Formation, properties and revegetation prospects for bauxite processing residue and the effects of seawater neutralisation

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Abstract: Partial neutralisation of bauxite residue (by treatment with seawater) prior to its deposition in land-based lagoons or impoundments minimises the need to treat the alkaline, sodic drainage both during operation of the alumina refinery and following its closure. Some of the Na present in the residue is replaced by Mg, Ca and K present in the seawater and reactive, soluble alkalinity is converted to poorly soluble alkaline solids (Mg and Ca hydroxides and hydroxycarbonates) with the result that the pH is reduced from 10–13 down to 8.5–9.0. However, the extent to which pH rises again during storage is unclear. There are, as yet, no reports of revegetation of seawater neutralised material. Growth limiting factors are likely to include alkalinity, sodicity, salinity, nutrient deficiencies and poor soil physical conditions but the severity of these constraints are as yet unknown. Research into the technology required for revegetation of this material is warranted.

Keywords: bauxite residue; red mud; revegetation; Bayer process; seawater neutralisation.

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Biographical notes: Y. Li is an environmental science researcher working on revegetation strategies for bauxite residue mud. Her research pays particular attention to the effects seawater neutralisation on the properties of residue mud and how this influences revegetation strategies.

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1 Introduction

The main source of aluminium is bauxite ore which contains gibbsite [Al(OH)₃], boehmite [γ-AlO(OH)] or diaspore [α-AlO(OH)]. The ore is typically excavated using open-cut mining techniques and then crushed and processed in an alumina refinery using the Bayer Process. This involves dissolving the Al-containing minerals in caustic soda (NaOH) at elevated temperature. The soluble product generates alumina, the precursor of aluminium, while the insoluble residue is separated and pumped out of the refinery as bauxite processing residue and deposited in land-based impoundments.

The engineered impoundments used for residue storage, often termed residue disposal areas (RDAs), typically occupy hundreds of hectares of land surrounding alumina refineries. Indeed, 1–2 tonnes of residues are generated per tonne of alumina produced (Hind et al., 1999; Kumar et al., 2006). On a global basis, bauxite residue production amounts to about 120 million tonnes per annum and the legacy of residue accumulation over the past 120 years is estimated to be approximately 2.7 billion tonnes (Power et al., 2011). Bauxite residues have a high pH (10–13) and possess high salinity and sodicity. As a result, drainage from the storage areas can pose an environmental risk and must be managed. Indeed, leachate from RDAs may need to be treated during operation of the alumina refinery and then for many decades after closure. In addition, wind-blown alkaline dust from drying residue can pose a threat to wildlife and humans. As a result, some refineries now partially neutralise their residues before they are deposited in RDAs. This reduces the need for costly ongoing intensive management of the RDA and its leachate after closure and also opens up opportunities for re-use of the residue which to date have been hindered because of the high pH (Kirwan et al., 2013).

Neutralisation may involve

a. direct carbonation whereby the residue slurry is treated with CO₂ gas (Cooling et al., 2007; Dilmore et al., 2008)

b. addition of spent acids (Kirwan et al., 2013)

c. reaction of residues with seawater (Hanahan et al., 2004; Palmer et al., 2009).

Seawater neutralisation was pioneered at the Queensland Alumina Limited refinery where, in order to conserve fresh water, seawater was used as a medium to transport residue from the refinery to disposal lagoons (Hanahan et al., 2004). An accidental consequence of this was partial neutralisation. The pH is reduced by converting soluble reactive alkalinity to less soluble caustic solids such as calcite (Hanahan et al., 2004). Modern alumina refineries are often located close to deep water ports since this allows for bulk shipment of incoming bauxite (sometimes from multiple sources) to the refinery and/or for bulk shipment of alumina to aluminium smelters situated elsewhere. There is therefore ample scope for the increasing use of seawater neutralisation technology for pretreatment of residues prior to their deposition in impoundments.

Revegetation of RDAs is a priority in closure strategies since it minimises dust, reduces leaching (through transpiration losses to the atmosphere) and forms a landscape which is a habitat for wildlife. However, the saline/sodic nature of residues makes them difficult to revegetate (Grafe and Klauber, 2011; Jones and Haynes, 2011). Although a number of workers have characterised the seawater neutralisation process (Hanahan et al., 2004; Menzies et al., 2004; Power et al., 2011), to date there are no reports on revegetation of this material. In this review we outline the processes of formation of
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Bauxite processing residues, its key properties, alteration of properties induced by seawater neutralisation and the prospects for its revegetation. It is not intended to provide an exhaustive review of papers on the subject but rather to highlight progress in the field, examine the mechanisms of formation and neutralisation, identify limitations to revegetation and highlight areas where future research should concentrate.

2 The Bayer process and formation of bauxite residue

The Bayer process is the most widely used industrial method of producing alumina (Hind et al., 1999; Sidrak, 2001). It involves five major steps: grinding and pre-desilication, digestion, clarification, precipitation and calcination to alumina (Figure 1). The bauxite is washed to remove residual materials, such as clays, and then crushed and ground to increase surface area. In many modern operations there is a pre-desilication step prior to digestion which removes reactive silica (predominantly present as kaolinite) that would otherwise cause scaling problems during digestion. This involves reacting the crushed material with hot (150–250°C) NaOH to produce a slurry. Silicate minerals begin to dissolve in the liquor to form soluble sodium silicate:

\[
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 6\text{NaOH} \leftrightarrow 2\text{NaAlO}_2 + 2\text{Na}_2\text{SiO}_3 + 5\text{H}_2\text{O}
\]  

(1)

The slurry is left in heated holding tanks for several hours to allow time for precipitation of desilication product (DSP):

\[
\Delta T \leftrightarrow 3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O})\text{Na}_2\text{X} + 12\text{NaOH}
\]

(2)

The sodium aluminium silicate DSP mineral formed, 3(Na₂O ∙ Al₂O₃ ∙ 2SiO₂ ∙ nH₂O)Na₂X is sodalite where X⁻ can be a variety of anions, commonly CO₃²⁻, OH⁻, SO₄²⁻. The structure of DSP is discussed in more detail below. Slurry storage usually transforms 80%–90% of the reactive silica into DSP, with the remainder being converted during digestion (Smith, 2008).

**Figure 1** A schematic diagram of the Bayer process
After desilication the bauxite undergoes digestion at elevated temperatures. The alumina phases are dissolved in the caustic solution to form sodium aluminate. Digestion conditions vary depending on the type Al-containing minerals present in the bauxite. Diaspore and boehmite are less soluble in NaOH than gibbsite and therefore require greater energy inputs. Indeed, gibbsite can be digested in 3M NaOH with a temperature of only 100–150°C but boehmites and diaspores require significantly higher temperatures and stronger NaOH concentrations (Lavalou et al., 1999; Authier-Martin et al., 2001; Mylona et al., 2008). The formation of sodium aluminate from bauxite minerals during Bayer digestion is as shown below:

\[
\begin{align*}
\text{(3)} & \quad \text{Al(OH)}_3(s) + \text{NaOH}(aq) \rightarrow \text{Na}^+ \text{Al(OH)}_2(aq) & \quad \text{(gibbsite)} \\
\text{(4)} & \quad \text{AlO(OH)}(s) + \text{NaOH}(aq) + \text{H}_2\text{O} \rightarrow \text{Na}^+ \text{Al(OH)}_2 & \quad \text{(boehmite and diaspore)}
\end{align*}
\]

Slaked lime [Ca(OH)$_2$] is often added to the liquor during digestion in order to remove impurities. These include carbonate, silicon, phosphorus and anatase and when lime is added sparingly soluble calcium carbonate, hydrogarnet, carbonate apatite and calcium titanate oxide are formed (Whittington and Fallow, 1997; Authier-Martin et al., 2001).

The next process is clarification in which the undigested bauxite residues are separated from the aluminate liquor and caustic soda is recovered. Firstly, via gravity, and sometimes cyclonic separators, the coarse particles (residue sand) are segregated. Secondly, in thickener vessels, synthetic flocculants such as polyacrylates, polyacrylamides are used for separating fine particles (residue mud) (Clifton et al., 2007; Pejcinovic et al., 2007). The mud, once separated, is washed using continuous counter current mud washers to recover liquor containing caustic soda and alumina.

In the precipitators, crystalline aluminium trioxide (gibbsite), which is termed hydrate, is precipitated from the digestion liquor:

\[
\text{(5)} \quad \text{Na}^+ \text{Al(OH)}_2(aq) \rightarrow \text{Al(OH)}_3(s) + \text{NaOH}(aq)
\]

In order to induce precipitation, small crystals of trihydrate alumina are seeded into the cooled liquor. The finished mix of crystals is settled from the liquor stream and separated. The last phase is where the washed hydrate is calcined to form alumina. It is heated to 1,000–1,200°C to drive off the water of hydration:

\[
\text{(6)} \quad 2\text{Al(OH)}_3(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O(g)}
\]

The final, white, sand-like product, alumina (Al$_2$O$_3$) is then transported to an aluminium smelter.
3 Bauxite processing residue

3.1 Storage/disposal

Throughout the world, the utilisation of bauxite processing residue is very low (Paramguru et al., 2005; Klauber et al., 2011) so that the vast bulk of material is discarded in areas close to the alumina refinery. The stockpiling of residues in RDAs, and their subsequent management, represents a substantial cost in alumina production and it is also a key environmental concern for the industry (Hausberg et al., 2000; Kumar et al., 2006). There are a number of different options for bauxite residue disposal.

Marine discharge is the simplest method and involves residue slurry from the washing circuit being carried by pipeline well offshore for discharge into the deep ocean (Hausberg et al., 2000; Power et al., 2011). This was historically favoured by French and Japanese refineries. In 1965, about 30% of global alumina production was associated with such residue disposal but by 2011 this had been reduced to only 2%–3% (Power et al., 2011). Due to increasing environmental awareness (Dauvin, 2010), increasingly strict environmental regulations, and international agreements with the International Maritime Organisation, the practice is scheduled to be discontinued by 2015.

The second residue management option is lagooning where the residue slurry from the washing circuit is pumped directly to land-based ponds. These are usually formed within natural depressions in the landscape and dams and other engineered earthworks are used to secure the residue containment. The alkaline liquid slurry can leach from lagoons and contaminate surface and/or groundwater (Cooling, 2007; Paramguru et al., 2005). Additional security can be achieved by using linings of compacted clay and/or synthetic membranes and the installation of engineered drainage networks (Hausberg et al., 2000). Storage problems can also be mitigated by partially neutralising the slurry prior to discharge into the lagoon using seawater and/or mineral acids. The slurry in lagoons dries and consolidates over a long period and rehabilitation is only possible after this has occurred (Mahadevan and Ramachandran, 1996).

The current trend in residue storage is to move towards dry stacking (thickened tailings disposal) as the preferred technology. In this method, residue slurry from the washing circuit is thickened to a paste (48%–55% solids) prior to discharge (Nguyen and Boger, 1998; Cooling, 2007). The paste is transported by pipeline to the RDA where it is deposited on sloped beds (2–6°) in layers up to 0.5 m thick. The layer is then allowed to dry (by drainage and evaporation) to about 70% solids (Cooling and Glenister, 1992; Cooling, 2007). Evaporative loss is often promoted by turning the surface using earthmoving equipment. Once the bed has dried, the process is repeated by depositing a fresh layer of mud and the deposit is built up into a progressive stack. The process is designed so that the dried paste becomes self-supporting and as a result it can be safely stacked to considerable heights within containment embankments. Although dry stacking includes the additional step of thickening, it has many advantages over lagooning including minimisation of
the size of the storage area
the structures needed for containment of the residue
the potential for leaching to groundwater and therefore contamination of ground and
surface waters.

At the present time there is interest in mechanically removing as much water as possible
from the residue (by a combination of thickening and filtration) to produce a dry cake
with a solids content greater than 65%. The dry cake is transported to RDAs by conveyer
belt or trucks. Such a strategy eliminates the need to remove liquids after deposition in
the RDA and greatly reduces the potential for environmental impact especially
contamination of surface and groundwater. Hyperbaric filtration of residue mud has been
carried out successfully at a pilot scale (Bott et al., 2002) and dry cake disposal
(following drying using vacuum drum filters) is already practiced at some refineries
(Shah and Gararia, 1995).

3.2 Properties of bauxite residues

Bauxite residues vary greatly in elemental composition depending primarily on the nature
of the parent bauxite ore. Typical ranges of elemental content (as oxides) are: Fe₂O₃
30%–60%, Al₂O₃ 15%–25%, SiO₂ 1%–20%, Na₂O 1%–10%, CaO 5%–40% and TiO₂
3%–15% (Paramguru et al., 2005; Power et al., 2011). The material has a low organic C
content (trace-0.3%) and is low in plant-available nutrients such as N, P, K, Ca, Mg, Cu
and Zn (Jones and Haynes, 2011).

Concentrations of some heavy metals (e.g., Pb, Cd, Co, Cu, Zn, As) and naturally
occurring radioactive materials (e.g., Th, U) are elevated compared to the parent bauxite
due to their concentration in the waste stream during refining (Paramguru et al., 2005;
Jones and Haynes, 2011). However, most metals are in non-mobile forms because of the
high residue pH and radioactivity is typically extremely low (Von Philipsborn and
Kuhnast, 1992; Qu and Lian, 2013).

3.3 Mineralogy

Bauxite residues typically consist of 70% crystalline mineral phases and 30% amorphous
materials (Grafe et al., 2011). Mineralogical composition of residues depends on the
nature of the bauxite ore used (since many minerals are carried over from the original
bauxite) and the nature of new minerals created during the Bayer process. The major
minerals in bauxite ores are gibbsite, boehmite, goethite, hematite, anatase, rutile,
ilmenite, kaolinite and quartz (Bardossy and Aleva 1990). Minerals commonly present in
bauxite residues include the iron oxides hematite (Fe₂O₃) and goethite (α-FeOOH), Al
oxides such as boehmite (γ-AlO(OH)) and gibbsite (Al(OH)₃), sodalite (Na₈Al₆(SiO₄)₆Cl),
quartz (SiO₂), anatase and rutile (both TiO₂) and cancrinite (Na₈Ca₂Al₅Si₃O₂₆(CO₃)₂)
(Table 1). Ilmenite (FeTiO₃), perovskite (CaTiO₃), tricalcium aluminate and hydrogarnet
are other minerals commonly present (Grafe et al., 2011).
<table>
<thead>
<tr>
<th>Country</th>
<th>Region</th>
<th>Hematite</th>
<th>Goethite</th>
<th>Boehmite</th>
<th>Gibbsite</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Sodalite</th>
<th>Cancrinite</th>
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<td>-</td>
<td>●</td>
<td>-</td>
<td>●</td>
<td>-</td>
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</tr>
<tr>
<td>Australia</td>
<td>Kwinana</td>
<td>●</td>
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<td>●</td>
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<td>●</td>
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<td>-</td>
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</tr>
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<td>●</td>
<td>●</td>
<td>●</td>
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<td>●</td>
<td>-</td>
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<tr>
<td>Turkey</td>
<td>Seydshir</td>
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<td>●</td>
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<td>●</td>
<td>●</td>
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Note: ● detected; - not found.
Table 2   Properties of some bauxite residues

<table>
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<tr>
<th>References</th>
<th>pH</th>
<th>EC (dS/m)</th>
<th>CEC (mmolc•kg⁻¹)</th>
<th>SSA (m²/g)</th>
<th>P (g/m³)</th>
<th>ANC to pH7 (mol H⁺/kg solid)</th>
<th>ESP (%)</th>
<th>SAR</th>
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<td>12.7</td>
<td>12.7</td>
<td>2.75</td>
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<td>28.4</td>
<td>883.6</td>
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<td>10.6</td>
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<td>17.3</td>
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<td>9.2</td>
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<td>8.2</td>
<td>26</td>
<td>0.88</td>
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<td>12.4</td>
<td>10.8</td>
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<td>11.1</td>
<td>37.7</td>
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<td>16.9</td>
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<td>198.57</td>
<td>53.4</td>
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<td>11.2</td>
<td>11.2</td>
<td>47.4</td>
<td>11.2</td>
<td></td>
<td>4.22</td>
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</tr>
</tbody>
</table>

Because of the lower digestion temperature, the residues of gibbsitic bauxites have more minerals from parent ores than those from bauxites containing boehmite and diaspore. That is, under high temperature digestion, many of the major minerals are dissolved or react with other chemicals (Authier-Martin et al., 2001). Hematite is ubiquitous in residues and commonly has a concentration range of 7% to 29% (Graf et al., 2011). Goethite occurs only when refining processes are at lower temperatures or the parent ores contain very large amounts of Al (Li, 1998; Li and Rutherford, 1996).

DSP (e.g., sodalite or cancrinite) are important components of bauxite residues because Na⁺ and OH⁻ ions are slowly released from the mineral structure (Barrow, 1982; Wehr et al., 2006; Wong and Ho, 1995). Their structure is made up from SiO₄ and AlO₄ tetrahedra and they contain ‘cages’ of negative charge (Figure 2). Sodium ions balance this charge (Whittington et al., 1998; Smith, 2008). For sodalite, the Na is present as (Na₄Cl)⁺ where Cl is tetrahedrally linked with four Na ions while for hydroxyl sodalite the Na is present as (NaH₂O)⁺. Cancrinite has a different structure to sodalite and has two possible locations for included ions, either in the cage structures or in larger linear channels (Figure 2) that form part of the hexagonal structure (Smith, 2008). Within these channels 2CaCO₃ can replace Naₓ resulting in the formation of Ca cancrinite (NaₓCaₓAlₓSiₓOₓ₂(CO₃)₂). This contains 25% less Na than sodalite. The Na⁺ in sodalite and cancrinite cations can be replaced by other monovalent cations in the following order: K⁺ > Li⁺ > NH₄⁺ (Wong and Ho, 1995) but divalent cations such as Ca²⁺ and Mg²⁺ are ineffective. Over time, Na is released from the DSP structure by sodalite/cancrinite dissolution and/or displacement by other monovalent ions.
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Figure 2  A structural model of negative charged cages and linear channels of cancrinite and sodalite

![Figure 2: A structural model of negative charged cages and linear channels of cancrinite and sodalite](source)

Source: Redrawn from Zhao et al. (2004)

Other DSPs include the tricalcium aluminate hexahydrate (TCA) (CaO•Al₂O₃•6H₂O) and the hydrogarnet series of minerals (Smith, 2008). TCA (CaO•Al₂O₃•6H₂O) is formed when lime is added to Bayer liquor. It is used as an aid to filtering during liquor clarification and it is also used as a desilication agent (Franca et al., 2010). For desilication, the TCA reacts with soluble silica to form a non-Na-containing DSP product, hydrogarnet [Ca₃Al₂(SiO₄)n(OH)₁₂-4n] (Whittington and Fallow, 1997; Yuan and Zhang, 2009) thus minimising the amount of soda lost with the residue mud.

3.4 pH and alkalinity

Residual NaOH is present in bauxite residues resulting in them being highly alkaline. The pH of untreated residue liquor typically varies from 10.0 to 13.0 (Paramguru et al., 2005; Jones and Haynes, 2011; Grafe et al., 2011) and in the liquor the main alkaline anions buffering the solution are OH⁻, CO₃²⁻/HCO₃⁻ and Al(OH)₆⁻. The alkaline buffering capacity of residues is maintained by alkaline solid phase minerals. These solids are formed during the Bayer process and the alkalinity originates from the NaOH and slaked lime [Ca(OH)₂] present during digestion. As well as calcite (CaCO₃), sodalite, cancranite, tri-calcium aluminate (TCA) and hydrogarnet are important buffering solids. For sodalite (Grafe et al., 2011), dissolution to form soluble alkalinity occurs as follows.

$$Na₆[Al₆Si₆O₂₄]·2NaOH + 24H₂O = 8Na^+ + 8OH^- + 6Al(OH)₃ + 6H₄SiO₄$$

Because of their alkalinity, bauxite residues have acid neutralising capacity (ANC). This is measured as the amount of acid needed to reach a target pH. The ANC of bauxite residues (to pH 7.0) can range from 0.45 to 1.64 mol H⁺ kg⁻¹ (Snars et al., 2003, 2004)
with an average of approximately 0.9 mol \( \text{H}^+ \) kg\(^{-1}\) (Grafe et al., 2011). There are several inflection points on ANC curves (Snars et al., 2004; Carter et al., 2008) reflecting the fact that, as noted above, there are a number of minerals contributing to the buffering capacity of residues (Khaitan et al., 2009). ANC values increase with increasing equilibration times up to several days (Liu et al., 2007; Carter et al., 2008) because neutralisation reactions are limited by rates of dissolution of the solid phases.

For developing vegetation, the alkaline nature of bauxite residues is growth-limiting in a number of ways. In alkaline solutions, \( \text{HCO}_3^- \) predominates between \( \text{pH} 6.0 \) and 9.5 and \( \text{CO}_3^{2-} \) and \( \text{OH}^- \) above 9.5. Very high \( \text{pH} \), with high concentrations of \( \text{OH}^- \), \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) in solution, can impair root growth and function and nutrient translocation to leaves (Gupta and Abrol, 1990). The toxic effects of \( \text{OH}^- \) and \( \text{HCO}_3^- \) ions are similar in that they both cause inhibition of root growth (Kopittke and Menzies, 2004). The high concentrations of aluminate \( [\text{Al(OH)}_4^-] \) present in solution at high \( \text{pH} \) (i.e., > \( \text{pH} 9.0 \)) are also phytotoxic (Fuller and Richardson, 1986; Ma et al., 2003; Stass et al., 2006; Brautigan et al., 2012). The main mechanism of toxicity may be that aluminate forms a central core to \( \text{Al}_{13} \) species which are known to be highly phytotoxic (Kinraide, 1990; Kopittke et al., 2004a). Aluminium toxicity has been forwarded as a major limitation to plant growth in unamended bauxite residues by several workers (Fuller and Richardson, 1986; Courtney et al., 2009; Woodard et al., 2008).

### 3.5 Salinity

Electrical conductivity (EC) is measured to estimate total dissolved salt content and values for untreated bauxite residues range from 3,000 to 18,000 mS m\(^{-1}\) (Fuller et al., 1982; Snars et al., 2004). In a soil, values are typically less than 400 mS m\(^{-1}\) (Meecham and Bell, 1977a; Woodard et al., 2008) so that bauxite residues are considered highly saline. Inhibition of plant growth (Maas, 1990) is usually slight at EC values between 200–400 mS m\(^{-1}\), severe between 400–600 mS m\(^{-1}\) and death typically occurs at > 600 mS m\(^{-1}\) (Maas, 1990).

As a result of salinity, and a more negative water potential in soil solution, water uptake by plants is reduced (Keren, 2000; Yadev et al., 2011). The root-pressure-driven xylem transport of water and solutes is reduced as is shoot and root growth (Lauchli and Grattan, 2007; Yadev et al., 2011). Thus, the salinity of freshly deposited bauxite residue will be a growth limiting factor for plants. However, over time the salts will be leached out of the surface horizons and down the residue profile. There is, nevertheless, the possibility that they may subsequently move back upwards in the profile by capillary action (particularly in residue mud deposits) (Wehr et al., 2006). Halophytic plants, tolerant to high salinity, are therefore appropriate for revegetation of bauxite residues (Bell et al., 1993; Jones and Haynes, 2011).

### 3.6 Sodicity

Exchangeable sodium percentage (ESP) and/or sodium adsorption ratio (SAR) are used to quantify sodicity (Sumner, 1995). The ESP is expressed as:

\[
\text{ESP} = \frac{100 \times \text{Exchangeable Na}}{\sum \text{(Exchangeable Ca + Mg + K + Na + Al)}}
\]  

(9)
Formation, properties and revegetation prospects

The SAR in soil solution, saturation paste extracts or soil/water extracts is defined as:

\[
\text{SAR} = \frac{\text{mmol Na L}^{-1}}{\sqrt{\frac{\text{mmol Ca L}^{-1} + \text{mmol Mg L}^{-1}}{2}}}
\]  

(10)

Soil sodicity is normally recognised when ESP values are > 15% or SAR values > 13 (Summer, 1995). The ESP of bauxite residues is typically 60%–90% (Meecham and Bell, 1977a; Fuller et al., 1982) so that it is sodic as well as highly saline.

Plant growth is inhibited by sodicity through a number of mechanisms. Excessive uptake and accumulation of Na leads to toxicity (Naidu and Rengasmy, 1995). Enzyme reactions can be inhibited by accumulation of Na in the cytoplasm while dehydration and death of leaf cells can occur where Na accumulates in the leaf apoplasm (Keren, 2000). In addition, high concentrations of Na in soil solution reduce Ca uptake and Ca deficiency often occurs (Kopittke and Menzie, 2005). A deficiency of Ca can influence membrane permeability and therefore restrict uptake of other ions resulting in deficiencies of N, K, Mn, Zn and Cu (Levy, 2000; Yadav et al., 2011).

3.7 Surface area and surface charge

The specific surface area of residue mud commonly ranges between 10 and 30 m\(^2\) g\(^{-1}\) (Grafe et al., 2011). Such values are similar to those for 1:1 phyllosilicate clays such as kaolinite but are an order of magnitude less than those for expanding 2:1 clays such as the smectites. The net negative charge or cation exchange capacity (CEC) of residues has been reported to be 111–173 mmolc•kg\(^{-1}\) by Meecham and Bell (1977a) and 42 mmolc•kg\(^{-1}\) by Wong and Ho (1995).

The Fe and Al oxide materials in bauxite residues have variable charge surfaces so their net charge is dependent on factors such as pH and ionic strength. The pH where equal numbers of positive and negative surface charges exist (the point of zero charge) varies greatly depending on the nature of the parent bauxite and details of the Bayer process (Grafe et al., 2011). It has been reported to be 7.8–8.5 (Pradhan et al., 1999; Chevdo et al., 2001; Zhang et al., 2008), 6.9 (Lopez et al., 1998) and 6.0 or lower (Lopez et al., 1998; Castaldi et al., 2008). The variable charge nature of the Fe and Al oxide surfaces means that residue can specifically adsorb both metal cations (e.g., Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\)) and anions (e.g., phosphate, molybdate, asenate, vanadate) and because of this, and its substantial specific surface area, residue mud has been forwarded as a suitable material to remove such ions from wastewater streams (Paramguru et al., 2005; Wang et al., 2008).

The high adsorption capacity of residues means that micronutrient cations/heavy metal cations such as Cu, Zn, Mn, Pb and Cd as well as macronutrients such as P can be ‘fixed’ to the surfaces of the residue mud. For this reason, during revegetation fertiliser P applications are often large (see Section 5.2). Adsorption of cations is favoured by high pH so that leaching of heavy metals from RDAs is minimal but in some cases micronutrients such as Cu, Zn and Mn may be deficient and need to be added.
3.8 Physical properties

Since bauxite ores are crushed and then digested by the Bayer process, the particle size is mostly of a fine textural class, ranging from 0.10 to 200 µm with an average range of 2 to 100 µm (Pradhan et al., 1996; Roach et al., 2001). Soil particles are traditionally divided into size classes: sand (diameter 0.02–2.00 mm), silt (2 µm–0.02 mm) and clay (< 2 µm) and residue mud is typically in the silt and fine sand textural classes (Gee and Bauder, 1986). There are, however, large differences in size class between refineries. For example, Wehr et al. (2006) working at Gove, northern Australia, found that more than 50% of particles were clay-sized while Newson et al. (2006) reported most of the residues from a Scottish refinery were a mixture of sand and silt. Where the residue is lagooned, large particles settle first so that the material can become increasingly fine with increasing distance from the discharge point (Fuller et al., 1982).

The particle density of residue mud has been shown to range from 3.4–3.8 g cm\(^{-1}\) (Li and Rutherford, 1996; Li, 1998; Courtney et al., 2009). Residue mud can consolidate to form a solid mass and the bulk density is often in the range 1.5–1.8 g cm\(^{-1}\) (Nikraz et al., 2007; Courtney et al., 2009) and total porosity is about 0.53–0.63 cm\(^{-3}\) cm\(^{-3}\) (Wong and Ho, 1991, 1994a; Courtney et al., 2009). Because of the fine particle size, the pores present are all in the small size classes. A lack of macroporosity results in a low hydraulic conductivity (e.g., 0.002 cm min\(^{-1}\)) (Bell and Meecham, 1978). Residue sand (which is much more coarse textured) has a lower water holding capacity than mud but a higher hydraulic conductivity (Wehr et al., 2005, 2006).

Because of the low macroporosity and hydraulic conductivity of mud, water tends to pond on the surface and the upper layers can become saturated during wet periods of the year. Such waterlogging can limit plant establishment (Wehr et al., 2006) and installation of drainage to depth (i.e., several meters) is essential. In addition, a massive, solid, structure can develop in the surface horizons as a residue mud lagoon progressively dries. This limits both penetration and water infiltration (Newson et al., 2006; Harris, 2009). Such solidification develops due to the presence of binding agents in mud through the combined effects of silica, goethite, gibbsite and sodium silicate, amorphous goethite and hydrosodalite (Pinnock and Gordon, 1992; Zhang et al., 2001; Newson et al., 2006). Upon drying and solidification the mud typically contracts and this can result in the formation of surface connected fissures and macropores to depth. In order to prepare the ground for revegetation, the profile may be deep ripped to a meter or more and then the surface layer (10–15 cm) tilled to form a seedbed using agricultural implements. This results in the formation of a mixture of size classes of solid peds and aggregates (bound together by the binding agents) and a physical environment which is sometimes satisfactory for plant growth.

4 Seawater neutralisation

4.1 Reaction mechanisms

Seawater typically contains 965 g of water and 35 g of salts (i.e., 3.5% salinity). The concentration of various salt ions in seawater is 55% Cl\(^{-}\), 30.6% Na\(^{+}\), 7.7% SO\(_4\)\(^{2-}\), 3.65% Mg\(^{2+}\), 1.17% Ca\(^{2+}\), 1.13% K\(^+\) and 0.7% other ions (Rai et al., 2013). For seawater neutralisation, bauxite residues are mixed with seawater in a specialised facility and the
neutralised residues are then rinsed with fresh seawater to remove entrained liquor. The process replaces some of the Na\(^+\) with Ca\(^{2+}\), Mg\(^{2+}\) and K\(^+\) on exchange sites and soluble alkalinity is precipitated as sparingly soluble hydroxides and hydroxycarbonates (Hanahan et al., 2004). Neutralisation is considered complete when the liquor from the treated residue mud has a pH less than 9.0 and a total alkalinity less than 200 mg l\(^{-1}\) (as CaCO\(_3\) equivalent alkalinity) (Rai et al., 2012). Under field conditions the pH of seawater neutralised residues is typically in the range of 9.0–9.5.

The addition of seawater to residue mud results in the formation of fine mineral particles that flocculate into larger agglomerates (Palmer et al., 2009). Multivalent cations (Ca\(^{2+}\) and Mg\(^{2+}\)) originating from the seawater form electrostatic bridges and these acts as nucleation sites for the precipitation of Ca and Mg hydroxides:

\[
\text{Mg}^{2+} + 2\text{(OH)}^- \rightarrow \text{Mg(OH)}_2 (s) \tag{11}
\]

\[
\text{Ca}^{2+} + 2\text{(OH)}^- \rightarrow \text{Ca(OH)}_2 (s) \tag{12}
\]

Formation of these solid phase hydroxides reduces the concentration of hydroxide in solution resulting in a decrease in pH. The decrease in pH also causes soluble aluminates to begin precipitating as AlO(OH) polymorphs and the concentration of extractable Al is decreased by seawater neutralisation (Anderson et al., 2011). As electrostatic conditions on the surfaces change, the agglomerates tighten pH decreases and elements that exhibited colloidal behaviour at high pH lose their stability. A further decrease in pH causes precipitation of hydroxycarbonates of aluminium, calcium, and magnesium, and precipitation of hydrotalcite-like compounds is favoured (Boclair and Braterman, 1999; Smith et al., 2005; Kirwin et al., 2013):

\[
\begin{align*}
6\text{Mg}^{2+} + 8\text{OH}^- + 2\text{Al(Oh)}_2^4+ + \text{CO}_3^{2-} &\leftrightarrow \text{Mg}_6\text{Al}_2\text{OH}_{16}\cdot\text{MgCO}_3\cdot4\text{H}_2\text{O} \text{ (hydrotalcite)} \tag{13}
\end{align*}
\]

Hydrotalcite is a layered double hydroxide. These compounds have the general formula:

\[
[\text{M(II)}]_{z-} [\text{M(III)}]_z (\text{OH})_2 [\text{A}]_z \cdot m\text{H}_2\text{O},
\]

where M(II) and M(III) are divalent and trivalent cations and A is an anion (e.g., CO\(_3^{2-}\), SO\(_4^{2-}\), OH\(^-\), Cl\(^-\), NO\(_3^-\)). Hydrotalcite is produced where M(II) = Mg\(^{2+}\), M(III) = Al\(^{3+}\) and A = CO\(_3^{2-}\) giving the general formula Mg\(_6\)Al\(_2\)(OH)\(_{16}\)CO\(_3\)4H\(_2\)O. Layered double hydroxides consist of layers of metal cations M\(^{2+}\) and M\(^{3+}\) of similar radii which are randomly distributed in octahedral positions that form brucite-like structures (Figure 3). The brucite-type layers are stacked on top of each other and held together by weak interactions. Substitution of divalent cations by trivalent ones gives rise to positively charged layers and in order to maintain neutrality, the interlayer region is occupied by an adequate number of anions, which are often hydrated (Figure 3). Carbonate is the prevalent anion present during seawater neutralisation and it is not readily exchanged with other anions. However, as pH declines during the neutralisation process, there is a decrease in OH\(^-\) ions, (and therefore CO\(_3^{2-}\) ions), and intercalation of other anions is possible (Palmer et al., 2009).
It is important to note here that although the pH has decreased to 9.5 or below, no H⁺ ions have been added to neutralise alkalinity. The alkalinity in the residue liquor has been neutralised by precipitation of sparingly soluble hydroxides and hydroxycarbonates. The alkalinity associated with the solid phase of the residue (Section 3.2.2) (i.e., sodalite, cancrinite, TCA and hydrogarnet), as well as the hydrotalcite, is still present so that over time, the pH of sea water-neutralised residue will tend to rise as these materials slowly dissolve.

4.2 Composition of neutralised residues

As expected the elemental and mineralogical composition of neutralised residues is similar to that of un-neutralised ones with hematite typically contributing about 60% of the mineral composition (Palmer et al., 2009). However, as already discussed, additional minerals are generated during neutralisation. During seawater neutralisation, Menzies et al. (2004) noted formation of a white precipitate which contained hydrotalcite, aragonite and pyroaurite. Hanahan et al. (2004) noted that the main additional minerals in seawater neutralised residue mud were hydrotalcite, hydrocalumite and p-aluminohydrocalcite.

4.3 Properties of neutralised residues

Depending on the solid to seawater ratio, neutralisation proceeds through two or three buffering stages before reaching a pH of 8.2–9.0 (Hanahan et al., 2004; Menzies et al., 2004). Following seawater neutralisation, residue surfaces have a greater Ca and Mg saturation although exchange sites are still dominated by Na [i.e., Na saturation is about 50%] (Hanahan et al., 2004)]. Thus, sodicity is decreased but there is an increase in salinity (EC) due to accumulation of cations in solution. These originate from those displaced from exchange sites plus those added in the seawater (Hanahan et al., 2004). The CEC remains essentially unaffected by neutralisation (Hanahan et al., 2004; Menzies et al., 2004). Neutralised residues have an increased acid neutralisation capacity due to the presence of large quantities of acid neutralising hydroxycarbonate and hydroxyl-Al minerals (Hanahan et al., 2004; Palmer et al., 2009). The phosphate adsorption capacity of residues is increased after neutralisation due to the anion adsorption capabilities of the
precipitated hydrotalcides (Hanahan et al., 2004; Palmer et al., 2009). These materials remove oxyanions from solution through a combination of intercalation and adsorption onto external surfaces (Palmer et al., 2009).

Whether seawater neutralisation significantly changes the physical properties of residue mud after deposition in the RDA is yet to be determined. Certainly, Rai et al. (2013) showed that in the laboratory, neutralised residue mud filtered twice as fast as un-neutralised mud and while the latter produced a reddish, turbid filtrate, that from neutralised mud was clear and devoid of colour. This was attributed to the fact that, as discussed previously, mud particles (< 5 µm dia.) flocculate into larger agglomerates (80–400 µm dia.) during seawater neutralisation (Hanahan et al., 2004). Visual observations suggest that the seawater neutralised mud still tends to form a compact, solid mass within the RDA.

5 Revegetation

Since as yet, there are no reports of revegetation of seawater neutralised bauxite residue, the appropriate amendments need to be deduced from the research literature on revegetation of un-neutralised residues plus the known physicochemical properties of the neutralised material. Apart from a lower pH, and the presence of some secondary minerals precipitated during neutralisation, seawater neutralised residue has a very similar composition to un-neutralised residue. The same limitations to plant growth are therefore likely to be operative apart from, perhaps, severe alkalinity.

There are a number of alternative strategies for revegetation of bauxite residues. The conventional remediation technique was capping in which a cap of soil from 20–200 cm deep was placed over the RDA (Wehr et al., 2005, 2006). A shallow cap can support grasses and herbs whilst deeper caps may support trees and shrubs (Mendez and Maier, 2008). Often, a capillary break needs to be installed to prevent upward capillary rise of dissolved alkaline salts which then limits plant growth (Wehr et al., 2006). Because of the need for large amounts of soil and the fact that phytotoxic conditions in the residue below are not conducive to plant root growth, there is an increasing trend towards amending the residue and then seeding/planting directly into it.

Where the alumina refinery produces a substantial portion of residue sand, this can be separated and used to cap the residue mud (Eastham et al., 2006; Cooling, 2007). This means revegetation is into a less alkaline material with better physical properties than the mud. This technique is carried out successfully by Alcoa in West Australia as part of their dry stacking procedure (Cooling, 2007). Another option, where less residue sand is available, is to mix sand into the surface of the RDA to about 15 cm at a rate of about 25% (Courtney and Timpson, 2004, 2005; Courtney et al., 2009) thus improving physical conditions, at least in the surface horizon. The least desirable option is to revegetate directly into a well-drained residue mud profile. In any of the cases, other than capping with soil, the plants are seeded/planted into saline/sodic bauxite residue which normally needs additional amendments to make it a suitable growth medium. In addition, plant species need to be chosen carefully based on their tolerance to saline/sodic conditions.
5.1 Field neutralisation

For un-neutralised residue, application of gypsum (CaSO₄·2H₂O) at 1%–10% w/w is commonly practiced (Jones and Haynes, 2011; Rai et al., 2011). The added Ca promotes precipitation soluble alkalinity (HCO₃⁻/CO₃²⁻) as CaCO₃ resulting in a decrease in residue pH (Barrow, 1982; Jones et al., 2012a). Added Ca²⁺ also displaces Na⁺ from exchange sites thus promoting leaching of Na⁺ with the added SO₄²⁻ as a counterion. Even with added gypsum, the leaching of Na out of the surface horizons can be slow and it can take months or even years before the medium is suitable for plant establishment and growth (Wong and Ho, 1993; Gherardi and Rengel, 2003). Following leaching, the ESP is typically reduced from 60%–90% down to about 2%–10% while pH is reduced from 10–12 down 8.0–9.0 (Wong and Ho, 1993, 1994b; Courtney et al., 2003; Jppolito et al., 2005; Xenidis et al., 2005). Since seawater neutralised residue typically has a pH around 8.5–9.5, it has been suggested by some that field neutralisation will not be required. However, as already noted, seawater neutralised residues have an ESP of about 50% (Hanahan et al., 2004; Kopittke et al., 2004b) while values of above 15% are usually considered sodic and potentially plant growth-limiting. Thus, displacement of exchangeable Na⁺ by added Ca²⁺ and other exchangeable bases (e.g., Mg²⁺ and K⁺) would seem necessary.

In addition, field experience suggests that the pH of seawater neutralised residues tends to rise up to values of around 9.5–10.0 or above over the ensuing years after its deposition in an RDA. Indeed, a slow release of Na⁺ and OH⁻ from residues is well documented due to the presence of DSP an in bauxite residues (Barrow, 1982; Wehr et al., 2006; Wong and Ho, 1995). As noted previously, Na in the cage-like structure of sodalite is slowly released through slow dissolution of sodalite and/or displacement by other monovalent cations such as K⁺. Other compounds which will contribute to residual alkalinity in residues include tricalcium aluminate and hydrogarnet. In addition, in seawater neutralised residues the newly precipitated Ca and Mg hydroxides and hydroxycarbonates represent another source of solid phase alkalinity that can potentially re-dissolve. Residual gypsum present in the residue may therefore be important since it will continue to dissolve releasing Ca²⁺, which helps neutralise this newly solubilised alkalinity as well as diapling released Na⁺ and promoting its leaching.

Thus, it seems likely that gypsum applications will be beneficial for revegetation of seawater neutralised bauxite residue. In all probability, lower rates of application than those commonly used for un-neutralised residue will be sufficient since partial neutralisation has already been achieved prior to deposition in the RDA. Added organic residues can have a similar neutralising effect to gypsum (see below) so that where they are incorporated into surface layers, their effect may be sufficient to render gypsum applications unnecessary.

5.2 Nutrient additions

Fertiliser nutrient additions are required for revegetation because bauxite residues have a very low nutrient content. Rates used are generally high in the order of 250–270 kg N, 97–300 kg K, 200–300 kg P, 6–10 kg Ca, 30 kg Mg, 6–15 kg Mn, 6–16 kg Mg, 0.2–0.25 kg Mo and 1.0–1.5 kg B•ha⁻¹ (Eastham and Morald, 2006; Meecham and Bell, 1977b). The application of P is typically high because of the high P fixation capacity of residue (due to its high content of Fe and Al oxides (Snars et al., 2004; Rai et al., 2011).
Rates will need to be high in seawater neutralised mud since, as noted by Palmer et al. (2009), the neutralisation process increases P fixation capacity.

The form of fertiliser nutrients applied may be important, particularly in the case of N. The high pH of bauxite residues favours NH₃ volatilisation losses when NH₄⁻ containing fertilisers are surface applied. In laboratory studies, Chen et al. (2010) measured very large losses of NH₃ (up to 95% of that added) when diammonium phosphate was applied to an un-neutralised residue sand (pH 11.6). The use of urea fertiliser should be avoided since when urea hydrolyses to form NH₄⁺, the pH around granules is further elevated (Sommer et al., 2004). Ammonium may also accumulate in residues due to the lack of autotrophic nitrifier bacteria (Meecham and Bell, 1977b) and high concentrations of NH₄⁺ can be phytotoxic. Where ammonium-containing or forming fertilisers are used they need to be incorporated below the surface to avoid NH₃ volatilisation losses. Fertiliser NO₃⁻ is an alternative that can be used. However, NO₃⁻ is highly mobile and could readily leach during periods of heavy rain. The use of controlled release fertilisers that release their nutrients (including NO₃⁻) slowly over a period of months or years (Shaviv and Mikkelsen, 1993) is probably the most practicable solution during revegetation of residues.

Use of such slow release materials is an important consideration otherwise there will be a need to apply regular side-dressings. Indeed, after five to ten years of revegetation, Courtney et al. (2009) observed nutrient deficiencies in plants growing in residue mud and stressed the importance of regular fertiliser applications. It would be desirable to practice regular soil and plant tissue analysis so that fertiliser nutrient rates could be altered based on the results obtained.

5.3 Organic matter additions

Organic matter performs many important functions in soils. These include

a increasing water retention capacity
b forming a stable soil structure
c increasing CEC
d supplying available nutrients (N, P, S) through mineralisation
d providing a source of nutrients and energy for soil microorganisms and many soil fauna (Stevenson, 1994).

Since the organic matter content of bauxite residue is extremely low, additions of organic matter are likely to be extremely beneficial for revegetation.

Thus, as expected, additions of manures, biosolids, composts and other organic wastes have been shown to greatly improve plant growth in bauxite residues (Fuller et al., 1982; Fuller and Richardson, 1986; Xenidis et al., 2005; Courtney et al., 2009; Jones et al., 2012a, 2012b). The positive effects of these materials are at least partially due to increased macronutrient supply (N, P, K, Ca and Mg). Often there is also a decrease in pH, soluble and exchangeable Na and ESP (Wong and Ho, 1991, 1994b; Courtney at al., 2003, 2009). Acidification occurs because the organic materials normally have a lower pH than the residue and a high buffering capacity. The reductions in soluble and exchangeable Na and ESP are mainly attributable to additions of Ca, Mg and K in the
manure which displace Na from exchange sites and this Na is subsequently leached. The increased CEC (and the additions of Ca, Mg and K) caused by organic matter additions also tends to lower the measured ESP (Jones et al., 2012a).

The addition of organic matter to the surface layers of bauxite residue will provide substrate for microbial activity. Indeed, bauxite residue is effectively a heat- and chemically-treated sterile inorganic material with an extremely low organic matter content. As a result soil microbial activity in the recently deposited material is low (Jones et al., 2010, 2011; Banning et al., 2011). Thus, the addition of organic manures, wastes and composts to bauxite residues causes a massive increase in the size and activity of the soil microbial biomass (Jones et al., 2010, 2011, 2012b). The microbial community (in association with soil fauna) carries out key functions including

a  synthesis and degradation of humic material
b  mineralisation of N, S and P
c  formation and stabilisation of soil aggregates.

The development of a functioning below-ground ecosystem is essential for a sustainable above-ground ecosystem (Harris, 2003; Wardle and Peltzer, 2007) so that organic matter additions are a key consideration.

Organic matter additions also have extremely important effects on soil physical properties including increasing porosity and hydraulic conductivity and decreasing bulk density (Jones et al., 2010, 2011). In soils, linkage (with the aid of polyvalent cations) between mineral components (mainly secondary clay minerals) and humic material results in the formation of microaggregates (< 250 µm dia.) (Edwards and Brenner, 1967) and these are then linked together to form macroaggregates (>250 µm dia.) by fungal hyphae, plant roots and other binding agents (Haynes and Beare, 1996; Bronick and Lal, 2005). Thus, addition of organic materials to residue mud is likely to initiate microaggregate formation through linkage of humified material to the Fe oxide surfaces of the residue mud. As noted above, flocculation of mud particles into larger agglomerates has been recorded during seawater neutralisation but how such processes would interact with organic matter-mineral particle-generated microaggregation has yet to be determined. Microbial activity, associated with the organic matter, along with root growth from planted vegetation is then likely to initiate macroaggregate formation. Thus, addition of organic matter to residues has been shown to increase macroporosity and stabilise structure (Wong and Ho, 1991; Jones et al., 2011). Large pores (macropores, > 30 µm) between macroaggregates can drain freely and are normally air-filled. They allow for gaseous exchange with the atmosphere, for percolation and drainage of water after heavy rainfall and growth of plant roots. Since the lack of macroporosity in fine-textured residue mud is a major constraint to plant growth, the effect of organic matter additions in generating aggregation is an important aspect that deserves future study.

Where solidification of residue mud is a problem, additions of organics (e.g., green manures) to the crushed surface mass can prevent re-solidification and create a more porous and stable topsoil structure (Harris and Rengasamy, 2004; Harris, 2009). In addition, an active soil microbial community helps in acidification of the residue. That is, CO₂ is produced by microbial respiration reacts with water to produce an acidic solution of carbonic acid which can then leach down the profile.
From the above discussion, it is evident that there are a multitude of benefits from adding organic amendments other than nutrient supply. Thus, Bell et al. (2003) demonstrated that fertiliser alone was a poor substitute for organic amendments when rehabilitating bauxite residues. A combination of organic amendments and inorganic fertilisers is likely to give best results (Bell et al., 2003; Jones and Haynes, 2011).

5.4 Introduction of soil biota

Colonisation of newly exposed parent material by soil microorganisms is rapid (Haynes, 2014). The major dispersal mechanism is aeolian transport of bacterial cells and fungal spores (e.g., in dust storms) although movement in water and by biological vectors can also be important. Microbial growth and activity is initially limited by low C and N availability so that during the initial stages of community assembly, heterotrophic microflora exist predominantly in resting stages. For example, Banning et al. (2011) found that bacterial and fungal communities developed rapidly on bauxite residues and diversity was similar to that under a coastal sand dune ecosystem after only 0.5 years of rehabilitation. Nevertheless, the size of the microbial biomass was very much smaller in the bauxite residue due to the low organic matter accumulation. The most practicable way of increasing microbial activity in residues is to add organic matter.

By contrast to microorganisms, colonisation or new sites by soil fauna is more problematic and slower, particularly for non-winged organisms. Development of an active earthworm community, for example, may take 30–50 years (Haynes, 2014). It has been suggested by a number of workers that inoculation with earthworms is an important strategy for mined land restoration (Snider and Hendrix, 2006; Butt, 2008; Boyer and Wratten, 2010) and earthworms have also been successfully introduced into mine tailings along with organic matter amendments (Jiemin and Wong, 2008; Rutherford and Arocena, 2012). In the case of residue mud, introduction of earthworms along with organic amendments could have a range of beneficial effects, particularly on physical properties including macroporosity. For example, endogeic earthworms live in the top 15 cm of soil and ingest soil with a preference for particulate organic matter. They continually burrow and back-fill some of their burrows and other voids with their casts. They ingest organic residues, humified organic matter and mineral particles, mix them together and egest the mixture as casts. These casts have a higher microbial activity and nutrient content than surrounding soil and they can become stable macroaggregates (Tolman et al., 1995; Laossi et al., 2010). In addition, their burrowing activity directly creates macroporosity in the surface horizon (Blanchard et al., 1999). In relation to physical properties, Marashi and Scullion (2004) showed that recolonisation with earthworms was a key factor in development of a macropore system in compacted soils formed after mining and that earthworm inoculation was an effective strategy.

Thus, introduction of earthworms to residue mud (along with organic amendments) could improve physical properties (particularly macroporosity) and plant growth and therefore be an important revegetation strategy. However, prior leaching to remove excess salts and reduce sodicity would be necessary since although the tolerance of earthworms to salinity/sodicity differs between species a high EC can bring about a cessation in reproduction (Owojori and Reinecke, 2009; Owojori et al., 2009) and even death (Guzte et al., 2011). Research on this aspect of revegetation is warranted.
5.5 Appropriate plant species

Selection of appropriate plant species is an extremely important aspect of successful revegetation. The species selected need to be able to tolerate high levels of salinity and sodicity and a high pH and most typically will come from maritime sand dune ecosystems or other systems where saline/sodic soils predominate. Mendez and Maier (2008) suggested successful revegetation of mine tailings involves biomass production comparable to uncontaminated soil, self-propagation, establishment of native colonisers, long-term survival and accumulation of only trace amounts of heavy metals in shoots. The long-term aspect of revegetation of bauxite residues (e.g., > 10 years) is not well studied since most workers have concentrated on the establishment phase (Wehr et al., 2006; Courtney et al., 2009). More long-term experiments are required.

In the field study of Courtney et al. (2009), residue was seeded with four grass species and two legumes but after 6–9 years, 47 species belonging to 38 genera and 15 families were present. *Holcus lanatus*, *Fescue rubra*, *Agrostis stolonifera*, which were seeded, were the dominant grass species. As well as the originally seeded legumes (*Trifolium repens, T. pratense*) several others were also present including *Lathyrus pratensis*, *Lotus corniculatus*, *Medicago lupulina* and *Vicia sepium*. Since legumes have the ability to fix atmospheric N\textsubscript{2} symbiotically, they have an advantage where the soil N supply is poor. Courtney et al. (2009) noted that in general, the dominant species that invade residues are those that have high seed production rates are easily dispersed and have tolerance to both local climate and the potentially damaging soil conditions. Other herbaceous species that have been successfully grown on residues include salt tolerant grasses such as Rhodes grass (*Chloris gayana*), Yorkshire Fog, (*Holcus lanatus*), perennial ryegrass, (*Lolium perenne*) and Wimmera ryegrass, *Lolium rigidum* (Meecham and Bell, 1977b; Bell et al., 1989; Courtney and Timpson, 2004; Eastham et al., 2006) as well as pasture legumes such as red clover *Trifolium pratense* (Courtney and Timpson, 2005; Courtney et al., 2003).

In many situations it may be desirable to revegetate with plants from a native woody shrub ecosystem so that the RDA blends back into its natural environment. Bell et al. (1993) screened 29 native Australian woody plants which grow naturally in saline conditions and found survival and growth in bauxite residue under field conditions was predicted by their short-term response under glasshouse conditions. Species which survived well included *Melaleuca nesophila*, *Tamarix aphylla*, *Eucalyptus loxophleba*, *Acacia saligna*, *E. gracilis*, *E. Conferruminata*, *E. tetragona* and *E. platypus*.

6 Discussion and conclusions

6.1 General considerations

Bauxite residue is an alkaline, saline/sodic material that is stored in large engineered lagoons and impoundments surrounding alumina refineries. The material represents an environmental risk since drainage may contaminate surrounding surface and groundwater and alkaline dust represents a risk to plants and animals. Closure of these areas will normally involve revegetation and the continuing expense of ongoing management of the impoundment and treatment of drainage. There are both chemical (salinity, sodicity and alkalinity) and physical (fine texture, low hydraulic conductivity, poor drainage)
constraints to revegetation of residue mud. While alleviation of soil chemical properties through addition of gypsum and leaching is well documented, amelioration of physical constraints is much less well understood. An important strategy could well be addition of organic matter (biosolids, composts, etc.) and earthworms to the surface horizon resulting in formation of macroaggregates and and macroporosity. This would involve:

- Linkage of organic matter molecules to the Fe oxide surfaces on residue mud resulting in the formation of microaggregates
- Microbial activity (associated with the added organic matter) and plant root growth then generating macroaggregation
- Development of macro pores within inter-aggregate spaces between macroaggregates
- Introduction of soil fauna (e.g., earthworms) which would generate further macroaggregation (through intimate mixing of organic and mineral components) and formation of macroporosity (through burrowing).

Further research is needed on the above topics because establishment and plant growth on residue mud is greatly restricted by physical constraints. Research is required to investigate these aspects since physical constraints to the establishment and growth of plants in residue mud are considerable.

6.2 Seawater neutralised residue

There is an increasing trend towards partial neutralisation of residues before they are deposited in storage areas. Several refineries having proximity to the sea have already installed dedicated seawater neutralisation plants and with the trend towards locating refineries close to deep water ports, there is scope for greatly increased use of this technology. By the addition of Ca and Mg from the seawater, alkaline buffering anions in the residue liquor are neutralised by precipitation of poorly soluble hydroxides (calcite and magnesite) and hydroxycarbonates (e.g., hydrotalcite). As a result, pH is reduced from 10–13 down to about 8.5–9.5.

To date, there are no reports on revegetation of seawater neutralised residue mud. Nevertheless, revegetation is an important component of closure strategies since it not only improves the aesthetic setting and minimises dust but the growing plants continually remove water via transpiration thus reducing drainage. Plant growth-limiting factors are likely to be similar, but less intense, to those for un-neutralised residues and include salinity, sodicity, alkalinity, deficiencies of macro- and micronutrients, lack of macroporosity and consequent waterlogging and solidification.

There are a number of unanswered questions that require future investigation related to the management of RDAs containing salt water neutralised residues. These include:

- To what extent does the initial pH of 8.5–9.5 rise during storage as a result of the presence of a buffering reserve of alkalinity? Unpublished observations have indicated a measureable rise to above 9.5.
- How does an increase in pH with time effect properties of the residue (e.g., alkalinity, sodicity, soluble Al content)?
• Does agglomeration of residue mud particles during seawater neutralisation substantially alter the physical properties of mud after its deposition in the RDA?
• What are the key limiting factors to revegetation in the short and longer-term. To what extent does seawater neutralisation require revegetation strategies developed for non-neutralised residues to be modified and/or changed?
• What are the most effective ameliorative amendments (organic wastes, gypsum, fertilisers) and how should they be applied and managed?

With large volumes of seawater neutralised residues now being produced, and prospects for much greater volumes in the future, it is important that these questions are answered promptly.

References


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Formulation, properties and revegetation prospects


