ii. economic viability (what is the estimate of benefit to expected cost? – includes green house gas benefits/costs)
- iii. size of benefit (how much soda can be potentially saved?)
- iv. applicability of process (does it apply to all bauxites or only to some?).

The following table lists the potential processes identified for strategy one (Smith 2008).

Table 1 Processes identified for strategy one (Smith 2008).

Process	Description	Strategy (type)
1	Screening / washing	One (beneficiation)
2	Gravity separation	One (beneficiation)
3	Flotation	One (beneficiation)
4	Bio-leaching	One (beneficiation / pre-treatment)
5	Magnetic separation	One (beneficiation)
6	Mechano-chemical treatment with lime	One (milling pre-treatment)
7	Roast-leach	One (thermal pre-treatment)

Figure 1 shows an assessment of “attractiveness” for each process listed in Table 1. The axes represent the technical and economic difficulty (viability) of the process. The size of the circle represents the size of the potential caustic savings. The colour represents whether the process is suitable for all bauxites (applicability) - blue indicates that the process is suitable for most/all bauxites and red indicates that it is restricted to a particular type of bauxite. In reality this “applicability” will have a continuous spectrum, but to simplify matters, only two extremes have been identified¹.

¹ In addition, the circles are shaded. This is meant to indicate that the potential caustic savings, and both estimations of technical and economic viability are subject to errors of judgement, and should not be considered to have been accurately determined.

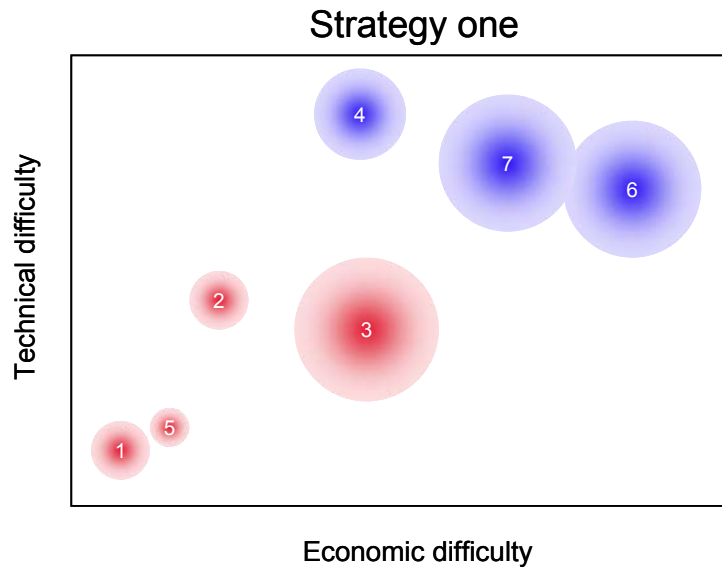


Figure 1 Attractiveness of processes in strategy one.

Options that have low technical and economic difficulty such as screening/washing (1), magnetic separation (2) and gravity separation (5) are mostly bauxite specific (red). Often these are processes that are already in place if they are applicable, and would be viewed as methods to raise the grade of the bauxite up to a minimum operating level. As such they are not regarded as having the potential to save significant caustic soda.

The process that shows the greatest level of attractiveness is flotation (3). This technique is in commercial operation, especially in China, where the almost unique mineralogy of the diasporic bauxites can be exploited. In these bauxites the reactive silica in the form of kaolin is in large, liberated particles that can be targeted by the flotation process and removed from the rest of the ore. Unfortunately this liberation does not occur in most lateritic bauxites and thus the technique is unsuitable for Australian bauxites. Flotation could be used to remove quartz from lateritic bauxites, but in this case the fraction of the reactive silica removed compared to the cost of the treatment would push the option significantly to right of its current position in the diagram.

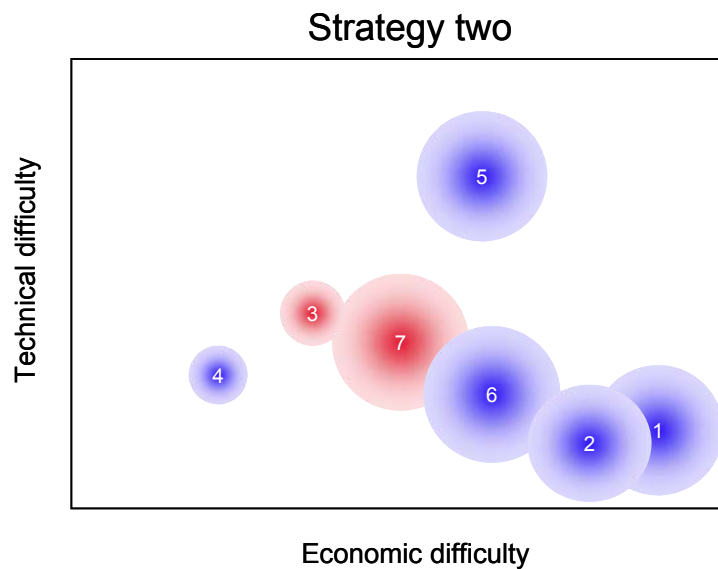
Bio-leaching is discounted due to very high levels of technical difficulty, and mechano-chemical treatment is not considered further due to the high cost of milling, downstream problems that would be caused by such fine feed material, and an unproven benefit.

The technique with the best potential to save significant soda, applicable to most bauxites, is the Roast-leach process (7). The difficulty here is the economic cost of roasting the bauxite feed, and some aspects of the subsequent removal of silica. Roast-leach is the technique chosen for more in depth study in the following sections of this report.

Table 2 and Figure 2 represent a similar analysis for options in strategy two.

Table 2 Processes identified for strategy two (Smith 2008).

Process	Description	Strategy (type)
1	Sinter process	Two (modified Bayer)
2	Combination process (Bayer-sinter)	Two (residue re-process in situ)
3	Bauxite activation	Two (lower digestion temperature)
4	Double digestion	Two (lower digestion temperature)
5	Low soda DSPs	Two (changing digestion chemistry)
6	Hydrothermal lime treatment	Two (residue re-process in situ)
7	Differential extraction processes	Two (exploiting digestion kinetics)

**Figure 2 Attractiveness of processes in strategy two.**

By contrast to the strategy one options, those in strategy two are less bauxite specific. The high cost of the sinter and Bayer-sinter options (1&2) rules them out of further consideration, whereas double digest and bauxite activation (3&4) are known processes with limited potential to save soda (except perhaps when combined with other options, see later sections).

The three processes to be examined in more detail are low soda DSPs (5), hydrothermal lime treatment (6) and differential extraction processes (7).

Table 3 and Figure 3 represent the analysis of options from strategy three.

Table 3 Attractiveness of processes in strategy three.

Process	Description	Strategy (type)
1	Lime sinter of DSP	Three (sinter of re-processed residue)
2	Weak acid leaching of DSP	Three (chemical breakdown of DSP)
3	Complex causticisation (mud causticisation)	Three (chemical breakdown of DSP)
4	Mechano-chemical treatment of residue	Three (chemical milling of residue)

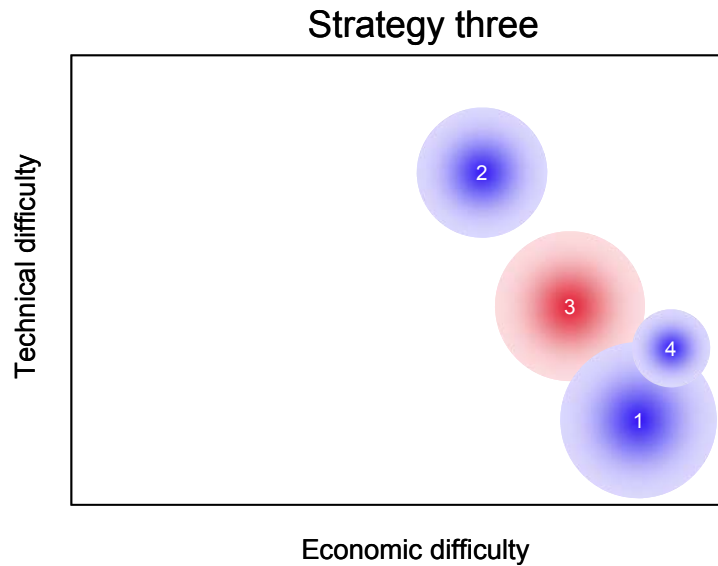


Figure 3 Attractiveness of processes in strategy three.

It is notable that for this strategy, there is no process that could immediately be considered economically favourable. The lime sinter of DSP (1) is similar to a Bayer sinter except that the DSP is produced at the beginning of the Bayer process, to improve the efficiency of the subsequent lime-sinter. However the cost of the enabling technology is not expected to make the overall process economically viable and so it will not be considered further. Complex causticisation is in red, not because of the nature of the bauxite itself, but rather that there is a requirement for a local, cheap source of sodium carbonate (see section 4.1). Mechano-chemical treatment (4) at present contains too many unanswered questions, not least of which is how to handle/separate/wash/dewater the ultra-fine material that is produced by the milling (this applies to mechano-chemical treatment of both bauxite and residue).

The processes to be examined in further detail from strategy three are complex causticisation (3) and weak acid leaching (2).

2. Strategy One – Beneficiation - selected processes

2.1 Roast-leach

A general description of the process has been given in the previous report (Smith 2008). The essentials are shown in Figure 4.

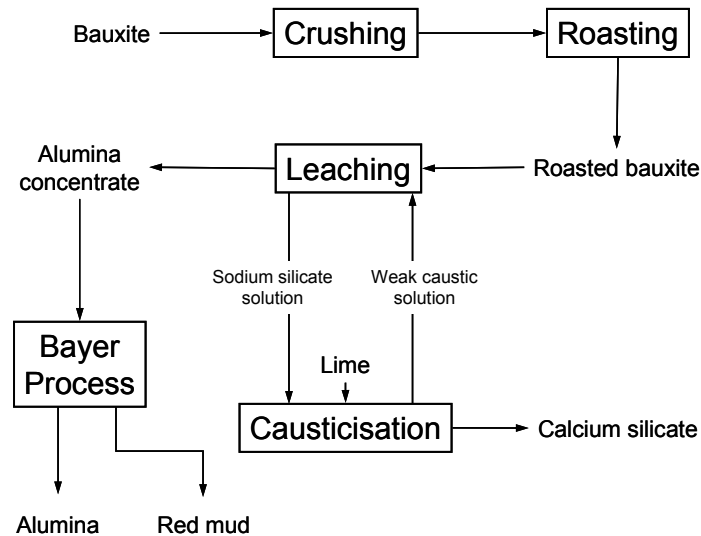
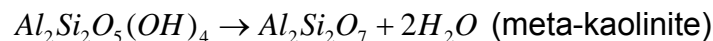


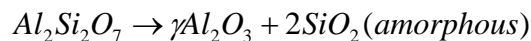
Figure 4 Schematic of the roast-leach process – re-drawn from Rayzman (Rayzman, Pevzner et al. 2003).

Detailed examination:

Roasting bauxite in an inert atmosphere causes many overlapping chemical reactions, mainly related to dehydration and structural re-arrangement of minerals. Focussing first on kaolin in the bauxite, heating to $\sim 550^\circ\text{C}$ causes a dehydration to meta-kaolinite.



After this a cubic phase is formed at $\sim 980^\circ\text{C}$. There is still controversy about the nature of this phase, with some authors suggesting the formation of gamma-alumina along with amorphous kaolin (Jiang, Li et al. 2000; Qiu, Jiang et al. 2004):

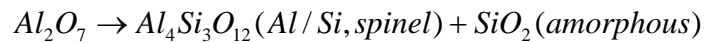


Under these same conditions the valuable alumina minerals (usually gibbsite and boehmite) also dehydrate to form so-called “transitional” aluminas (Al_2O_3) although the exact forms (usually denoted by a Greek letter) will be dependent on the history and conditions of the heating process.

For the purposes of the roast-leach process, we need go no higher in temperature, although it is noted that around 1100°C the amorphous silica recombines into mullite (which is insoluble under most Bayer digestion conditions):



Other authors (Brown, MacKenzie et al. 1985; Chakraborty 2003; Santos, Campos et al. 2005) have suggested that the cubic phase is in fact an alumino-silicate spinel:



with the spinel also degrading at temperatures $>1100^\circ\text{C}$ to mullite and (in this case) to a crystalline silica called cristobalite. The controversy comes about because the X-ray diffraction patterns of the spinel and gamma alumina are very similar, and hard to differentiate.

The key to this process is the realisation that there is a distinct difference in solubility between the amorphous silica and the alumina (produced from both kaolin and from the dehydration of gibbsite/boehmite) in a weak caustic leach. The applicability of this process to produce a desilicated bauxite feed to the Bayer process depends on a delicate balance. To maximise the difference in the solubility of the silica and the alumina (and thus the efficiency of the weak caustic leach), high temperatures ($980\text{--}1100^\circ\text{C}$) would be recommended. However the higher the roast temperature, the more insoluble the alumina becomes during Bayer digestion. More aggressive Bayer digestion conditions would increase the cost, but more importantly would increase the attack on quartz if it is present in the bauxite, increasing the reactive silica and compromising the objective of the whole pre-treatment.

This compromise in roasting conditions introduces problems for both the weak caustic leach and the subsequent Bayer digestion. Low charges of the roasted bauxite in the weak caustic solution help maximise the difference in solubilised alumina and silica in solution (Qiu, Jiang et al. 2004) and thus there will be a technical and economic problem with large inventories of weak caustic liquor required. Rayzman (Rayzman, Pevzner et al. 2003) circumvented this problem to some extent by using a percolation system that is in essence a counter-current leaching system.

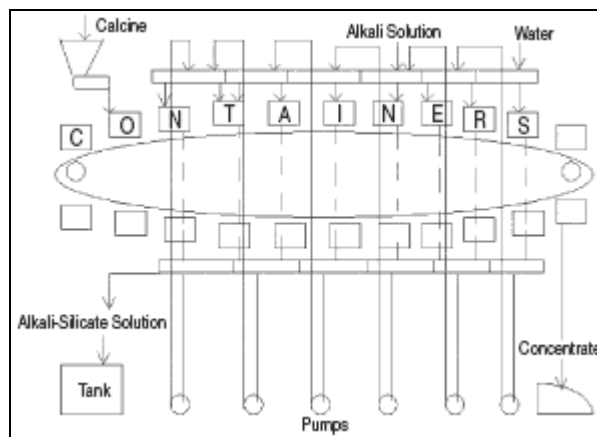


Figure 5 Percolation device used described by Rayzman (Rayzman, Pevzner et al. 2003) for the weak caustic leach of the roasted bauxite (termed calcine in the figure).

Whichever system is used for the weak caustic leach, it will contribute substantially to the overall cost of the pre-treatment.

After leaching the weak caustic liquor is predominately a sodium silicate solution which is subsequently limed (CaO is added) in order to precipitate calcium silicate – a saleable by-product) and regenerate the weak caustic solution. The inefficiency of the leach comes about when non-trivial amounts of alumina also leach, and the calcium silicate by-product is contaminated by regular sodalite DSP. The DSP also removes caustic

from the leach liquor further compromising the leach efficiency. This is an outstanding problem for this process.

However the most important technical drawback of the roast-leach process (at least as applied to Australian high silica bauxites) is the more severe Bayer digestion conditions needed to extract the roasted alumina. Higher digestion temperatures and/or longer digestion times will increase attack on quartz, therefore increasing the effective reactive silica of the bauxite. This is seen by the authors to be a major technical hurdle to implementation.

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

3. Strategy Two – Process modification – selected processes

3.1 Low soda DSPs (cancrinite production)

The previous report (Smith 2008) described the production of cancrinite during high temperature Bayer digestion. Cancrinite has a molar soda to silica ratio of $\frac{1}{2}$ compared to the $\frac{2}{3}$ characteristic of the more usual sodalite. Encouraging cancrinite precipitation instead of sodalite therefore has the potential to save up to 25% of the soda lost to sodalite (the majority of DSP).

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

3.2 Hydrothermal lime treatment

Detailed examination:

As noted in the previous report (Smith 2008) the hydrothermal lime treatment process is a hydrothermal version of the Bayer-sinter process in which residue from the Bayer process – containing significant soda and alumina in DSP – is treated with lime and a high caustic, low alumina solution at $\sim 270\text{-}280^\circ\text{C}$. The conditions of this reaction produce di-calcium silicate (Ca_2SiO_4) which is an efficient desilication product containing no soda or alumina.

The problems identified with this process were:

1. the residue from the Bayer digestion is typically flashed, deliquored and re-heated back to digestion temperatures, which is energy intensive and wasteful, and
2. the second digestion is conducted with a high caustic low alumina stream (i.e. low A/C liquor) produced by “salting out” sodium aluminate (a complex and expensive procedure).

This process is most attractive if the refinery is already processing boehmitic bauxite and therefore has the heating capacity to produce the temperatures required for the second digestion. The increase in temperature from $\sim 250^\circ\text{C}$ (normal boehmitic digestion temperature) to $270\text{-}280^\circ\text{C}$ has, until recently, been considered prohibitive, mainly from the standpoint of materials of construction. However the Yarwun refinery digestion facilities have been designed around these temperatures (albeit in tube digesters) suggesting that these conditions are workable.

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

3.3 Differential extraction processes – the Sumitomo process and counter-current digestion

Detailed examination:

The Sumitomo process is the latest in a series of processes designed to exploit the different leaching kinetics of alumina and silica minerals. By digesting rapidly and solid-liquid separating the slurry, almost complete extraction of gibbsite can be achieved whilst only a fraction of reactive silica (kaolinite) has dissolved over the same period. The difference in the kinetics becomes more marked as the temperature of the digestion is reduced. On the other hand, productivity of the liquor (alumina loading in the Bayer liquor) increases with increasing temperature. The Sumitomo digestion temperature (~130 °C) has been chosen as a compromise between these two opposing factors.

There are several outstanding issues with the Sumitomo process (some of them common to other differential extraction processes) which, if solved, will increase the attractiveness of the process to treat high silica bauxites. These include optimisation of digestion parameters for individual bauxites, increased efficiency of pressure decanters (especially scaling issues and the use of flocculants that are effective at digestion temperatures) and the development of green liquor desilication.

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

4. Strategy Three – Soda recovery - selected processes

4.1 Complex causticisation

Detailed examination:

The general description of the process has been given previously (Smith 2008).

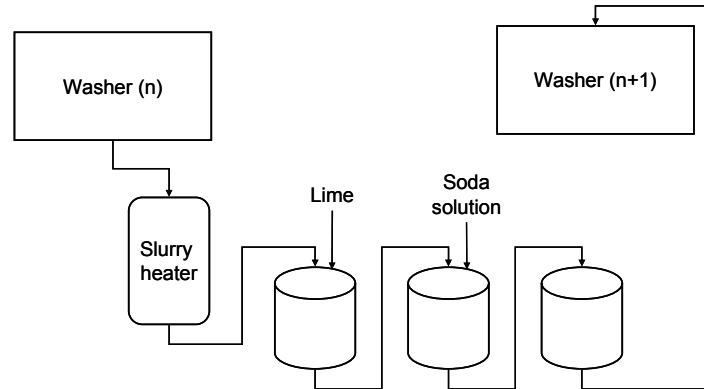


Figure 6 Schematic of the complex causticisation of red mud residue – redrawn from Baksa (Baksa, Vallo et al. 1986).

Lime is added to a partially washed residue to encourage the dissolution of sodalite DSP and the formation of calcium silicate and silica substituted TCA – hydrogarnets. It is generally thought that the TCA and the hydrogarnets form initially until the alumina in the solution (plus that released from the DSP) is exhausted, and after this the more efficient calcium silicates are formed. The amount of lime required for this operation is excessive, since the Ca:Si ratio in the hydrogarnets is high.

In addition to the inefficiency of hydrogarnet formation mentioned above, there are problems with the second stage of the causticisation. As proposed by the Hungarian inventors (Baksa, Vallo et al. 1986), the residue now containing hydrogarnets is suspended in a concentrated solution of sodium carbonate, sourced from the mineral trona. The suspending liquor is now low in caustic soda but high in sodium carbonate. These conditions favour the transformation of TCA (and hydrogarnets) into calcite.

The problems are thus twofold:

1. The lime efficiency is poor because of the high ratio of Ca:Si in hydrogarnets, and the production of TCA or hydrogarnets from residual alumina in the wash-water.
2. Refineries cannot easily produce a concentrated sodium carbonate solution from any Bayer liquor stream, and importing sodium carbonate would probably not be economic unless a cheap local supply happened to be available.

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

4.2 Electrolysis of salt solutions produced by weak acid dissolution of DSP

Detailed examination:

The extraction of caustic soda from DSP using (weak) acids was described in the previous report (Smith 2008). Technically the recovery by this method will always be better with a DSP concentrate than for an untreated residue, but the economics of this process for both materials (including the extra cost of producing the concentrate) needs to be evaluated. For almost all versions of this process there are two distinct stages:

1. The extraction of sodium from DSP by an acid to form the sodium salt of that acid, and
2. The causticisation of the salt to produce caustic soda suitable for return to the Bayer process.

In the first stage, “soda” can be extracted either by using an ion exchange resin (Wightman, Naden et al. 1992), by direct treatment by SO₂ (Yamada and Harato 1982) or by using mineral acids. If the pH of the acid treatment is below ~4, then the cage structure of the alumino-silicates breaks up, liberating not only soda but also alumina and silica. An example is the sulphurous acid (sulphite) process (Cresswell 1992) in which the dissolved silica must be precipitated out as a by-product before the causticisation reaction. Alternatively the use of ion exchange resins can be used to exchange soda from DSP for hydrogen in alkaline environments, after which the loaded resin is regenerated in acid solution, releasing the soda for further treatment. Presumably the advantage of the ion exchange resin over treatment with acids is that sodium can be extracted in an alkaline liquor without the need for neutralisation.

The causticisation step is traditionally through the use of lime, with the greatest efficiency coming from the use of an acid whose anion which produces the most insoluble calcium salt. The most convenient anion would be carbonate (so that the calcium could be recycled), but carbonic acid has too low a pK_a. Other acids producing insoluble calcium salts will not be easily recycled, and thus have an added complication.

An alternative is an electrochemical (membrane) separation which produces caustic at one electrode and the acid of the sodium salt at the other. The main drawback of these methods (there are several) is the purity of the salt solution and the consequent fouling of the membranes.

Some text has been removed here concerning potential innovation of this process. The authors would welcome enquiries from interested parties seeking collaboration with a view to further development.

5. Conclusions and further work

From the 18 process options examined in the previous report (Smith 2008) this report has selected 6 for further consideration. The selection process was made on the basis of the authors' experience against four distinct selection criteria.

The 6 selected processes have been examined to identify their current shortcomings and, in each case, innovation has been suggested either to circumvent these shortcomings or in other ways enhance the technical (and possibly economic/ecological) viability of the process.

The applicability of these processes to particular bauxites will be heavily dependent on how they can be retro-fitted to existing facilities and operations.

The knowledge gaps identified in the body of the report can be, in future work, translated into laboratory based work programs designed to address issues/problems with the processes. Prior to this, it is the intention of the authors to garner support from the alumina industry and other prospective partners. The objective will be to elicit engagement with one or more interested parties.

It is not expected that all six processes will be pursued, but once engagement with the collaborators has been established, a project will be set up to further develop the chosen alternative(s).

6. Acknowledgements

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The views expressed herein are not necessarily the views of the Commonwealth, and the Commonwealth does not accept responsibility for any information or advice contained herein.

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