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AMIRA P1038: Bauxite residue *in situ*
modification project

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It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the state of a residue particle.

- adapted from Heisenberg's Uncertainty Principle

EXECUTIVE SUMMARY

The future management of bauxite residue is of increasing environmental concern. The aim of this literature review is to identify, on the basis of the open (public) literature, possible ways in which the “*in situ*” remediation of bauxite residues might be undertaken and in particular to define specific objectives for the industry in the context of the most promising research pathways. This review was conducted under CSIRO Consulting Services Agreement # 2009124224 (December 2009). The focus is on lessening the potential for environmental impacts over the long term with the primary approach the potential for biological activity to enhance any natural remediation and the limitations imposed by pH, solid alkalinity and sodicity. Whilst it was anticipated that this might be compared (for example) to natural (rainfall) leaching as a base case for long-term remediation, insufficient public domain information exists to assess the long-term impact of continuing current management practices for the generic bauxite residue disposal area (BRDA). Any such “natural” remediation would be very dependent on actual BRDA design and local climate and environment. The idea of practical leaching of the deposit (with different reagents) to either, modify the nature of entrained alkalinity or modify the leaching characteristics of the residue, is at the opposite technological end to rainfall remediation and is equally absent as a concept in the open literature. This review has thereby focused on the key deliverables to the contract:

- Physical and chemical characteristics of residue that mitigate against its remediation and rehabilitation.
- Knowledge gaps around these physical and chemical characteristics.
- Identifying existing technologies/fields that could assist in the *in situ* remediation of bauxite residue.
- Collation of the available fundamental chemical and physical parameters that may be relevant to *in situ* residue remediation.
- Through the knowledge gaps and physical/chemical barriers to remediation, indicate what research may be required as a next step.

The key to properly understanding or developing strategies for remediation is to first define the rehabilitation goals for minimal long-term environmental impact. Herein we have defined criteria that support eco-system development. Specifically residue characteristics of stable residue solution such that; pH of 5.5-9.0, sodium adsorption ratio (SAR) of ≤ 7 , exchangeable sodium percentage (ESP) of ≤ 9.5 , residual sodium carbonate (RSC) of ≤ 1.25 , electrical conductivity (EC) of < 4 mS/cm. Concomitant is a requirement that Na, Al, and heavy and trace metal content in the residue solution is below toxic threshold levels to plants and microbes as described by the Australian and New Zealand Environment and Conservation Council (ANZECC). There is also a specific physical requirement of a bulk density of ≤ 1.6 . An additional critical requirement is the provision of adequate macro- (N, P, K, Ca, Mg) and micronutrients (Cu, Zn, Mn, Fe, B) consistent with the requirements of the eco-system and its development stage. How best to approach the problem to transform the residue to an eco-supporting medium?

The most promising pathway for *in situ* rehabilitation would appear to be bioremediation based on strategies developed for saline-sodic soil, i.e. using halophyte plants to effectively farm sodium from the system. On bauxite residue

surfaces the advantages and similarities should closely parallel saline-sodic agricultural soils. Halophytes provide great potential to accomplish some of the rehabilitation goals indicated above. Foremost is that they can directly reduce Na content in solution (SAR) and on the bauxite residue solids (ESP) independent of drainage. Applied gypsum can further displace Na^+ from the residue exchange complex and in conjunction with other divalent cation strategies control pH within halophyte tolerance. Both halophyte produced organic acids and halophyte promoted microbial populations provide H^+ and increase the partial pressure of CO_2 in the rooting zones to further the rehabilitation process. Drainage strategies, along with other additions (organic waste, sewage sludge, macro and micro-nutrients) will also assist the outcome. Whilst this approach would not be envisaged to be either capital or operating intensive, it is not a "quick-fix". Bio-remediation is a process that would require multiple seasons, but well within the typical lifetime of a refinery operation.

To successfully implement this approach requires an improved understanding of both the abiotic and biotic aspects of the problem, especially as the halophyte farming would be progressing into such an extreme environment. Those practical studies to date, on simpler re-vegetation systems for residues, appear to have been designed with a limited understanding of the residue chemistry and lacking detailed information on individual plant responses and tolerances. Research design should commence with more rigorous plant, fungi and microbe selection in conjunction with residue chemistry. Attempting actual BRDA trials in the absence of this type of information would seriously impede ultimate progress. The knowledge gaps and suggested research requirements are tabulated in the report.

The report has been prepared for AMIRA International on behalf of five sponsoring companies (Alcoa World Alumina, BHP-Billiton, Hydro Aluminium, Rio Tinto Alcan and UC Rusal) and approval has been given for distribution to the members of the International Aluminium Institute (IAI), notwithstanding that under the terms of the CSA Agreement CSIRO retains full copyright. Any distribution of this report or its contents must include the original authorship and copyright statements. Extraction of components is permissible provided that the authorship is clearly acknowledged. Please refer to the original CSA Agreement with AMIRA International Limited.

1. REHABILITATION GOALS

In this report, *in situ* rehabilitation is taken to define a final outcome in which bauxite residues, in an impoundment situation, exist in an improved state compared to their original state. This is a narrow interpretation of the concept of rehabilitation, which would be a complete restoration to a previous condition, i.e. to have the same impact as the unmined bauxite (which is not possible). The act of remediation defines the pathway by which the required improved state is accomplished. This is an important distinction, i.e. rehabilitation is not equal to remediation. The interplay between rehabilitation as a final outcome and the remedial pathway assumes that the current state of the bauxite residue is deficient (poses a negative environmental impact) and a correction is required to remove any identified deficiencies or faults via an act of remediation. In the physical and chemical description in this report (Section 2), these deficiencies are defined in the context of the rehabilitation goals. The rehabilitation goals for bauxite residues are to *achieve and sustain* the following five principal characteristics (chemical and physical) in order to support the development of ecosystems on closed-down bauxite residue disposal areas:

1. Stable residue solution pH below 9.0 and above 5.5 (Tisdale et al., 1993).
2. Sodium adsorption ratio (SAR) of 7 or less (ESP of 9.5 or less), and a residual sodium carbonate (RSC) value of 1.25 or less (McBride, 1994).
3. Electrical conductivity of $< 4 \text{ mS/cm}^1$ (McBride, 1994).
4. Na, Al, and heavy and trace metal content in the residue solution below toxic threshold levels to plants and microbes and in part described by the ANZECC guidelines (Australian and New Zealand Environment and Conservation Council, 2000).
5. Bulk density² of less than or equal to 1.6 (Fredlund and Rahardjo, 1993).

In addition to these five primary goals, the provisions of adequate macro- (N, P, K, Ca, Mg) and micronutrients (Cu, Zn, Mn, Fe, B) consistent with the requirements of the specific plant type and development stage are essential. Whilst critical, the nutrient issue is not included in the set of five primary goals as it is species dependent. Table 1 illustrates a qualitative relationship matrix of the key factors that need to be considered for residue rehabilitation.

¹ Conductivity of Siemens per unit length. By comparison sea water (for example) with an SI conductivity of 4.8 S/m has a cgs value of 48 mS/cm or $4.8 \times 10^4 \mu\text{S/cm}$ or "EC units", i.e. 48,000 EC units.

² This arises from a critical limit for root growth and inter-relates with both void ratio and hydraulic conductivity. As is noted in section 2.1.4 the bulk density limit does have a dependence upon particle size distribution.

Table 1. Interaction of the residue solution and solids properties and how they impact on the residue's ability to support living organisms. Top-left quadrant summarizes the chemical matrix. Response arrows indicate an increase (↑) or a decrease (↓) for a property based on the increase of the chemical value in the dark grey cells. Measure of qualitative impact given by the number of arrows.

Solution → Solids ↓		High pH		Residual Sodium Carbonate, TDS, Sodium...		... Adsorption Ratio		Effects on residue physical properties			
		OH ⁻	Al(OH) ₃ / CO ₃ ²⁻	Al(OH) ₃ / CO ₃ ²⁻	Na	K, NH ₄ ⁺ / Ca ²⁺ , Mg ²⁺	Impact	Bulk Density	Porosity	Permeability or HC	
Acid neutralising capacity	OH ⁻	pH	pH buffering	Surface charge	Mineralization / solubility						
	Al(OH) ₃ / CO ₃ ²⁻	pH buffering	Alkalinity	Sodic alkalinity	Base saturation						
Exchangeable Sodium Percentage	Na	Surface charge	Sodic alkalinity	Sodicity vs.	Base saturation						
	K, NH ₄ ⁺ / Ca ²⁺ , Mg ²⁺	Mineralization/ solubility	Base saturation		CEC/ Fertility						
Effects on residue bio-support properties	Floral & microbial toxicity	↑↑	↑↑↑	↑↑↑	↓↓↓						
	Water potential	↓↓	↓↓↓	↓↓↓							
	EC	↑	↑	↑	↑						
	Root penetration	↓	↓	↓	↓						

A plethora of research supports the importance of all five factors for sustainable plant growth (e.g., Tisdale et al., 1993; Doran et al., 1994; McBride, 1994), and these should not be considered as issues for either debate or negotiation. If and when met, residues whose characteristics are consistent with these five goals will be able to support plants and microbes, which will mark a significant improvement to the current abiotic, barren, and erosion-susceptible states of bauxite residue surfaces. The rehabilitated physical and chemical qualities of the residues and the solutions in contact with them will markedly improve the residues' micro-, meso- and macro-structural properties thus improving hydraulic conductivity, and providing a basis to remove Na-based salts from the residues on an ongoing basis. The remediated chemical qualities of the residue will furthermore diminish the potential for adverse effects on the integrity of the sealants of the bauxite residue disposal area (as far as present) thus minimizing the potential of leaking remaining sodic-alkaline plumes potentially loaded with other hazardous chemicals.

Discussion is warranted with regards to the most effective remedial pathways. The complexity of rehabilitating bauxite residues is due to the inter-dependence of the five principal characteristics; they cannot be considered in isolation. Furthermore, imbedded in the condition of sustainability is the time dependence of maintaining the five conditions. Because of the sheer volume of bauxite residues, imparting a buffering capacity against the recurrence of the current physical and chemical conditions (alkaline pH, high Na, Al, CO_3^{2-} contents, cementation, low permeability, etc.) should be seen as one of the key remediation outcomes. Principally, it requires that either an equal amount of counter-active substance (e.g., a source of H^+) is provided from the start or that these counter-active substances are provided over time in response to the stimulus arising from the chemical gradients trying to achieve homeostasis (akin to a titration with fixed endpoint).

Throughout this review we have chosen to default to the units, concepts and definitions commonly in use for soil science. A glossary of commonly used terms is provided at the end of the document with sources of definitions cited.

2. CHEMICAL AND PHYSICAL CHARACTERISTICS OF BAUXITE RESIDUES

Bauxite residues are the slurry by-products generated from the treatment of bauxite in concentrated NaOH under elevated temperatures and pressure, following, in principle, the Bayer process to produce alumina. Despite washing the solid remnants in counter-current decantation washer trains, bauxite residues remain strongly sodic-alkaline at the time of their disposal into purpose-built tailings ponds (bauxite residue disposal areas, BRDAs) independent of the disposal method (e.g., dry-stacking vs. lagooning). Although the Na-dominated solution liquor typically has an average electrical conductivity of 7.4 ± 6.0 mS/cm (range: 1.4-28.4 mS/cm, Table 2), this is lower than expected based on total dissolved solids (TDS). In untreated residues, the counterions are primarily composed of CO_3^{2-} and associated OH^- , which have a lower actual conductance. As the slurries dry a structureless, massive, and highly compacted bauxite residue stack ($\text{BD} = 2.5 \pm 0.7$, Table 2) develops, which, at its surface will form an evaporation crust with a light-colored, evanescent salt layer (Klauber et al., 2008).

Table 2. Selected chemical and physical characteristics of untreated bauxite residues.

	average	std ¹	max	min	n ²	target
pH	11.3	1.0	12.8	9.7	44	5.6-8.9
EC, mS/cm	7.4	6.0	28.4	1.4	46	4
[Na ⁺]	101.4	81.6	225.8	8.9	9	See SAR
SAR	307.2	233.1	673	31.5	10	< 7
ESP	68.9	19.6	91	32.1	10	< 9.5
ANC (pH=7.0)	0.94	0.3	1.64	0.68	13	n/a
ANC (pH=5.5)	4.56	-	-	-	1	n/a
PZC	6.9	1.0	8.25	5.1	11	n/a
BD	2.5	0.7	3.5	1.6	13	≤ 1.6
SSA	32.7	12.2	58.0	15.0	30	n/a

void ratio (e)

¹ std = standard deviation of the population (n)

² n = population size from which the average and std were calculated.

[Na⁺] = concentration of Na⁺ in solution expressed as mmol of charge per liter (mmol_c L⁻¹)

SAR = sodium adsorption ratio: $[\text{mmol Na L}^{-1}] / [(\text{mmol Ca}^{2+} \text{ L}^{-1} + \text{mmol Mg}^{2+} \text{ L}^{-1})^{1/2}]$

ESP = exchangeable sodium percentage: $\text{ESP} / (\text{ESP} + 100) = 0.015 \text{ SAR}$

ANC (pH=7.0) is acid neutralisation capacity normalised to the weight of the residue to a pH endpoint of 7.0 using a strong acid

ANC (pH=5.5) is acid neutralisation capacity normalised to the weight of the residue to a pH endpoint of 5.5 using a strong acid. Only one study is quoted in this table. Additional studies are discussed in text where the ANC (pH=5.5) was estimated from graphs.

PZC = point of zero charge. Measurements include bauxite residues with and without flocculant addition.

BD = dry density of the solids, referred to as the bulk density (Fredlund and Rahardjo, 1993).

SSA = specific surface area with units of m² g⁻¹.

Trace metals can be of concern and may exceed regulatory levels in certain circumstances (Goldstein and Reimers, 1999; Kutile et al., 2004). Some bauxite residues may emit ionizing radiation above natural background rates due to the presence of naturally occurring radioactive materials (NORMs): ^{238}U and/or ^{232}Th and members of their decay chains (Bardossy and Aleva, 1990; Pinnock, 1991; von Philipsborn and Kuhnast, 1992; Wong and Ho, 1993; McPharlin et al., 1994; Cooper et al., 1995; Somlai et al., 2008).

The physical and chemical characteristics of the residues make re-vegetation particularly challenging, and established floras are difficult to sustain without amendments (Meecham and Bell, 1977a; Meecham and Bell, 1977b; Wong and Ho, 1991; Wong and Ho, 1992; Wong and Ho, 1993; Wong and HO, 1994; Wong and Ho, 1994; Wehr et al., 2006; Woodard et al., 2008). Bulk densities commonly encountered in bauxite residues of fine silty to heavy clay textures do not permit root penetration. In addition, the high salt content that rapidly re-dissolves upon wetting the residues lowers the matric potential of the residue pore water substantially and causes adverse osmotic potentials across both microbe and plant root membranes, effectively negating the possibility of water and (thus) nutrient uptake.

2.1 Basic Mineralogy and Chemical Composition of Bauxite Residues

Bauxite residues are solid-solution mixtures ranging in solids content from 20 to 80 wt % depending on the disposal method. The elemental abundance in bauxite residues is typically $\text{Fe} > \text{Si} \sim \text{Ti} > \text{Al} > \text{Ca} > \text{Na}$ (see Table 3). Bauxite residues consist on average of approximately 70% (by weight) crystalline phases and 30% amorphous materials (Gräfe et al., (2009), and references therein). Hematite is ubiquitous (7 – 29 wt%), whereas goethite is abundant in bauxite residues generated from Jamaican and Darling Range bauxites which contain significant amounts of goethite in the original ores (Li and Rutherford, 1996; Li, 1998). Magnetite (Fe_3O_4) is a transformation product that occurs in bauxite residues generated from bauxites sintered with soda to solubilise boehmite or diaspore. Boehmite ($\gamma\text{-AlOOH}$), gibbsite ($\text{Al}(\text{OH})_3$), anatase, rutile (both TiO_2), ilmenite (FeTiO_3), perovskite (CaTiO_3) and quartz (SiO_2) are the other minerals commonly present in bauxite residues.

Table 3. Elemental and mineralogical composition of bauxite residues. Points of zero charge were taken from Stumm (1992), Hanawa et al., (1998), Hu et al., (2003) and Sparks (2003). Bayer process characteristic solids (BPCSs) are identified by bold lettering.

Element (n ¹)	content			Minerals	Unit cell formula	PZC ²
	Min	avg±std ³	max			
Fe ₂ O ₃ (63)	6.8	40.9±15.6	71.9	Hematite	α -Fe ₂ O ₃	8.7-9.8
				Goethite	α -FeOOH	7.5-85
				Magnetite	Fe ₃ O ₄	6.8
Al ₂ O ₃ (62)	2.12	16.3±6.4	33.1	Boehmite	γ -AlOOH	8.2
				Gibbsite	γ -Al(OH) ₃	5.0
				Diaspore	α -AlOOH	6.4
				Sodalite	Na ₆ [Al ₆ Si ₆ O ₂₄]·[2NaOH, Na ₂ SO ₄] ⁴	n/d ⁶
SiO ₂ (63)	0.6	9.6±6.7	23.8	Cancrinite	Na ₆ [Al ₆ Si ₆ O ₂₄]·2[CaCO ₃]·0[H ₂ O] ⁵	n/d
				Quartz	SiO ₂	< 2.0
				Other	illite, muscovite	
				Rutile	TiO ₂	4.6
TiO ₂ (61)	2.5	8.8±4.4	22.6	Anatase	TiO ₂	5.9-6.3
				Ilmenite	Fe ^{II} Ti ^{IV} O ₃	n/d
				Perovskite	CaTi ^{IV} O ₃	8.1
				Calcite	CaCO ₃	8.3
				Perovskite	CaTi ^{IV} O ₃	8.1
				Whewellite	CaC ₂ O ₄ ⁷	n/d
CaO (76)	0.6	8.6±9.4	47.2	TCA	Ca ₃ Al ₂ (OH) ^{12, 8}	n/d
				hydro-calumite	Ca ₄ Al ₂ (OH) ₁₂ ·CO ₃ ·6H ₂ O ⁸	n/d
				Sodalite	Na ₆ [Al ₆ Si ₆ O ₂₄]·[2NaOH, Na ₂ SO ₄] ⁴	n/d
Na ₂ O (78)	0.1	4.5±3.3	12.4	Cancrinite	Na ₆ [Al ₆ Si ₆ O ₂₄]·2[CaCO ₃]·0[H ₂ O] ⁵	n/d
				Dawsonite	NaAl(OH) ₂ ·CO ₃	n/d
LOI (46)	4.4	10.0±2.8	21.1			

¹ n = number of samples

² PZC = point of zero charge of the corresponding mineral. n/a = not applicable, n/d = not determined.

³ avg±std = average ± standard deviation of the population.

⁴ Sodalite has between 0 and 6 waters of hydration (Whittington, 1996; Whittington et al., 1998).

⁵ Cancrinite has 0 to 2 waters of hydration depending on the ions in the cage (Whittington, 1996): 0 for 2CaCO₃, 1 for 2NaOH, and 2 for Na₂SO₄.

⁶ possibly similar to that of feldspar, ~ 2-2.4 or zeolites

⁷ calcium oxalate.

⁸ see Vieillard and Rassinoux, (1992).

The Bayer process transforms soluble phyllosilicate and tectosilicate clay minerals into sodalite, cancrinite, tri-calcium aluminate (katoite and hydrogrossulars), hydrocaluminites, calcite/aragonite and Na-carbonates. These minerals contain primarily Si^{4+} , Al^{3+} , Ca^{2+} , Na^+ , OH^- and CO_3^{2-} . Sodalite is the most common desilication product forming during pre-desilication, while cancrinite forms in the presence of excess SO_4^{2-} , and at elevated digestion temperatures that are required to dissolve boehmitic bauxites. Sodalite concentrations of 16-24% (Castaldi et al., 2008) and up to 50% cancrinite (Garau et al., 2007) have been measured in bauxite residues from Eurallumina, which processes Weipa bauxites. Perovskite (CaTiO_3) and calcite/aragonite (both CaCO_3) are common in bauxite residues in China due to the addition of lime during the Bayer process (Liu et al., 2007). Hydrated Ca-silicates, tri-calcium aluminates and hydrocaluminites form from adding slaked lime during digestion and causticisation. The formation of sodium carbonates (e.g., trona or nahcolite) at the surfaces of residues in the drying areas due to evaporation emphasises that the solution contains a substantial concentration of Na^+ and CO_3^{2-} . Other minor mineral constituents often found in bauxite residues are ilmenite (FeTiO_3) usually because they are contained in the parent ore and are not affected substantially by the digestion conditions. Very significantly, both the chemical and physical properties of deposited residue will depend on the deposition management and aging processes. Figure 1 illustrates a residue profile from field data for a BRDA in Mobile (Alabama) based on the work of Fuller et al., (1982).

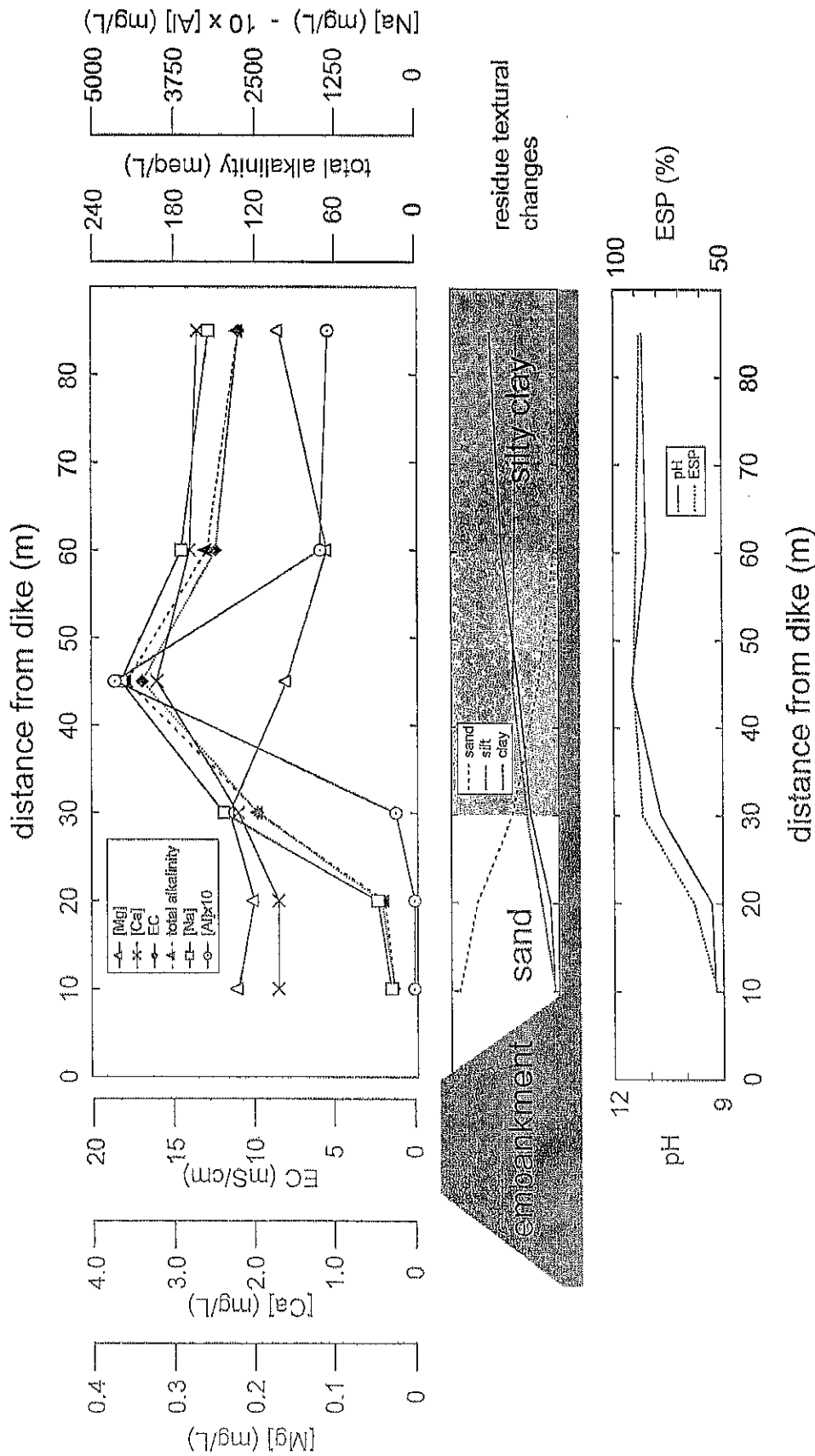


Figure 1. Textural distribution of bauxite residues deposited at the BRDA of the Alcoa Mobile plant (Alabama, USA). The textural class influences the chemical properties of the residues from pH to Na, Ca and Mg and therefore ESP. Figure based on data reported by Fuller et al., (1982)

2.1.1 pH, RSC, SAR & ESP

The pH, the amount of residual sodium carbonate (RSC), the sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) in bauxite residue are all closely related to each other in the context of the Bayer Process inputs (NaOH, Ca(OH)₂) and the mineralogy of the residues (see Table 3). Remnant NaOH and Na₂CO₃ concentration in solution impart an average solution pH of 11.3±1.0 (Table 2). This average value is lower than one might expect, however, this table includes the pH of aged bauxite residues that have experienced at least partial neutralization by atmospheric CO₂ (Liu et al., 2007). Carbonate in solution originates in part due to the diffusion of CO₂(g) into the liquor, but also due to the decomposition of organic matter in bauxite under Bayer process conditions into water, CO₂, and various organics particularly short-chain (low molecular weight) aliphatic dicarboxylates. The RSC is thus a partial evaluation of the alkalinity of the residue solution and is quantified by:

$$\text{RSC} = [\text{HCO}_3^- + \text{CO}_3^{2-}] - [\text{Ca}^{2+} + \text{Mg}^{2+}] \quad [1]$$

where all units are expressed in millimoles of charge (mmol₊) per litre (L⁻¹). In bauxite residue solutions with an average pH of 11.3, the RSC is effectively equal to the CO₃²⁻ concentration as at this pH the contribution to the RSC from HCO₃⁻ is negligible, and any Ca²⁺ or Mg²⁺ will exist as precipitated species (presumably Ca/Mg carbonates). If the Caustic/Soda ratio of last washer underflow can be taken to be approximately as 0.85 with C and S, respectively, measuring 8.5 and 10.0 g Na₂CO₃ per L, then the RSC would be approximately 28 mmol L⁻¹.

Removing the alkaline-sodic components from bauxite residues is complicated by the presence of alkaline solids such as sodalite and/or cancrinite and undissolved Na₂CO₃, among others, which exist in a quasi-equilibrium with the residue solution. Thornber and Binet (1999) sequentially exchanged bauxite residues with H₂O and determined that while the mass of the solids decreased with sequential washings, neither the pH, Na⁺, Al(OH)₄⁻, CO₃²⁻ nor the OH⁻ concentration changed in solution. The buffering properties of the solution with respect to these ions occurred due to the dissolution of alkaline solids such as undissolved Na₂CO₃, alunite, sodalite and/or cancrinite and may be quantified as the acid neutralization capacity (ANC) of the residues. The average ANC (pH 7.0) is 0.94±0.3 mol H⁺ kg⁻¹ residue. Snars et al., (2004) investigated the buffering capacity of an Alcoa supplied desilication product and showed that its ANC (pH 7.0) was about 3 moles H⁺ per kg of DSP. The dissolution behavior and mechanisms of the major ANC contributing mineral phases thus presents an important knowledge base requirement for neutralizing and mitigating against Na⁺, OH⁻, Al(OH)₄⁻, H₃SiO₄⁻/H₂SiO₄²⁻ and CO₃²⁻ in solution. This is particularly true for Na bearing solids such as sodalite and cancrinite as their dissolution would contribute to the sodium adsorption ratio (SAR) of residue solutions and the exchangeable sodium percentage (ESP) of the cation exchange complex.

The SAR is, like pH and the RSC value, a solution parameter (McBride, 1994) but it is dependent on the nature of the solid with which the solution is in contact.

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

SAR values for solutions in contact with untreated bauxite residues have an average value 307.2 ± 233.1 (Table 2).

In contrast to the SAR, the ESP value approximates the composition of the cation exchange sites on the residue surface based on the solution composition of Na, Ca and Mg:

$$\text{ESP} = \frac{1.5 \times \text{SAR}}{(1 + 0.015 \times \text{SAR})} \quad [3]$$

An average ESP value of 68.9 ± 19.6 (Table 2) has been computed for 10 bauxite residues based on residue solution data. At a pH above 9.5, calcium (Ca) and magnesium (Mg) solid phases (primarily as carbonate minerals: calcite, aragonite, dolomite) are sparingly soluble and therefore neither mitigate the SAR or ESP (Gustafsson, 2006).

2.1.2 Electrical Conductivity

Electrical conductivity is related to cation and anion concentrations in solution and therefore to ionic strength (IS). Electrical conductivity is related to total cation and anion concentrations in solution by approximately a factor of 10 provided that the solution is neither highly acidic nor highly alkaline (McBride, 1994):

$$\text{Total cations (mmol}_{(+)} \text{ L}^{-1}) \sim \text{EC (mS cm}^{-1}) * 10 \quad [4]$$

$$\text{Total anions (mmol}_{(-)} \text{ L}^{-1}) \sim \text{EC (mS cm}^{-1}) * 10 \quad [5]$$

In the absence of detailed solution compositional data, electrical conductivity is the most feasible quantity to measure to investigate total cation and anion concentrations and to estimate ionic strength. In natural aqueous solutions, Griffin and Jurinak (1973) determined that:

$$\text{IS} \sim 0.0127 * \text{EC} \quad [6]$$

In addition, the EC is related to the quantity of total dissolved solids (TDS, (McBride, 1994)):

$$\text{TDS (mg L}^{-1}) \sim \text{EC (mS cm}^{-1}) * 640 \quad [7]$$

The ionic strength of a solution is relevant as it determines the double-layer thickness of charged particles and therefore in turn relates to physical behavior such as dispersion and coagulation of particles. In addition, the ionic strength indicates the osmotic potential of a solution, which, as ion concentration in solution increases,

becomes increasingly negative and therefore suppresses the total water potential (or activity). As water will flow from high to low potentials, the electrical conductivity of a saturated residue paste helps to define water quality (e.g. in leaching salts from residues to a specified target value).

It is important to note that equations [4] through [7] will apply when the remediated residue starts to approach target values. Untreated residue is so alkaline that the ionic species are not fully dissociated and the concept of equivalent conductances at infinite dilution has no meaning. In particular, how applicable equations [6] and [7] are for bauxite residues has not been ascertained to date.

In bauxite residues, high EC values are due to high Na^+ concentrations in solution that are replenished from Na-bearing solids. Calcium, magnesium and other cations do not contribute significantly to the EC as their concentrations are negligible in solution at pH above 10. The average electrical conductivity (EC) of bauxite residues in deionized water is $7.4 \pm 6.0 \text{ mS cm}^{-1}$ and ranges from 1.4 to 28.4 mS cm^{-1} (Table 2, (Fuller et al., 1982; Liu et al., 2007)). In amended residues, the EC varies from as low as 0.3 (Castaldi et al., 2008) to as high as 60 mS cm^{-1} (Woodard et al., 2008). Acid neutralised residues tend to have lower EC's, whereas seawater-neutralised residues have higher EC's (Meecham and Bell, 1977a; Snars et al., 2004; Castaldi et al., 2008).

2.1.3 Particle Size Distribution

The particle size distribution of bauxite residues depends on the separation of sand size particles after the alumina extraction step. Menzies et al., (2004), for example, show that red sand from Gove has a particle size distribution between 10 and $>1000 \mu\text{m}$ with more than 50% of the particles being larger than $250 \mu\text{m}$. In contrast, the fine or mud fraction has a particle size range from less than 0.1 to about $100 \mu\text{m}$. Summers et al., (1996) reported sand/silt/clay size distribution of 3.6/65.6/30.8 and 4/85/11 for bauxite residues from Suriname and Pinjarra (WA, Australia), respectively, while Newson et al., (2006) reported a particle size range for bauxite residues from the UK (likely Burntisland, Scotland) between 1 and $300 \mu\text{m}$ with 50% of the particles being larger than $5 \mu\text{m}$. More recently, Snars and Gilkes (2009) reported particle size ranges ($< 2 \mu\text{m}$, $2\text{-}20 \mu\text{m}$ and $> 20 \mu\text{m}$) for bauxite residues from 11 different refineries. On average 31% of the particles were less than $2 \mu\text{m}$, 46% were between 2 and $20 \mu\text{m}$, and 23 % were greater than $20 \mu\text{m}$. Approximately the sand and fine fraction combined bauxite residues would thus have a particle size of 2 to $100 \mu\text{m}$ with a range of 100 nm to $200 \mu\text{m}$ and places it into the range between clay loams to fine sand textural class (Gee and Bauder, 1986). In addition to actual practices at the refinery, Fuller et al. (1982) have shown that the texture of the residues is dependent on the disposal method. The particle size separation with distance from embankment (see Figure 1) suggests that the residues were disposed of as wet slurries in lagoons rather than as thickened pastes discharged for dry-stacking. The chemical characteristics of the residues and their solutions including pH, Ca, Mg and Na content and consequently RSC, SAR and ESP vary with textural class, suggesting that disposal method and aging strongly influence the physicochemical characteristics of the deposited residues.

2.1.4 Bulk Density

The average bulk density of bauxite residues is reported as $2.5 \pm 0.7 \text{ g cm}^{-3}$ (Table 2). The cited literature values are however a problematic comparison as the authors fail to specify under what moisture potentials the bulk densities were measured and consequently any shrink-swell influences on residue volume cannot be quantified. Consequently, the bulk density values range from 1.6 to 3.5 g cm^{-3} , effectively describing the bulk density from a well graded sand-silt-clay sized residue matrix (1.6 g cm^{-3}) all the way to what would be a highly compacted, non-porous material (3.5 g cm^{-3}). As the apparent particle size distribution may be a function of the sampling and disposal methods, the bulk density will vary across a BRDA, with the finer, clay-sized residues settling out further away from the embankment. Chemistry aside, bulk densities exceeding 1.7 g cm^{-3} in the sandy residue zones, 1.55 g cm^{-3} in fine silty zones and 1.4 in clayey (> 45 % clay-sized particle content) zones will impede root penetration and therefore plant establishment.

Nikraz et al., (2007) worked with residues that had a BD of 1.85 prior to treatment, and treatment with CO_2 resulted in a BD of 1.8 g cm^{-3} . Bitterns treated residues had a bulk density of 1.62 g cm^{-3} , a level at which root penetration is potentially possible. The void ratio achieved with bitterns treatment was 2.84, a 44-81% improvement over untreated and CO_2 treated samples (1.57-1.97) and a consequently improved hydraulic conductivity of 0.4 mm h^{-1} , up from $0.1\text{-}0.2 \text{ mm h}^{-1}$ for untreated and CO_2 treated bauxite residues. The increased ability of bitterns treated bauxite residues to conduct and drain water relates to the size and inter-connectivity of the void spaces or pores. Void space is a function of the ability of individual particles to form stable flocs and aggregates, which in turn create (empty) space between aggregates. As indicated above, particle aggregation, flocculation and coagulation is a function of electrical conductivity, but more directly, ionic strength and solution composition (in particular, Na^+ levels in solution) play a critical role. In clay-water mixtures, Na^+ is associated with clay dispersal, poor aggregate structure, cementation and dust formation upon drying at the surface (McBride, 1994; Klauber et al., 2008). Its presence in significant quantities at alkaline pH is a significant inhibitor to the creation of aggregate structure, hydraulic conductivity, and total water potential conducive to plant growth. In addition, the presence of large concentrations of Na^+ elevates the electrical conductivity of the solution beyond tolerable limits for plants.

2.1.5 Trace Metals

The speciation of trace metals in bauxite residues is virtually unexplored (Goldstein and Reimers, 1999) however, public concerns over the presence and potential bioavailability of trace metals are real (Ryle, 2002). Trace metals such as chromium, vanadium and arsenic may build up in residue solutions when supernatant liquor from the residue area and the counter-current decantation washer trains is successively recycled within the plant (Kutle et al., 2004).

As a first step in determining whether trace metals pose a potential (ecological / human) health risk, measurements of elemental concentrations in residue liquors and solids need to be made. In Australia, ANZECC (Australian and New Zealand Environment Conservation Council) and NEPC (National Environment Protection Council) guideline values (see Table 4) can then be used to assess whether the residue

is considered a low risk or a high risk hazardous waste³. However, as total concentrations in solid phases are poor indicators of potential bioavailability, and leach tests (e.g., TCLP or Toxic Characteristic Leach Procedure) are only valid under their operational (and legislative) parameters, solid phase speciation via spectroscopy of trace metals is highly warranted. Changes in the solid phase speciation of potentially toxic trace metals may occur as a result of the remediation process, and this may render post-remediation leach waters more contaminated or transform the solid phase complex of a specific metal to be more soluble, i.e., more bioavailable to plants and microbes. Understanding the chemical dynamics of potentially toxic trace metals in bauxite residues provides validation whether the quality of the rehabilitated bauxite residue is truly improved. Due to the refinery specific operational parameters and the (often unique) origin of the bauxite ore, these assessment tests need to be conducted on a per-refinery/ per-bauxite residue basis. These also help in defining whether micro-nutrients⁴ (e.g., Cu, Zn) and toxic metals/ metalloids (e.g., As) are potential health risk factors during remediation and in the rehabilitated state.

³ At present the practical hazardous waste classification for residue relates more narrowly to its alkalinity rather than trace metal composition or availability.

⁴ A micro-nutrient applied in excess to tolerance limits of micro-organisms and plants is toxic Tisdale, S. L., Nelson, W. L., Beaton, J. D. & Havlin, J. L. (Eds.) (1993) *Soil Fertility and Fertilizers*, New York, Macmillan Publishing Co.,

Table 4. Guidelines on the investigation levels for soils, drinking water, water for recreational purposes and irrigation.

Metal/Metalloid	SIL Parks (mg/kg)	SIL Industrial Sites (mg/kg)	WA Class IVA		QLD Industrial Refuse (lined) (mg/L)	DW (mg/L)	WRP (µg/L)	Irrigation Water	
			STC (mg/kg)	LCC (mg/L)				Plants (mg/L)	Livestock (mg/L)
Aluminium	n/d	n/d	n/d	n/d	n/d	n/d	200	5.0	5.0
Arsenic	200	500	3000	7	0.007	5.0	50	0.1	0.5
Beryllium	40	100	n/d	n/d	n/d	n/d		0.1	0.1
Cadmium	40	100	500	2	0.002	0.5	50	0.01	0.01
Chromium (III)	24%	60%	2500	50	n/d	5.0	50	1.0 (total Cr)	n/d
Chromium (VI)	200	500	(total Cr)		0.05	(total Cr)		0.1	1.0
Cobalt	200	500	5000		n/d	5.0		0.05	1.0
Copper	2000	5000	10000	2000	n/d	100	1000	0.2	0.5
Lead	600	1500	30000	10	0.01	5	50	0.2	0.1
Manganese	3000	7500	n/d	n/d	0.5	n/d	100	2.0	n/d
Methyl Mercury	20	50	200	1.0	0.001	0.1	1.0	0.002	0.002
Inorganic Mercury	30	75	(total Hg)	(total Hg)	0.001	(total Hg)	(total Hg)	(total Hg)	(total Hg)
Nickel	600	3000	10000	20	0.02	5	100	0.02	1.0
Sodium							300 mg/L		
TDS							100 mg/L		
Uranium	n/d	n/d	n/d	n/d	0.02	n/d		n/d	n/d
Vanadium	n/d	n/d	n/d	n/d	n/d	5		0.1	0.1
Zinc	14000	35000	50000	n/d	n/d	500		2.0	20.0

SIL = soil investigation level (National Environment Protection Council, 1999)
 WA Class IVA = The values shown in the table for STC and LCC represent the maximum total concentration allowed in Western Australian wastes classified as "low hazard wastes". In making this classification, if either the STC or LCC criteria are exceeded, the waste must be treated or classified as Class V (hazardous waste) (Australian and New Zealand Environment and Conservation Council, 1999)
 QLD Industrial Refuse (lined) (Australian and New Zealand Environment and Conservation Council, 1999)
 STC = soil total concentration (Australian and New Zealand Environment and Conservation Council, 1999)
 LCC = leachable contaminant concentration (Australian and New Zealand Environment and Conservation Council, 1999)
 TDS = total dissolved solids (Anon, 2000 #2.194)
 DW = Drinking Water (National Environment Protection Council, 1999)
 WRP = water for recreational purposes (Australian and New Zealand Environment and Conservation Council, 2000).
 n/d = not determined

2.2 Previously Attempted Remediation Strategies and Revegetation Trials

2.2.1 Laboratory & Greenhouse Studies

Meecham and Bell, (1977b) showed that Rhodes grass (*Chloris gayana*) responded well to improved physical conditions of red sand (QAL: red sand treated with seawater during transport to BRDA) mixed with fly ash (80:20 ratio) as the unconfined compression strength (kg cm^{-2}) was significantly reduced from ~ 2.5 to 0.9 kg cm^{-2} due to the fly ash amendment. Under adequate nutrient supply conditions, Rhodes grass had a combined dry matter yield of circa 15 g, which improved to over 40 g in the 80:20 red sand-fly ash mixture. An optimal dry matter yield for Rhodes Grass on red sand was determined to exist for N application rates of circa 200 kg ha^{-1} , while supplying at least 200 kg P ha^{-1} .

Fuller et al., (1982) and Fuller and Richardson (1986) evaluated the performance of desert saltgrass (*Distichlis spicata var. stricta*) as a function of dry matter yield and fertilizer applications including sewage sludge. The dry matter yield of desert saltgrass is negatively correlated to shoot concentrations of Al and Fe. In a separate hydroponic experiment, the toxicity of aluminate at pH 9.5 and 10.0 was suggested by increased uptake of Al in above-ground (shoot) tissues. The application of sewage sludge is seen as advantageous insofar that it significantly increased biomass production, which was in part attributed to the complexation capacity of sewage sludge for Al. Uptake of Mg, Ca, K, N, P were all positively correlated to biomass production highlighting the necessity to provide macro-nutrients to rehabilitated bauxite residues. In line with Fuller's work, Thiyagarajan et al., (2009) showed that micronutrients such as B, Mn, and Zn can significantly limit plant growth even though the overall physical (drainage) and chemical properties (SAR/ESP) are improved. In the HCO_3^- pH regime established with gypsum amendments, Cu and Zn become significantly limited which is consistent with micronutrient management dogma (Tisdale et al., 1993). Mn and Fe pools were limited due to the low solubility of the common Fe and Mn oxide forms. These studies highlight the necessity of the supplementary rehabilitation goal of supplying adequate nutrient levels specific to the plants' requirements.

Studies by Wong and Ho (1992, 1993, 1994) investigated the physicochemical properties (pH, EC and ESP) of bauxite residue from Kwinana following gypsum and or sewage sludge applications and their effect on the emergence and development of tall wheat grass (*Agropyron elongatum*) and Bermuda grass (*Cynodon dactylon*). The initial residue pH (10.2-10.5) was suppressed to 8.7 by applications of at least 5 wt% gypsum (8.7) and ESP lowered from 70.4 to less than 12. As a consequence of the decreased pH, water-soluble Al decreased from 1.04 to less than 0.15 mg kg^{-1} (solid solution ratios used in the experiment are unknown). By comparison the addition of sewage sludge to the residues did not suppress the pH, however, water-soluble Na concentrations decreased suppressing the ESP to 42-47 and making Na non-exchangeable, i.e., not bioavailable to either grass. As a consequence to the addition of sewage sludge and the lack of a pH suppressing effect, Al bound by the sewage sludge was released into solution, which had a devastating effect on *A. elongatum* dry matter yield consistent with the study by Fuller and Richardson (1986) on desert

saltgrass. In the presence of 8 wt % gypsum, however, the aluminate toxicity effect was suppressed by the lower pH regime in which soluble Al precipitates as gibbsite. Similar work carried out on bauxite residues from Alumine de Grece (AdG) and multiple plant species salt cedar (*Tamarix sp.*), Chinese cheesewood (*Pittosporum chinense*), mastic tree (*Pistacia lentiscus*), Sea Orach (*Atriplex halimus*) and Mediterranean saltbush (*Centaurea spinosa*) showed the same efficacy of sewage sludge and gypsum on sustaining plant growth. In addition, these authors identified that adequate P nutrition was vital to enhance plant growth. Of the plants investigated, salt cedar gave the most promising survival results.

Polcaro et al., (2000) investigated the physicochemical changes of bauxite residues from Eurallumina as a function of a fresh-water leach that percolated through gypsum-amended bauxite residues. Residues from the final thickening filter (RMF) and seawater-slurried bauxite residue (RMP) from the BRDA holding ponds were tested. Gypsum loadings of 5 and 10% are indicated (assumed to be dry weight percentage) and leachate quantities reported as liquid/solid washing ratios (volume of water per gram of dried residue). For the filtered residue the pH of the leachate decreased from 12 to about 10.5 by $\sim 30 \text{ ml g}^{-1}$, while the Na^+ release (reported in terms of integrated release per unit mass of residue) in the leachate increased from ~ 0.5 to more than 8 mg g^{-1} , providing evidence for the displacement of Na^+ by Ca^{2+} (the residue liquor only having an initial Na level of 7.4 mg L^{-1}). In the case of the seawater treated residue the leachate pH increased from 9 to about 10.5 over the experiment, while the Na^+ release increased from ~ 5 to 16 mg g^{-1} . As the pond residue has almost twice the Na level it is not clear whether this has any significance, although the authors appear to conclude that seawater treatment is a major hindrance to the extraction of Na^+ and more gypsum is required. Importantly though the gypsum treatment improved particulate agglomeration and permeability. Work by Menzies et al., (2004) similarly showed that the pH of solutions from 1:1 and 1:2 solid-seawater ratios (Gove, NT) increased slightly from 10.4 to 10.6 and from 10.7-11.0 over a 26-hr period. For lower solid-seawater ratios, the solution pH decreased over time to 9.7-9.0 with decreasing solid-seawater ratios ranging from 1:5 – 1:50.

Ippolito et al., (2005) determined that an effective method of lowering pH, SAR (ESP) and Na content, while raising Ca and Mg concentrations was to apply acidic gypsum and wood waste. The ameliorating effect of the acidified gypsum was due to its greater solubility, while the effects from wood chips are not entirely clear, but they did not appear to improve permeability.

2.2.2 Field Scale Work

Wong and Ho, (1991) conducted field experiments on the Kwinana BRDA F lake using tall wheat grass (*Agropyron elongatum*) to investigate the effects of gypsum and or sewage sludge on the physical qualities of bauxite residue, viz. bulk and particle densities, total porosity and hydraulic conductivity. The amendments were worked

into the residue using a roto-tiller⁵. Sewage sludge decreased bulk density and improved hydraulic conductivity, whereas gypsum was most instrumental in reducing the ESP and thus contributing to a 25-fold increase in hydraulic conductivity (from ~ 0.001 to 0.025 mm hr⁻¹). The water field capacity of red mud was positively correlated to the organic matter content, which increased with the rate of sewage sludge application. The long term efficacy (*achieve and sustain*) of the applied sewage sludge and gypsum on the survival of *A. elongatum* was unfortunately not determined. No information concerning the actual ESP (SAR), pH and RSC were made available in the study.

In an application of seawater to red sand (Gove, NT) Menzies et al., (2004) showed that via a 0.8 m column leach study, breakthrough of the major cations occurred in an order typical for the lyotropic soil cation exchange series. K appeared after 1 m of sea water, Mg after 1.7 m and Ca after 2.6 m. The authors suggested that Na⁺ was replaced via cation exchange, whereby the more abundant Mg initially replaced Na, until Ca began to replace Mg from the exchange complexes consistent with the lyotropic series of Helfferich (Helfferich, 1962). The exchange reactions occurred progressively from the surface implying the formation of a saturation front slowly moving through the red sand profile. With divalent Ca and Mg being strongly retained by the red sand, Na retained in the Bayer process liquor was leached quickly and Na concentrations fell to that of the input seawater.

Courtney and Timpson, (2004) determined that nutrient levels in sewage and gypsum amended bauxite residues (Aughinish) must be actively managed in order to adequately supply ryegrass (*Lolium perenne*) and fog grass (*Holcus lanatus*) with nutrients. Their two-year field study showed deficiencies to be particularly apparent for N, Ca, Mn, Mg, P and K. The nutrient deficiencies were further expressed by significant reductions in biomass production in aboveground tissues. Courtney and Timpson, (2005) also investigated the effects of gypsum and red sand additions on the ability to reclaim the fine fraction of a bauxite residue (Aughinish) with red clover (*Trifolium pratense*), and observed that the addition of 25 wt % red sand improved permeability of the bauxite residue/gypsum/sand mixture. Woodard et al., (2008) arrived at a similar conclusion that a combination of gypsum and improved drainage enhanced the removal of soluble Na⁺, Al(OH)₄⁻ and other toxic species, which was critical for their plant species (bermudagrass (*C. dactylon*), oldman saltbush (*Atriplex nummularia*) and fourwing saltbush (*Atriplex canescens*)) to survive on bauxite residues (Alcoa Point Comfort, Texas, USA). Later work by Courtney et al., (2009) investigated the effects of spent mushroom compost (SMC, a material high in Ca due to gypsum amendments) and additional gypsum applications on bauxite residue (Aughinish) physical properties. The authors determined that SMC additions improved the organic C content of the residues while decreasing bulk and particle densities and increasing porosity. SMC and gypsum in combination improved porosity due to improved micro-aggregation, which, under mechanical disturbance did



⁵ Illustrative example of the type of roto-tiller used.

not result in the dispersion of the otherwise clay-size matrix. This was in part attributable to the solubilization of Ca from the SMC and or CaCO_3 , decreasing SAR and ESP.

In light of the consistent apparent successes achieved with gypsum and sewage sludge applications, contrary evidence from a review of field studies in Jamaica are noteworthy (Harris, 2009). The author reports studies conducted by Alcan on bauxite residues deposited at the BRDA of the Kirkvine alumina refinery, in which gypsum and poultry sewage sludge did not succeed in initially establishing and sustaining a viable/ self-supporting plant cover. After 7 years it resulted in a 15-cm deep, brick-hard layer at the surface with little or no porosity and no permeability ($\text{HC} = 0 \text{ cm/h}$). Part of the failure was attributed to a so-called "un-activated" sewage sludge, which did not permit resident microbes to decompose and make available nutrients to plants. Harris (2009) studied these gypsum-hardened residues further and determined that mechanical break-up of the surface alone did not improve permeability in contrast to phyto-organic amendments, which increased HC from 0 to 10 cm/h and also increased water-stable aggregation of the residue particles. The main mechanism behind the improved permeability and aggregate stability was ascribed to the solubilization of Ca bearing compounds including the phyto-organic amendment and CaCO_3 ⁶ dissolution due to the presence of organic acids. It should be noted that in relation to the Kirkvine residue site, Riffaud and James (2010) have observed that after a period of 14 years extensive vegetative cover had established itself on the same site. Physiochemical conditions of the site would be important to establish in order to determine the factors contributing to the successful re-vegetation bearing in mind the climatic conditions of Jamaica.

2.2.3 Microbial Studies

Williams and Hamdy (1982) determined that in bauxite residue metabolically injured bacteria exist, which, if provided nutrients through either standard laboratory agars or hay, will repair their injuries and begin to become metabolically active. The consequence of the metabolic activity is (i) a multiplication of the number of bacteria, (ii) their respiration, and (iii) their exudation of organic acids. Within a two week period, the respiratory activity (effectively carbonation) and the exudation of organic acids dropped the pH of the solutions from >10 to circa 6.5.

In later work by Hamdy and Williams (2001), scanning electron micrographs showed that microbial colonies effectively dispersed otherwise clumped particles. Hay-treated residues supported the growth of several plants and pine trees, and earthworms for more than periods between 6 and 12 months. Hay treatments effectively improved water filtration and helped to remove soluble salts.

⁶ The formation of CaCO_3 in the cemented layer is presumably the consequence of the gypsum application: $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 (\text{s}) + \text{Na}_2\text{SO}_4$. CaCO_3 is a well-known cementing agent of clay-sized particles and is customarily removed with NH_4 -acetate (pH 5.5) to isolate the clay fraction in soils (Jackson, M. L. (1956) *Soil chemical analysis - Advanced course*, Madison, WI, University of Wisconsin.).

2.3 Other *in situ* remediation techniques

2.3.1 Soil Capping

Wehr et al., (2006) have reported on the 30-year old and ongoing revegetation program of sections of Gove (NT, Australia) alumina refinery's BRDA using a soil cap. The bauxite residues were originally deposited as a wet slurry with an east-to-west gradient of increasing particle size and increasing seawater neutralization. The pH in the finer (eastern) fraction was 10.5, whereas the western, sandier, residue fraction had a pH of 9.7. The cap consisted of a 75-150 cm clayey subsoil overlain by a 15 cm sandy topsoil. The total soil cap pH was less than 7.6 and the EC was less than 0.1 mS cm⁻¹ and it was fertilized with 1200 kg ha⁻¹ NPK (12/5/15) and an additional application of 300 kg ha⁻¹ superphosphate fertilizer. A plethora of naturally occurring vegetation was sown or transplanted, which was complemented by natural invasion of additional plants. Within 5 years of the revegetation program, the pH in the residue had decreased from 10.5 to 9.5 and roots had penetrated some 60 cm into the residue. By 1990 aerial surveillance showed that the finer eastern side of the revegetated area was dominated by grasses and shrubs, whereas the sandier western end was dominated by trees. Where the surface cover became increasingly sparse (grasses, east and western ends), soil testing revealed that the soil become sodic and alkaline (pH > 8.5, EC > 1.0 mS cm⁻¹). These areas had thin soil caps (0.6±0.3 m), while thicker soil caps (1.4±0.4) supported dense vegetation including trees, and maintained a pH between 5.5 and 8.8 and an EC of less than 1.0 mS cm⁻¹. Completely bare areas showed signs of salt crusting at the surface. In 1994, the barren areas were recapped and replanted and in some areas, drainage lines were installed. In the drained areas, soil testing in 1996 revealed that the pH remained about neutral and had an EC of < 0.1 mS cm⁻¹. In the bare areas, the pH had risen to 10 and the EC exceeded 0.6 mS cm⁻¹. By 2003, the drained areas were well populated with plant species including trees, while the bare areas occurred in poorly drained and waterlogged areas during the annual wet period.

Analyses of plant root propagation showed that roots were most prominent in the sandy topsoil cap and only few roots were present in the clayey subsoil cap. The main difference between these two cap zones being the Na content, which was up to 15 times higher in the clayey subsoil than in the sandy topsoil. Some roots had penetrated beyond the soil cap and were present in cracks that had developed in the red mud due to shrinkage; however, no penetration of bauxite residue pedes was observed, indicating that no intimate association to bauxite residues actually occurred.

The observations made by Wehr et al., (2006) are consistent with the behavior of uncapped bauxite residues ameliorated with sewage sludge and or gypsum in that drainage, soil fertility and the maintenance of plant suitable pH and EC (i.e., low Na levels) are critical for plant survival.

2.3.2 Bioremediation of saline-sodic soils in arid and semi-arid climates: Farming for Sodium

Analogous to achieving and sustaining plants on bauxite residues are the challenges faced by farmers in arid climates irrigating crops with saline ground water causing their soils to become saline-sodic (Qadir et al., 2006a; Qadir et al., 2006b; Shekhawat

et al., 2006; Qadir et al., 2007). Because chemical amendments and drainage with low salt content water is usually prohibitively expensive, many subsistent farmers resort to cropping sodic -saline soils with halophytes to remove excess Na^+ (Qadir et al., 2006a). Halophytes (in contrast to glycophytes, e.g., Bermuda grass) are salt resistant plants (as opposed to tolerant species), which thrive in salt-affected soils, and take up a significant amount of salt (wt% of dry matter yield), in order to complete their lifecycle (Jennings, 1968; Flowers et al., 1977). The limits of survival for *Atriplex* species, for example, appear to lie between 300 and 700 mM NaCl (17 to 40 g NaCl L⁻¹) with optimal growth conditions between 20 and 500 mM NaCl (Flowers et al., 1977). The growth response of halophytes is positive to NaCl, whereas KCl, CaCl₂ and MgCl₂ trigger various reactions depending on halophyte species from no effect at all, to a synergistic effect to an outright toxic effect. For example, *Suaeda maritime* grows slowly in MgSO₄, while *A. halimus* benefits from the presence of KCl and NaCl (*ibid.* and references therein).

The major difference between a halophyte (e.g., *Atriplex nummularia*) and a glycophyte (e.g., *Cynodon dactylon* (Bermuda grass)) is the way in which each respond to high salinity. Glycophytes tolerate high salinity by excluding Na^+ from their leaves (restriction to stem and roots or no entry of Na^+ into the plant at all), whereas a halophyte is resistant to high salinity by accumulating high concentrations Na^+ in the vacuoles of their leaves. In contrast to an uncontrolled inflow of Na^+ into a plant, Na^+ uptake has positive ramifications for the halophyte. For example, *Suaeda salsa* members of the *Chenopodiaceae* family are halophytes native to coastlines of China and accumulate between 10-12 wt % (dry weight basis) of salt in their roots and 23-27 wt % (dry weight basis) salt in their shoots (Zhao, 1991). Once in the leaf, research for *Atriplex* and *Suaeda* species suggests that Na^+ is not remobilized or exuded (unlike K^+) thus suggesting a near irreversible compartmentalization in the leaves (Flowers et al., 1977). For a more complete description of the salt tolerance mechanism in halophytes, consult with Flowers et al., (1977), Jennings (1968) and/or Ungar (1991).

Halophytes provide great potential to accomplish some of the rehabilitation goals stated in this report. Reducing the Na content in solution (SAR) and on the bauxite residue solids (ESP) by farming residue profiles for Na using salt resistant halophytes may be an effective means of removing Na^+ from bauxite residues. Amshot grass (*Echinochloa stagninum*) reduced the ESP of a salt-affected soil (0-15 cm) from 30 to 20.2 and 10.1 after one and two years, respectively (Helalia et al., 1992). In the same study, corresponding SAR and EC values in the soil solution of the upper 15 cm were reduced from an initial 30.9 and 27.6 mS cm⁻¹ to 12.9 and 4.3 mS cm⁻¹ after two years of cultivating with Amshot grass. Similar results were achieved with other members of the *Chenopodiaceae* family (*A. indicum*, *S. fruticosa*) and with *Sesuvium portulacastrum* (Rabhi et al., 2009). In addition to the reclamation of salt-affected agricultural land, halophytes have been evaluated to lower salt contents in oilfield brine contaminated soils. *Atriplex* removed up to 17 % of Na^+ from its rhizosphere and accumulated around 600 meq 100 g⁻¹ DW ~ 13.8 wt % Na in its leaf and stem tissues (Howes Keiffer and Ungar, 2002).

The use of halophytes on bauxite residue surfaces offers a number of interesting possibilities, advantages and similarities to their use on saline-sodic agricultural soils: 1) Na^+ removal is less dependent of drainage, a major hindrance factor for sustaining plant species on BRDAs, 2) Gypsum is applied in order to displace Na^+ off the

exchange complex and make it available to halophytes, 3) gypsum and any other divalent cation applied to bauxite residues controls the pH within the tolerance limits of halophytes (see further discussion below), 4) the halophyte exude organic acids and promote microbial populations thus providing H^+ and increasing the partial pressure of CO_2 (p_{CO_2}) in the rooting zones. Halophytes also have the capacity to absorb heavy metals such as Cd and As.

Increasingly, research is conducted on alkaline stresses on the physiological performance (e.g., relative growth rates, photosynthesis, Na uptake) of halophytes. Yang et al., (2009) evaluated the effects of alkaline buffering capacity on the performance (relative growth rates, photosynthesis, Na uptake) of *Chloris virgata* in solutions of pH between 9.5-9.7 and ANC between 0 and 316 $mmol H^+ L^{-1}$. The authors showed that relative growth rate and photosynthetic activity declined with increasing buffering capacity, while Na^+ accumulation in tissues was highest (4.6 wt %) from solutions buffered at 316 $mmol H^+ L^{-1}$ acid neutralizing capacity. The study showed that pH does not reflect the stress that is induced by the acid neutralizing capacity of the surrounding medium. The ability of the halophyte to function and survive at a pH of ~ 9.6 and low ANC suggests that some direct or indirect Na^+/H^+ exchange at the root counteracts the buffering capacity of the alkaline solutions. Several authors have reported that under alkaline stress and combined saline and alkaline stress, the physiological performance of otherwise alkali-resistant halophytes diminishes (among others, see for example Zhang and Chun-Seng (2009), Guo et al., (2010) and Li et al., (2010)). A common effect measured is the increase in organic acid accumulation (e.g., citric, oxalic and succinic acids) in the shoot and roots of *Puccinellia tenuiflora*, *Spartina alterniflora*, and *Lathyrus quinquenervius*. Despite the measureable stress levels in these and other halophytes, Na accumulation in above-ground tissues is usually maximized at high levels of alkalinity. Figure 2 shows a schematic representation of this type of bio-remediation approach and some of the residue chemistry changes.

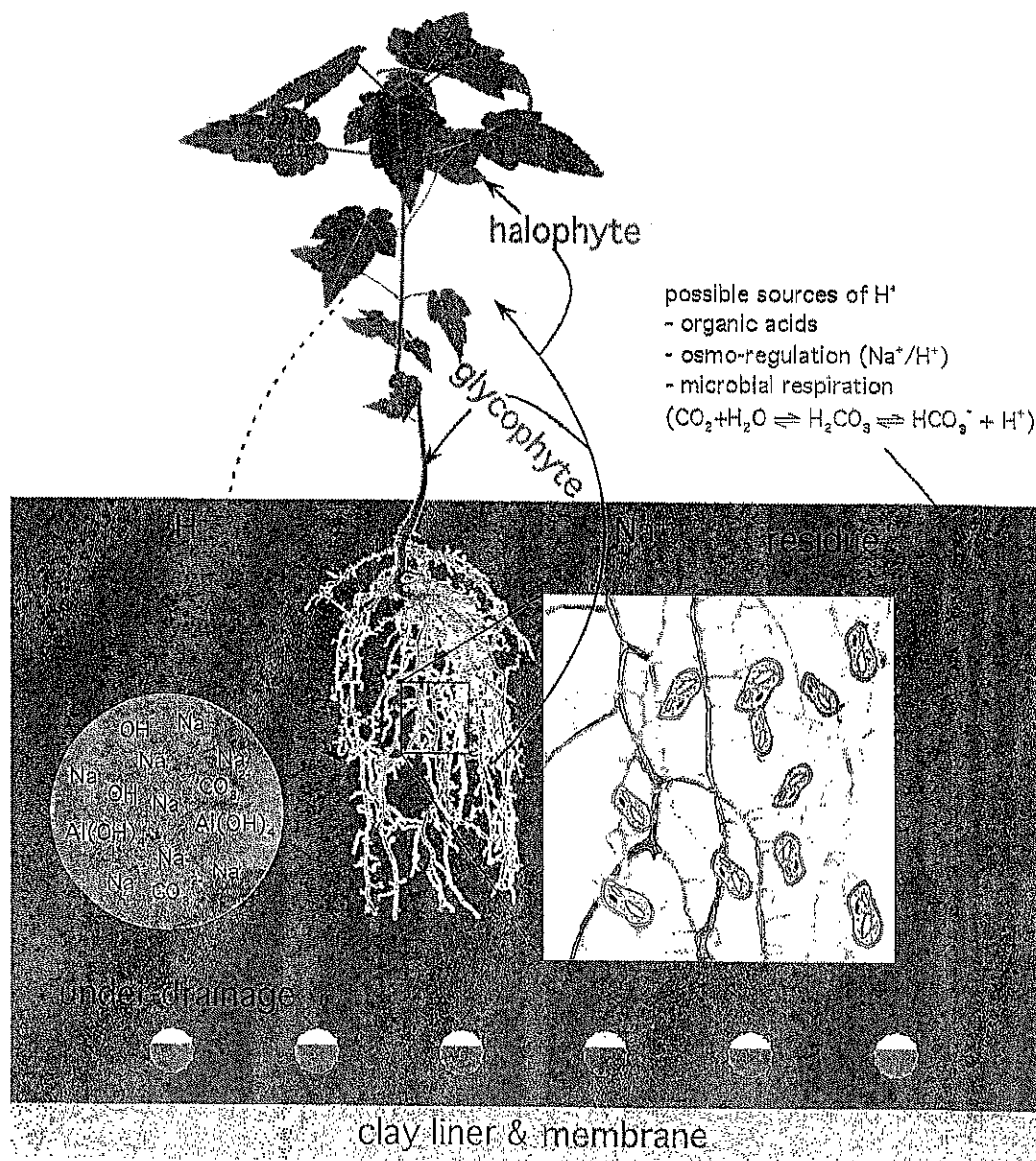


Figure 2. Schematic representation of the idea of "farming for sodium" as a bio-remediation strategy. With the appropriate choice of halophytes it is possible to both remove sodium from surface residue and reduce the residue alkalinity.

There are numerous additional research studies investigating saline and alkaline stresses on halophytes, however, they are outside the scope of the deliverables for consideration herein. For bauxite residue rehabilitation goals and remediation pathways, employing halophytes specifically for optimal removal of Na⁺ from residue profiles provides a challenging yet exciting new pathway to initiate bauxite residue remediation. Of the remediation strategies discussed above, those using *Atriplex* species can generally be considered as halophytes (see Table 5). Research in halophyte biochemistry and salt and alkali tolerance mechanisms indicate that a critical first step in choosing a halophyte species is to identify its optimal growth parameters (including climatic adaptability) with respect to salt, alkalinity and buffering tolerances and their effects on nutrient uptake and/or demand in order to achieve more optimal growth conditions.

Table 5. Plant species used in revegetation programs or greenhouse trials of bauxite residues classified into glycophytes (G), halophytes (H) or unknown tolerance (U) (Flowers et al., 1977).

Species (common name, where known)	G/H/U	Reference
<i>Chloris gayana</i> (Rhodes grass)	G	(Meecham and Bell, 1977b)
<i>Distichlis spicata</i> var. <i>stricta</i> (Desert saltgrass)	H	(Fuller et al., 1982) (Fuller and Richardson, 1986)
<i>Hardenbergia comptoniana</i>	U	(Thiyagarajan et al., 2009)
<i>Acacia cyclops</i> (Western Coastal Wattle)	G	(Thiyagarajan et al., 2009)
<i>Grevillea crithmifolia</i>	U	(Thiyagarajan et al., 2009)
<i>Eucalyptus gomphocephala</i>	U	(Thiyagarajan et al., 2009)
<i>Agropyron elongatum</i> (tall wheatgrass)	G	(Wong and Ho, 1992; Wong and Ho, 1993; Wong and HO, 1994)
<i>Cynodon dactylon</i> (Bermuda grass)	G	(Woodard et al., 2008)
<i>Tamarix sp.</i> (salt cedar)	H	(Xenidis et al., 2005)
<i>Pittosporum chinense</i> (Chinese cheesewood)	U	(Xenidis et al., 2005)
<i>Pistacia lentiscus</i> (mastic tree)	U	(Xenidis et al., 2005)
<i>Atriplex halimus</i> (Sea Orach)	H	(Xenidis et al., 2005)
<i>Centaurea spinosa</i> (Mediterranean saltbush)	U	(Xenidis et al., 2005)
<i>Quercus coccifera</i> (Kermes Oak)	U	(Xenidis et al., 2005)
<i>Lolium perenne</i> (ryegrass)	G	(Courtney and Timpson, 2004)
<i>Holcus lanatus</i> (fog grass)	G	(Courtney and Timpson, 2004)
<i>Trifolium pratense</i> (red clover)	U	(Courtney and Timpson, 2005)
<i>Atriplex nummulari</i> (oldman saltbush)	H	(Woodard et al., 2008)
<i>Atriplex canescens</i> (fourwing saltbush)	H	(Woodard et al., 2008)

2.4 Key physical and chemical parameters relevant to remediation strategies

In summary, laboratory/ greenhouse, microbial and field studies come to the conclusion that:

1. Na^+ , $\text{Al}(\text{OH})_4^-$, EC, pH, SAR and ESP levels must be reduced to plant tolerable levels. Research on halophyte tolerances also point to the necessity of reducing alkali buffering capacity.
2. Drainage of irrigation waters must occur in order to remove Na^+ . This may be accomplished with sewage sludge, divalent cations (Mg, Ca) and or other (structural) amendments such as red sand that lower bulk density, improve aggregation and aggregate strength (avoids cementation and dispersion), and increase porosity, permeability, and hydraulic conductivity.
3. The application of divalent cations such as Ca and Mg from sources such as gypsum or seawater enhances the removal of Na particularly under improved drainage conditions by ion exchange processes consistent with the lyotropic series and improves the saturation of the exchange complex with macro-nutrients.
4. It is essential to supply adequate amounts of nutrients (macro- and micronutrients) and available water to plants and microbes establishing seedlings/ populations and to guarantee their survival irrespective of saline and or alkaline tolerance levels.

5. Microbes are effective pH suppressants and in combination with hay additions achieve similar effects as gypsum and seawater with respect to pH, ESP and permeability.

In order to lower SAR/ESP values, residue solution conditions need to be amended such that either Ca or Mg bearing minerals become soluble and/or such that Ca and Mg additions to the residues do not precipitate. With respect to the stated rehabilitation goal of an SAR value 7 or less ($ESP \leq 9.5$), a key research component must entail a means to *achieve and sustain* the target SAR value. Ion exchange reactions are at the heart of lowering SAR and ESP to acceptable values and are thus fundamental reaction mechanisms that require thorough understanding. While gypsum and bitterns applications are capable of lowering pH, RSC, SAR and ESP, the choice of plant must consider the effect of such amendments on EC and tolerance by the plant. For example, certain halophytes and glycophytes have reduced physiological functioning in high SO_4 , Ca and or Mg environments. Provided that drainage is in good operation (sufficient permeability) and that water sources have a high water potential (low ion content \rightarrow low EC), excess salts (including Ca and Mg) will be flushed away. A salt resistant halophyte may provide assistance in achieving target SAR and ESP levels by removing Na^+ from solution, provided that it can survive the substantial pH buffering capacity. An amendment with Ca and or Mg to suppress pH in the presence of a halophyte would appear necessary. Farming for Na^+ on bauxite residues using halophytes has as such not been reported in the literature yet, although several studies have employed *Atriplex* species to vegetate bauxite residue surfaces (see section above).

3. KNOWLEDGE GAPS AND RESEARCH RECOMMENDATIONS

The knowledge gaps apply primarily to the remediation steps required to achieve the rehabilitation goals, i.e., the rehabilitation goals in themselves do not require further research. The knowledge gaps with respect to the remediation pathway can be separated into biotic and abiotic knowledge gaps. The biotic knowledge gaps concern the development of a thorough understanding of the stress and tolerance levels of halophytes, glycophytes and microbes (including resident, injured microbes, alkaliphilic microbes and fungi) to salinity and alkalinity, such that the amendments can be dosed and applied in a maximally beneficial way for the plants and microbe populations to be established. It should be emphasized that the halophyte bioremediation approach is not a rapid solution. The time involved and the influence through the BRDA height profile will depend not only on the remediation pathway, but the BRDA design and climate. Understanding aspects such as salt transport (A6) and the sodic-alkaline buffering chemistry are intimately linked to the final outcome.

Table 6. Abiotic knowledge gaps, research requirements, and research outcomes.

Knowledge Gap/ Research Requirement	Research Outcome
A1. Solution compositions of entrained liquors in bauxite residue deposited at the BRDA particularly with respect to plant and microbe limiting species such as OH, CO ₃ ²⁻ , SO ₄ ²⁻ , B(OH) ₄ ⁻ , Al(OH) ₄ ⁻ , Cl ⁻ , NO ₃ ⁻ , AsO ₄ , VO ₄ , CrO ₄ , PO ₄ , Mg ²⁺ , Ca ²⁺ , Na ⁺ , NH ₃ /NH ₄ ⁺ , etc.	Defines the limits of stress and tolerance for plants and microbes (see B2 below).
A2. Understanding the dissolution mechanisms of sodalite and cancrinite over the target pH range (8.9-5.6) is critical, because these minerals are the primary solid buffering agents for Na, OH, Al, and CO ₃ ²⁻ , all of which tend to be toxic to plants and microbes.	For a particular pH, the rate of Na, OH, Al, and CO ₃ replenishment into solution can be predicted based on the kinetics of the dissolution reactions and secondary reaction products.
A3. Ion exchange is a key reaction that supplies plants and microbes with nutrients stored in soils/residues and affects micro-aggregation, bulk density, porosity, and permeability of bauxite residues. Binary and ternary ion exchange reactions in bauxite residues and desilication products (e.g., sodalite, cancrinite) need to be evaluated as a function of pH (8.9-5.6) and counterions (e.g., SO ₄ vs. Cl vs NO ₃).	The thermodynamics of Ca:Na-, Mg:Na, and Ca, Mg:Na-exchange define upper limits for the saturation of the residues with Ca and Mg, which can be evaluated further in terms of their, when studied <i>in situ</i> (e.g., lysimeter studies) or in column experiments in the laboratory.
A4. Chemical speciation and mineralogical partitioning of trace metals, metalloids, heavy metals and other potentially toxic elements contained in the last-washer underflow liquor and in bauxite residues. These investigations must entail a laboratory-scale type experiments whereby the partitioning of soluble metals/metalloids is evaluated as a function of pH and ionic strength, and a molecular/atomistic-scale spectroscopic experiments (e.g., X-ray absorption spectroscopy, X-ray photoelectron spectroscopy) that determine the chemical states of the contaminants.	Research in this area will supply the data necessary to predict bioavailability of contaminants to plants and microbes and therefore will help to understand their impact (if any) on the biological remediation agents. Understanding the chemical dynamics of potentially toxic trace metals in bauxite residues provides validation whether the quality of the rehabilitated bauxite residue is truly improved.
A5. Evaluation of the presence and form of macro- and micronutrients including organic carbon: N, P, K, Ca, Mg, Cu, Zn, Fe, B, Mn, among others, in amended bauxite residues. This research cannot rely simply on determining totals, but must in addition define plant available levels through basic agriculture tests (e.g, Mehlich 3 test for P).	This data, in conjunction with B1 (see below), will help establish fertilization rates that will be required to keep plants and microbes alive.
A6. Generic salt transport and deposition model for predicting bauxite residue salts profile behaviour during the remediation process.	This would assist the time-line prediction of remediation progress; especially for varying BRDA designs (e.g. drainage, residue depth, climatic impact).

Table 7. Biotic knowledge gaps, research requirements, and research outcomes.

<p>B1. A detailed literature review of the tolerance and resistance levels and mechanisms of glycophytes and halophytes.</p>	<p>This literature review will identify the most promising species for remediating bauxite residues.</p>
<p>B2. Detailed tolerance and resistance studies of the species indentified in B1 with respect, but not limited, to salinity, alkalinity, and tolerance to divalent cations and anions such as Mg, Ca, and SO₄, and soluble trace metals (e.g., Cu, Zn, Al), metalloids (e.g., CrO₄, AsO₄, VO₄), and heavy metals (e.g., Pb).</p>	<p>This data is of paramount importance in order to define proper residue amendments and to maintain microbes and plants in optimal conditions during the first months and years of establishment.</p>
<p>B3. A detailed literature review of alkaliphilic microbes and fungi. Microbes and fungi, in particular obligate aerobes, are potentially the first level of biological agents to be introduced to bauxite residues in order to suppress pH and create pore space. Knowing the most promising species and their minimum nutritional and moisture/oxygen requirements is an important first step to establish such populations on bauxite residue surfaces.</p>	<p>Will identify suitable microbial species and fungi capable of surviving the harsh conditions of bauxite residues and in addition identify chemical and physical conditions conducive to their survival.</p>

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GLOSSARY

Aggregation: the property of solid particles to adhere to each other to form an aggregate. Aggregates in the soil science context have size distribution (dry and wet) and a stability (dry and wet). The inter-particle attraction is largely electrostatic. Aggregation is the opposite of dispersion.

Bulk density (ρ): Aka the total density, it is the ratio of the total mass of the residue to the volume it occupies (Fredlund and Rahardjo, 1993). It is affected by the moisture content of the residue as it affects the shrink-swell behavior of the residues. Therefore, in order to compare bulk densities, it is important to cite the moisture content, e.g., oven dry. Oven dry bulk densities are sometimes referred to as dry density (ρ_d).

Cementation: the consolidation of solid particles by virtue of an inter-particle cement, e.g. carbonate, precipitating and physically binding particles together. Cementation is a direct consequence of solution chemistry.

Degree of Saturation: describes the ratio of water-filled pore volume relative to the total volume, and ranges from 0 to 1. At full saturation (1), the water content is equal to the porosity of the residue sample (Topp and Ferre, 2002).

Dispersion: the breakdown of soils aggregates into individual component particles, most commonly used in the context of hydrodynamic dispersion, but dependent on surface charge.

EC: Electrical conductivity with units of siemens per unit length. In this work EC values are quoted in mS/cm (consistent with common usage in soil science). This should not be confused with the incorrect usage of water salinity "EC units" which are measured conductivities in $\mu\text{S}/\text{cm}$ with the units often ignored.

ESP: stands for exchangeable sodium percentage and is defined according to equation [3] in the text. It is related to the SAR by cation exchange processes occurring between Na, Ca and Mg. The ESP predicts the composition of the exchange sites that are filled with Na

Field capacity (FC): describes the moisture content *in soils* between -15 and 100 ft of moisture potential (-9.1 and -30.5 m moisture potential = -90 to -300 kPa) (Jarrett, 1997). In bauxite residues, the dissolved salt content will affect field capacity similarly as the wilting point.

Gravimetric water content (w, %, kg kg^{-1}): is the mass of the water (M_w) relative to the mass of solids (M_s) expressed as a percentage.

Hydraulic conductivity (K): is the movement of water through the residue. Saturated hydraulic conductivity (K_s) refers to the movement of water through the residue when all the pore space is filled with water, while unsaturated refers to the movement of water through the residue when the pores are partially filled with gas (presumably air) and water.

Matric potential: the total soil water potential which is the sum of all adhesive forces between water and the soil components (effectively all the surface tension components).

Permeability: A measure of the ease with which water and or air move through a residue (Jarrett, 1997) or the ability of the residue profile to transmit and drain water.

pH: the power of hydrogen (pH) is equal to the negative log (base 10) of the hydronium ion concentration ($\text{mol H}^+ \text{L}^{-1}$) in solution. It is important to note that pH is a solution attribute although it is often referred to as the pH of the residues. The latter is both inappropriate and misleading as it deflects from the ion exchange processes that occur as a residue comes into contact with water.

Porosity (%): is the ratio of the total volume of pores or voids (V_v) to the total volume (V) of the sample expressed in percent (Fredlund and Rahardjo, 1993; Jarrett, 1997). Porosity (S_T) can be calculated from bulk (ρ_b) and particle density (ρ_p) according to the equation:

$$S_T = 1 - (1 - \rho_b / \rho_p) \quad [8]$$

RSC: stands for residual sodium carbonate value (mmol charge per litre) and is equivalent to equation [1] in the text. For an average pH of 11.8 in bauxite residue solutions, the RSC value is essentially equivalent to the CO_3^{2-} concentration in solution multiplied by 2 to account for the charge on CO_3^{2-} .

SAR: stands for sodium adsorption ratio and defines the ratio of soluble sodium to soluble magnesium and calcium according to equation [2] in the text. SAR is dimensionless, however, evaluation of SAR requires Na, Ca, and Mg have units mmol of charge (mmol+) per litre (L^{-1}) (McBride, 1994).

Total soil water potential: is the sum of forces that act or retain water and thus affect its energy state. These forces are gravitational, matric, pneumatic, osmotic and overburden potential. In the context of bauxite residues, all except the pneumatic and overburden potential affect the total residue solution potential, whereby the overburden potential, affects the matric potential reading at greater depths of the residue stack. In order to convert among different units of water potential, it is useful to note that $1 \text{ Pa} = 1.02 \times 10^{-4} \text{ m H}_2\text{O}$ or $1 \text{ kPa} \sim 10 \text{ cm H}_2\text{O}$ (Topp and Ferre, 2002).

Gravitational Potential (J kg^{-1}): The amount of work required to move a unit mass of water from a reference elevation to the point of measurement.

Matric Potential: The combined potential due to adsorptive forces between soil/ residue particle and water and capillary forces at the air-water interface. The matric potential is equal but opposite in sign to these combined forces.

Osmotic Potential: exists at the root membrane/residue interface that acts as a semi-permeable membrane. The osmotic potential will be more negative in solutions of increasing salt content, which decreases the overall or total soil water potential. The osmotic potential illustrates the importance of the solution composition as any liquid with a higher (more positive) water potential will infiltrate into the residue and equilibrate as the precipitated salts dissolve into solution until the osmotic potential is equal throughout the wetted profile.

Unconfined compressive strength: special case test of the deformability of soil for those soils that possess the cohesion to be tested unconfined (ASTM D2166).

Void Ratio (e): is the ratio of the volume of pores (V_v) to the volume of solids (V_s) for a given sample volume (V).

Volumetric water content (Θ_w , $\text{m}^3 \text{m}^{-3}$): the volume of water relative to the total volume of the residue sample (V). The maximally achievable volumetric water content is equal to the porosity of the sample (Jarrett, 1997).

Wilting point (W_p): describes the moisture content of the residues at which plant growth is not possible due to a lack of water (Jarrett, 1997). In *soils* it occurs at circa -5000 ft moisture potential ($-1524 \text{ m} = -15,117 \text{ kPa}$), whereas in bauxite residues, the wilting point will be significantly affected by the presence of dissolved salts that lower the free energy of water. As water flows from high to low energy, water will not be available to plants although the moisture content in the residues might suggest otherwise (McBride, 1994).



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