

## **Drivers for seawater neutralisation of bauxite residue**

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### **Abstract**

Proponents and designers of greenfield alumina refineries face many constraints when planning new refinery projects, and the need for environmentally sustainable residue management practises is chief among them. Regulators, local communities, and project owners are increasingly demanding solutions that minimise the long term environmental liabilities of an alumina refinery and its associated bauxite residue disposal area. The seawater neutralisation of bauxite residue is one way to achieve this, however there is only a handful of refineries in the world today that have adopted the practice. This paper discusses the drivers and enablers for implementing sea water neutralisation of alumina refinery residues, with an emphasis on greenfield projects. It reviews benefits of a non-hazardous residue, competing treatment options, and implications of site selection on residue treatment.

**Keywords:** Seawater neutralization; bauxite residue.

### **1. Introduction**

The global inventory of bauxite residue is estimated to be in the order of 4 Gt as of 2015 and increasing at a rate of ~ 170 Mtpa at current global alumina production rates. Analysts have predicted that alumina production will increase at a rate of 3.1 % p.a. over the next 5 years to 2019 [1]. Based on the current world production of ~ 108 Mt of alumina, this means that an additional 14 Mtpa of new capacity is predicted to come on-line in the next 5 years.

It is becoming increasingly important that the bauxite residue management practises adopted for these new projects are environmentally sustainable, and do not leave an enduring legacy to be managed long after the bauxite reserve is depleted and the refinery decommissioned. The strategy for achieving this should be two fold: firstly, to maximise the amount of residue that is re-used, and secondly, to eliminate the need for active ongoing management of the residue storage facility after closure so as to permit transfer of ownership and alternative land use.

When the project conditions are conducive, seawater neutralisation may be one way to achieve this; however only a handful of refineries in the world today have adopted the practise. This paper considers the drivers and requirements for a seawater neutralisation process so that informed process selections can be made during the early development phases of greenfield projects.

### **2. Environmental Considerations**

Environmental issues weigh heavily in the selection of a residue disposal strategy and whether or not neutralisation should be adopted. Sea water neutralisation is differentiated in the following areas which are discussed below:

- Post closure ground water management
- Seawater discharge
- Dust
- Hazardous Material classification
- Water balance management
- Re-vegetation potential

- Improved properties for re-use

## 2.1. Post closure ground water management

Bauxite residue disposal areas continue to yield leachate and seepage long after their closure due to infiltration of water and further consolidation of the residue. To prevent ground water contamination this water will usually need to be recovered via a basal drainage system. How the recovered water is managed after the refinery is decommissioned is a significant issue, as it is generally not suitable for direct discharge to the environment. There is much uncertainty about how this effluent should be managed; it will require active treatment for many years and without the revenue from a refinery to pay for this treatment it will be a legacy burden either for the former operator of the refinery (as long as they remain in business) or for the state. The timeframe over which this can be expected to occur is in the order of many decades [2].

The challenge for new projects is to design a residue disposal system that does not result in a long lasting legacy requiring ongoing management after refinery closure. If the residue can be treated so that its leachate is non-hazardous to the surrounding environment, then this can be achieved. Sea water neutralisation is therefore of particular benefit where the residue disposal area can be located in a saline ground water environment. In this case, a low permeability liner may not be required (subject to assessment of groundwater impacts) and the enduring requirement for collection and treatment of basal drainage water may be reduced or eliminated. Queensland Alumina in Australia is an example where this applies [3], [4] – and similar opportunities may exist for new refinery developments in the Middle East where there are extensive areas of hypersaline ground water.

## 2.2. Seawater discharge

In the seawater neutralisation process large volumes of effluent must be discharged to the marine environment. This discharge is most often a point of contention when deciding whether or not to adopt seawater neutralisation for a new project. This is because of the risk of harm to the marine environment. However, this risk can be effectively managed providing sufficient seawater is always made available with adequate  $Mg^{2+}$  and  $Ca^{2+}$  ions available.

Studies at Queensland Alumina have shown that the seawater discharge has very low impact on the receiving environment. The trace element concentrations in the sediments, waters, mangroves, and oysters near the outfall site, as well as a survey on benthic fauna, showed no significant differences when compared to pristine control sites [5]. Concentrations of signature species Al, V, Ga, and Mo were all below ANZECC/ARMCANZ guidelines and the discharge waters were not toxic [6]. Similar results have been repeated in other toxicological studies [7], [8]. This low impact is thought to be due to the capacity of the neutralised residue to trap metal ions. When the neutralisation reaction takes place in the presence of the residue solids, the efficiency of metal removal is increased. This is because heavy metals are adsorbed by the solids and prevented from being discharged in the supernatant liquor [9], [10]. The residue also helps bind the hydrotalcite precipitate and improve dewatering/clarification of the discharge waters. These aspects highlight the importance of the presence of the residue solids in the neutralisation process – neutralisation of decant liquor alone does not achieve the same results.

Dissolved oxygen levels, turbidity, concentration and temperature are also important considerations for the discharge water. Where these parameters differ greatly from the receiving environment there is potential for impacts on benthic flora and fauna. The design of a sea water neutralisation system may need controls built in to ensure that these parameters are within the required levels. Specialist design of a sub-sea diffuser may also be required if there are buoyancy differences to ensure good mixing of the discharge with the receiving waters.

### 2.3. Dust

The clay minerals in bauxite residue have significant cation exchange capacity due to charge imbalances in their mineral structure. In un-neutralised residue the negatively charged sites are mostly taken up by exchangeable  $\text{Na}^+$  ions, making it highly sodic. High sodicity has a significant impact on the structural characteristics of a soil. The  $\text{Na}^+$  ions are large in diameter, low in charge density, and highly hydrated; consequently, the distance of separation between  $\text{Na}^+$  ions and charged clay particles is large, resulting in a weak electrostatic attraction. This weak electrostatic attraction between particles weakens aggregates, which leads to crusting and formation of dust on the surface of a residue deposit [11].

Seawater neutralisation of bauxite residue displaces these exchangeable  $\text{Na}^+$  ions, replacing them with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , thereby reducing the residue's sodicity [12]. The greater charge density and lower rates of hydration of these bivalent cations results in stronger particle attractions. One of the positive effects of sea water neutralisation then is to increase the ability of the residue to form aggregates. This binds the residue into clumps at the surface and reduces the propensity for dust generation.

In untreated residue disposal areas fugitive dust is one of the main concerns to surrounding communities. Extensive irrigation systems are required to wet down the surface of the residue using fresh water to suppress the dust, particularly in dry periods of high winds. This is not necessary when the residue has been neutralised with sea water. There is a significant reduction in fresh water usage, as well as a reduction in capital cost associated with reticulation systems.

This reduced propensity for dusting is a significant consideration for residue re-use if the material is to be stockpiled, handled and transported. Handling the dry, untreated residue can create fugitive dust emissions and a risk of occupational exposure to a respiratory irritant.

### 2.4. Hazardous material classification

A significant body of work has been assembled in the last decade on the topic of re-use or valorisation of bauxite residue but to date up-take of these emerging technologies by alumina producers has been very slow. One of the significant barriers (among others) has been the hazardous material classification of the bauxite residue and contingent liabilities associated with transfer of its ownership [13].

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is perhaps the most widely accepted standard in the world for classification of Hazardous materials. In accordance with the GHS system, alkaline bauxite residue could be classified as a corrosive substance (GHS section 3.2.2.4) if it, or its leachate, causes damage to human skin tissue (generally applies where pH exceeds 11.5), otherwise it may be classified as an irritant (GHS section 3.2.2.5).

The impact of this classification is significant, because alumina producers have justifiably shied away from any potential re-use option where the risks of loss of containment and human exposure cannot be tightly controlled. This limits the scope of potential re-use options to ones whereby only a small number of industrial consumers convert large volumes of residue into alternative benign products. These types of uses have so far proved to be elusive. Conversion of the residue into a non-hazardous form has the potential to break down this barrier and broaden the scope for residue reuse applications.

When treated by a seawater neutralisation process the hazardous properties of the residue are minimised, and it becomes safe to transport and handle in a wide range of applications. According to the Basel Convention, when treated to a pH < 11.5, bauxite residue is exempted from classification as hazardous material (Annexe IX, Item #B2110) for trans-boundary movements between signatory states. Furthermore, the treated residue has been shown to be non-toxic [14] and non-hazardous to the environment [15]. This is significant, because it makes practical the materials handling and transportation operations that are required for a multiplicity of simple re-use operations, and most importantly increases the likelihood of community acceptance of such operations. It also makes the residue safe to store indefinitely if it cannot be completely utilised as a resource.

For example, the Australian company, Virotec, has been successful at using residue neutralised by seawater or Ca and Mg enriched brines for a range of environmental remediation projects [16]. In these projects, the neutralised residue is mixed with a range of additives depending on the application, and applied without risk of harm to people or the environment. Most importantly, use of the neutralised residue in this manner has gained acceptance within the community.

This is in stark contrast to the trials conducted by the Department of Agriculture in the 1990's that used untreated (except for atmospheric carbonation) bauxite residue from Alcoa as a soil amendment in the south west region of Western Australia. Whilst the trials were deemed to be a success by the Department of Agriculture [17], there was a significant amount of controversy surrounding them at the time. Some of the landowners made claims of livestock sicknesses, heavy-metal contamination of run-off waters, and dust emissions caused by the residue [18]. As a result Alcoa sought indemnity from the state government as a condition of releasing residue for the trials. Subsequent detailed studies have found no basis for the claims of negative effects [19]. Despite the indemnity being granted and technical success of the trials, Alcoa withdrew the availability of the residue and the practise of using untreated residue as a soil amendment has not been revisited in the state of Western Australia.

## **2.5. Water balance management**

Refineries located in tropical climates with high rainfall often collect more run-off than the refinery can use and it becomes necessary to discharge excess water to the environment. Seawater neutralisation may be employed as a way to safely treat and release this excess water. This method is superior to neutralisation with mineral acid, as metal ions such as Al, V, Ga and Mo are removed from the effluent through the seawater neutralisation process, so it is likely to have lesser impact on the receiving aquatic environment.

The imperative for sea water neutralisation of excess run-off water is strong wherever thickened tailings disposal and dry stacking is used in a high rainfall climate. For this disposal methodology a large catchment of open residue area is required for drying of the residue, and so the volume of rainfall harvested will be large. This is not the case if a filtered tailings disposal methodology is employed – this is discussed further in section 4.1 below.

## **2.6. Re-vegetation potential**

Given the lack of uptake of residue re-use technologies discussed in 2.3, there is a strong possibility that most residue deposits in the world today will end up being stored indefinitely after closure and will ultimately need to be re-vegetated. Over time, the surface of an unamended residue area will be neutralised by atmospheric carbonation and microbial activity to a pH that supports plant growth, however this is a process that takes decades, and only occurs on the surface [20]. The process can be accelerated by the addition of organic matter [21]. The

alkaline bauxite residue has a high initial pH, high sodicity, and very low concentrations of important nutrients such as calcium, magnesium, manganese and phosphorus. Additionally the extremely fine texture of the residue is a barrier to root penetration and water absorption. Sea water neutralisation can change these characteristics - it reduces pH and sodicity and improves soil structure as discussed in 2.3. It also adds Ca, Mg, and K nutrients thereby making it a better medium for plant growth [22]. The initial salinity precludes plant growth, however after natural leaching by rainfall the sea water neutralised residue becomes a suitable medium for growing salt tolerant species.

## **2.7. Improved properties for re-use**

During the seawater neutralisation process the alkalinity of the residue slurry is converted to solid forms, such as brucite, hydrocalumite and hydrotalcite. These reaction products all have very high acid neutralisation and pH buffering capacities. Work by both Fergusson [16] and Hanahan [12] showed that the acid neutralisation capacity of bauxite residues from a number of refineries increased by 40 - 60 % after seawater neutralisation. This combined with the high metals removal capacity of the residue and the fact that it is safe to handle and use in the environment (as discussed in section 2.4) makes it very successful at treating acid sulphate soils and acid mine drainage [23]. Once absorbed, the metal cations are very stable in the environment, are not bioavailable, and hence are no longer present in toxic a form [24].

Phosphate absorption capacity of the residue is significantly increased by seawater neutralisation - up to five times that of un-neutralised residue [12]. Unlike absorbed metal cations, the absorbed phosphate is bio-available, and it has been shown that when applied to soil with phosphate fertiliser it acts as a slow release agent and reduces the loss of water soluble phosphate [16].

A significant body of work has assessed the suitability of seawater neutralised residue for use in concrete. As this is a potential avenue for large scale quantities of residue to be re-used its consideration here is important. Whilst there is little direct comparison with un-neutralised residue, it has been shown that the neutralised material is suitable for use in Ordinary Portland Cement concrete at rates of up to 10 % by weight of cement as a replacement for natural sand without detrimentally affecting its physical properties [25]; in fact, the addition of the residue improved the acid resistance of the concrete [26]. Whilst no conclusions are drawn here on whether or not seawater neutralisation improves the residue for use in building materials, it does not appear to have significant detrimental effects.

## **3. Economic considerations**

Sea water neutralisation is often dismissed as too expensive, or an 'unnecessary cost'; however when the right project conditions are met, it can in fact be the most economic process selection for residue disposal. The following factors need to be considered:

- Site Selection
- Organics control

### **3.1. Site Selection**

Perhaps the most important factor affecting the viability of a seawater neutralisation process is location, and it is critical in the site selection phases of a greenfield project that the potential for sea water neutralisation is considered. The ideal site for a residue disposal area should have:

- Access to seawater (or a Ca/Mg rich brine)

- Access to a discharge location with good tidal exchange or currents, and devoid of sensitive receptors (e.g. coral reefs)
- Saline ground water system
- Favourable topography for storage of residue and rainfall catchment diversion
- Suitable in-situ materials for its construction
- Low-value competing land uses

Seawater neutralization processes require large volumes of seawater to be pumped between the coast, refinery, and possibly the residue storage area. The pipelines and pumping costs required for this can become prohibitively expensive if they are more than a few kilometers long. Ideally the refinery and residue area should be located immediately adjacent to the coast to minimize these costs and increase the viability of seawater pumping. Previous studies undertaken by Hatch for Australian projects have estimated direct capital costs in the range of ~AUD \$4-5M per km for the required pumps, pipelines and access roads between the coast and the neutralization plant, although this is variable depending on project location and specifics.

More often than not coastal land is viewed as 'high-value' real estate and there is a tendency to locate residue storage areas which may be seen as a low-value land use, further inland. During the site selection process this tendency needs to be balanced with the long term impacts of the residue area. If the distance from the coast is too large, then seawater neutralization becomes prohibitively expensive.

### **3.2. Organics control**

Most bauxites contain a small amount of organic matter that, when digested, creates organic impurities in the Bayer liquor and causes a number of undesirable effects. Due to the cyclic nature of the Bayer process, the concentration of organics builds up until the amount leaving the circuit is in balance with the amount coming in. The major route for organics leaving the circuit is via the last washer underflow.

Refineries that operate alkaline residue disposal systems, recover bleed water and run-off from the residue stack and return it to the refinery. Some of the organics in bleed water end up coming back into the refinery process. Alternative methods of organics removal, such as thermal destruction, are often required to maintain reasonable organics level in the refinery liquor - these installations are typically costly to build and difficult to operate.

In contrast, a sea water neutralised residue disposal system operates in open circuit and there is no recovery of organics back to the process. Instead they are purged from the refinery along with the effluent from the sea water neutralisation process. As discussed in section 2.2, studies have shown that this effluent is not toxic and has very low environmental impact. Depending on the amount of organics in the bauxite, this can be an effective way of managing organics in the refinery, that is, if it avoids the cost of building and operating a thermal destruction process.

Trade-off studies by Hatch have concluded that the cost of building and operating a seawater neutralisation system can be more than offset by the cost of building thermal destruction process providing the refinery is located close to the coast. A case study for a proposed refinery in Australia with thickened tailings disposal, and a neutralisation plant located approximately 10 km from the coast, is presented below as an example:

**Table 1. Case study - Cost of residue disposal and impurity destruction facilities for a proposed Greenfield alumina refinery project in Australia.**

|                                       | <b>Alkaline Recycle<br/>+Thermal Organics<br/>Destruction</b> | <b>Seawater<br/>Neutralisation</b> |
|---------------------------------------|---|------------------------------------|
| <b>Capital Costs</b>                  |   |                                    |
| Years 1-5                             | \$287.3 M   | \$199.4 M                          |
| Years 6-30                            | \$122.7 M   | \$140.8 M                          |
| <b>Operating Cost Differentiators</b> |   |                                    |
| Pumping Energy Cost                   | \$1.0 M   | \$1.6 M                            |
| Heating Energy Cost                   | \$2.5 M   | -                                  |
| Soda recovery benefit                 | -\$6 M  | -                                  |
| Water recovery benefit                | -\$0.7 M  | -                                  |
| O&M costs                             | 4.4   | 2.0                                |
| Subtotal                              | \$1.2 M   | \$3.6 M                            |
| <b>Net Present Cost</b>               |   |                                    |
| Simple NPV @7 % discount rate         | \$368 M   | \$320 M                            |

#### 4. Competing technologies for residue treatment

There are a number of alternative processes for treatment of bauxite residue to reduce pH and hence its environmental impact.

- Pressure filtration – low soda filter cake
- Pressure carbonation

##### 4.1. Pressure filtration – low soda filter cake

High pressure filtration is emerging as the preferred technology for dewatering of bauxite residue prior to disposal. In the past it has been employed as an alternative to sea water neutralisation in high rainfall locations as it minimises catchment area to maintain water balance. There are however, numerous other benefits of pressure filtration and it is rapidly being adopted as ‘best practise’ regardless of climate for the reduced footprint and high consolidation strength it provides in the RDA. Indeed, studies by Hatch have concluded that residue filtration is an economically favourable option in most cases due to a reduction in civil construction costs regardless of any water balance considerations.

With high filtration pressures, cake solids up to 70 % can be achieved and this combined with a high efficiency displacement wash can produce a filter cake with soda content as low as 5 kg/t as Na<sub>2</sub>CO<sub>3</sub> [27].

Organics and impurity control is a particularly relevant issue when considering pressure filtration of residue. Whilst it is possible to reduce the soda content in residue to as low as 5 kg/t, this is only possible for refineries with very low impurity inputs. Few producers could afford to operate with soda losses this low for a long period of time due to the lack of impurity purging that goes with it. The trend in the industry appears to be for refineries to maintain soda loss, and therefore impurity levels at historical levels (typically > 20 kg/t) even if the technology being installed has the capability to achieve better.

Best practice recommendations of the International Aluminium Institute are that “there should be an overarching goal to reduce and/or stabilise the residual soda content in residue” [28]. With this goal in mind, there will be an increasing need for refineries to reduce their impurity bleed to tailings and employ alternative impurity removal practices. Therefore, there is an argument for sea water neutralisation to be considered in conjunction with residue filtration. This would provide a design philosophy that takes advantages of the civil cost savings associated with pressure filtration and dry disposal of residue, as well as a cost effective method of organics control which is not affected by the choice to produce a low-soda filtered residue cake. Whilst this would be a first for the industry, it opens up the possibility of having a low-cost, benign residue stack, whilst still allowing the refinery to operate with an economic precipitation yield.

It is also worth noting, that in laboratory scale tests, the filtration rate of seawater neutralised residue was approximately doubled when compared to un-neutralised residue [29]. If a filtered residue disposal methodology were to be implemented with seawater neutralisation, it may reduce the amount of filtration equipment required. The improved filterability of the residue is a result of the same mechanism that reduces dusting, as discussed above in section 2.3.

#### **4.2. Residue carbonation**

Residue carbonation involves the treatment of last washer underflow with pressurized CO<sub>2</sub> and is equivalent to seawater neutralisation in rendering bauxite residue less hazardous [4]. The reduction in pH of carbonated residue opens up a range of potential re-use options; however, compared to sea water neutralised residue it will have lower acid neutralising capacity, higher sodicity, and lower capacity for phosphate absorption. Properties of the carbonated residue will not be beneficial to the same extent as seawater neutralised residue in many applications.

Major benefits of residue carbonation are that the refinery doesn't need to be located close to the coast, and no contaminants are added to the process so soda and water can be recovered from the residue area and returned to the refinery.

The process requires a source of > 95 % pure CO<sub>2</sub>; and unless there is a waste stream readily available (as is the case at Alcoa's Kwinana Refinery where it has been successfully implemented) a significant investment in a CO<sub>2</sub> recovery plant is required to purify CO<sub>2</sub> from powerhouse flue gas. The CO<sub>2</sub> absorption process requires thermal energy to operate, and electrical energy to compress the product gas - these are significant operating costs. Absorption of CO<sub>2</sub> from flue gas is a complex operation – if the refinery is located near to the coast, seawater neutralisation is a simpler and cheaper process in comparison.

#### **5. Conclusions**

There are many factors that should be considered when selecting a residue disposal strategy for a greenfield refinery project. Seawater neutralisation of the residue can provide a facility with very low environmental impact, and minimal post closure legacy. The residue produced has lower associated dust risks, is non-hazardous to handle and transport and it has enhanced properties for many re-use applications. Moreover, its re-use for other beneficial purposes is also more likely to gain acceptance from the wider community than an alkaline residue. In addition, seawater neutralisation can also be an economically attractive choice in the right set of project conditions. Site selection is key to realising these benefits and it is imperative that this is considered in the very early phases of the project lifecycle.

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