

Review of Bauxite Residue Alkalinity and Associated Chemistry

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EXECUTIVE SUMMARY

This report addresses Items 2 (residue chemistry – general) and 5 of ATF-06-3 project on the Management of Bauxite Residues for the Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia.

Item 2 (chemistry) and Item 5 are respectively a general and detailed literature review covering the alkalinity and associated chemistry of bauxite residue (BR). It examines those aspects of Bayer process that relate to the creation of the alkalinity of BR, and discusses in detail the complex chemical reactions that govern the neutralisation behaviour of BR. The implications that this has for future management, remediation and rehabilitation of BR disposal areas are outlined. A set of Research Priorities is provided to address the knowledge gaps that need to be filled to support the development of alternative uses of BRs, improve storage practices, and reduce of the environmental impacts.

pH is the “master variable” in the chemistry of BRs because it is dominated by the presence of alkaline solids. The pH in BR solutions is 11.3 ± 1.0 and ranges between 9.7 and 12.85. Thus BRs are in general highly alkaline, and as such are hazardous and will not support plant life. The pH is highly buffered by the presence of alkaline solids (hydroxides, carbonates and aluminates) that are formed by the action of caustic soda on bauxite in the Bayer process refinery. We refer to these solids, which generally are identified mineral phases but which are nevertheless characteristic of the Bayer process, as “Bayer process characteristic solids”, or BPCSs.

The buffering action of multiple BPCSs causes the acid neutralisation behaviour of BRs to be highly complex. It is impractical to remove the alkalinity from BR by washing with water. This chemistry has profound implications for all aspects of BR, including storage requirements, raw materials usages and recoveries, neutralisation, physical properties including bulk density, sedimentation rates and compaction, hydraulic conductivity, drying rates and dusting behaviour, and physical strength after drying.

Future progress on improved storage practices, remediation, rehabilitation and reuse will be dependent upon the development of better understanding of the complex buffering and neutralisation chemistry of BR. Developing an understanding of how surface charge develops, distributes and abates in the residue mineral assemblage as a function of acid input will be paramount in order to understand neutralisation reactions overall, to successfully model them, and ultimately to implement the most effective neutralisation measures that create conditions at the surface conducive to plant growth. Support for fundamental research to develop of a model for the neutralisation behaviour of bauxite residue based on an understanding of the underlying mineralogy and its relationship to surface charge is warranted.

Data relating dissolution behaviour over time in specific buffering pH regions is absent from the literature, but is critical if a well-founded, mineralogy-based acid neutralisation model is to be realised. Support for the establishment of a

comprehensive data set relating to the dissolution behaviour of bauxite residue specific solids is also warranted.

The reactivity and longevity of the naturally-occurring and synthetic sealants that are used to improve the security of bauxite residue storage areas in relation to leaching of alkaline waters to ground and surface waters are not well documented in the literature. Support for a review of the sealants and research on their reactivities under accelerated test conditions would be appropriate.

The establishment of techniques for creating self-managing, sustainable ecosystems from bauxite residue impoundments is the most realistic solution to the large and increasing inventory (currently 2.7 Bt increasing to 4 Bt by 2015) of bauxite residue globally. Applied research to support implementation in the following areas is required as a matter of priority:

- Microbiologically assisted bio-remediation of bauxite residues;
- Hydrological modelling of liquid flow in bauxite residues impoundments;
- Optimised amendments for the development BR structure conducive to plant growth;
- Effective vegetative covers in bauxite residue disposal areas; and
- Best agronomic practices for managing vegetative covers overlying bauxite residue disposal areas.

A range of trace metals and NORMs are known to be present in residue, but little is known of their mineralogy, chemical speciation or leaching behaviour, especially in relation to neutralisation. A significant research effort is needed to provide the basic information about the speciation of these constituents for evaluation of long-term storage practices, remediation and rehabilitation strategies, and reuse options. Support for research in this area is needed.

The key Research Priorities identified in relation to residue alkalinity and associated chemistry, and the APP Objectives which they support, are:

Research Priority	APP Objectives Supported
Develop thermodynamic and kinetic models for the neutralisation behaviour of bauxite residue and their component minerals and their relationship to surface charge.	Development of best practice residue management options More environmentally acceptable storage Improved potential for re-use options
Establish a comprehensive data set relating to the dissolution behaviour of Bayer process specific solids	Development of best practice residue management options More environmentally acceptable storage Improved potential for re-use options Improved raw materials usages Improved potential for re-use options
Review the materials used for lining residue storage areas and research their reactivities under accelerated test conditions	Development of best practice residue management options More environmentally acceptable storage
Develop the science and practice of microbiologically assisted bio-remediation of bauxite residues	Development of best practice residue management options More environmentally acceptable storage
Establish a hydrological model of liquid flow in bauxite residues impoundments	Development of best practice residue management options More environmentally acceptable storage
Develop methods for the optimisation of residue amendments for the development soil structure conducive to plant growth	Development of best practice residue management options More environmentally acceptable storage
Develop selection criteria for vegetative covers in bauxite residue disposal areas	Development of best practice residue management options More environmentally acceptable storage
Develop a set of best agronomic practices for managing vegetative covers overlying bauxite residue disposal areas	Development of best practice residue management options More environmentally acceptable storage
Progress detailed investigations into the nature, concentrations, speciation and leaching behaviour of trace metals and radionuclides in bauxite residues under a range of neutralisation, storage, rehabilitation and reuse scenarios.	Development of best practice residue management options More environmentally acceptable storage Improved potential for re-use options Improved potential for re-use options

1. INTRODUCTION

1.1 Scope

This review is part of the ATF-06-3 project on the Management of Bauxite Residues for the Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia, and represents completion of Items 2 (residue chemistry – general) and 5 in the schedule of Contract for the Provision of Services number 2490. As such it also represents part of the overall commitment of the Australian Government toward the Asia-Pacific Partnership on Clean Development and Climate (<http://www.app.gov.au/>). China and India are also involved in research components of the ATF-06-3 project. Please also refer to the three parallel review documents that relate to Items 3, 4 and 7:

DMR-3608 Review of bauxite residue storage practices (Item 3)

DMR-3609 Review of bauxite residue reuse options (Item 4)

DMR-3611 Priority research areas for bauxite residue (Item 7)

1.2 Purpose of the Asia-Pacific Partnership (clause 6.2)

The Asia-Pacific Partnership on Clean Development and Climate (APP) brings together Australia, Canada, China, India, Japan, Korea, and the United States to address the challenges of climate change, energy security and air pollution in a way that encourages economic development and reduces poverty. The APP represent around half the world's emissions, energy use, GDP and population, and is an important initiative that engages, for the first time, the key greenhouse gas emitting countries in the Asia Pacific region. With its focus on the development, deployment and transfer of cleaner more efficient technologies, the APP is also unprecedented in the way business, government and researchers have agreed to work together. The APP is also the first time that industry has been afforded an opportunity as equal partners in global climate change discussions.

The objectives for the APP include to:

- *Meet the growing energy needs, reduce poverty and achieve the development goals of partner countries and reduce greenhouse emissions and intensity of partner economies;*
- *Strengthen cooperative efforts to effectively build human and institutional capacity in partner countries;*
- *Actively engage the private sector with considerable marshalling of financial, human and other resources from both public and private sectors;*
- *Demonstrate substantial practical action in the near term as an approach to addressing climate change;*
- *Develop and deploy clean fossil and renewable energy technologies and practice including longer-term transformational energy technology; and*
- *Develop and disseminate best management practice and technology in:*
 - *Aluminium, steel, cement and coal mining industry sectors*

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- *Energy efficiency in building appliances, and*
- *Power generation and transmission.*

The Project aims to address the high volume of bauxite residue (red mud) produced during the processing of alumina from bauxite. It will identify, develop and deploy technologies and practices for the alternative use of bauxite residues or improved storage practices. Thus the project will enable the development of best practice residue management options to reduce the reliance on stockpiling and storage, or to make stockpiling and storage more environmentally acceptable.

1.3 Focus Areas of ATF-06-3: Managing Bauxite Residues

The Aluminium Task Force (ATF) of the Asia Pacific Partnership (APP) identified the following three key focus areas in relation to the management of bauxite residues [1]:

- The productive utilization of bauxite residue in various end-uses including those applications specific to the steel and cement industries (including the extraction of oxides and trace metals).
- Better stabilizing the residue (mechanical stability and chemical inertness).
- Utilizing minimum land for storage and ensuring faster rehabilitation of landfill sites.

Bauxite residues have to date not been integrated into existing industrial processes to any major extent. This has meant that the overwhelming majority of the bauxite residue that has ever been produced (2.6 Bt by 2007) has been disposed of, mostly into land-based impoundments. This implies a responsibility to ensure that the impounded residues do not cause harm to surrounding environments including humans and wildlife, nor diminish the amenity and aesthetics of the landscape. Vertical and horizontal embankment integrity is necessary to ensure that bauxite residues maintain bulk mechanical stability and that the reactive components are confined. At the surface, dust formation has to be controlled to minimise airborne dispersal of bauxite residue. Re-vegetation of the surface to integrate the bauxite residue disposal area into the landscape can, by binding loose particles, simultaneously inhibit dust formation and dispersal by wind erosion. In order to establish sustainable vegetation cover however, the physical and chemical conditions at the residue surface have to be changed.

The alkalinity of bauxite residues is the central issue in relation to sustainable re-vegetation, dust prevention and embankment integrity, because the alkaline constituents prevent vegetation from establishing on the surface, cause the formation of friable dust-prone surfaces, and contribute to embankment failure in the long term.

While it is feasible to overlay residues with several layers of fertile materials to prevent dusting and help plants to establish, continuous management in the long and short term is required to ensure the ongoing effectiveness of the cover. Investigations at the Gove refinery have shown that the success of this method is critically dependent on drainage and the ability to withstand resurging alkalinity from lower lying residues [2]. Alternatively, *conversion of bauxite residues at the surface into material which*

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promotes plant life and is able to buffer against the effects from underlying alkaline layers is arguably the most sustainable approach for the future of bauxite residue management.

2. ITEM 2: GENERAL LITERATURE REVIEW (RESIDUE CHEMISTRY)

2.1 Bauxite Residue: Generation and Composition

Bauxite residue is the slurry by-product generated during the treatment of bauxite ores using the Bayer process to produce alumina. Bauxite residue is also referred to in the literature as red mud, Bayer process tailings, or bauxite process tailings. In this review “bauxite residue” (BR) is the preferred term.

In 2008, 60.5 million tonnes (Mt) of alumina were produced worldwide [3]. As a global average, the production of a tonne alumina generates 1.5 tonnes of bauxite residue, so approximately 91 Mt of bauxite residue was produced in 2008. Historically, we estimate that the total production of bauxite residue reached 1 billion tons (Bt) by 1985, 93 years after the first Bayer plant was established. It took only 15 years for that to double, and we estimate that it will likely double again to 4 Bt by 2015. Given that virtually all of this ends up in land-based storage, these figures highlight the urgent need for a sustainable storage methodology [4].

Bauxite residues are strongly alkaline, have a high salt content and electrical conductivity (EC) dominated by sodium (Na^+), and the particles are compacted (high bulk density (BD)). Trace metals can be of concern and may exceed regulatory levels in certain circumstances [5-7]. Some bauxite residues may emit ionising 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 [8-14]. Little is known about the speciation of trace metals and NORMs in bauxite residues, particularly with regard to pH neutralisation and the accompanying changes in the mineral and solution phases. Typical residue characteristics are listed in Table 1.

The physical and chemical characteristics of the residues make re-vegetation challenging, and established floras are difficult to sustain without amendments [2, 11, 15-21].

GENERAL LITERATURE REVIEW

Table 1: Selected chemical and physical characteristics of unamended bauxite residues.

	average	std ^a	max	min	n ^b
pH	11.3	1.0	12.8	9.7	44
EC	7.4	6.0	28.4	1.4	46
[Na ⁺] ^c	101.4	81.6	225.8	8.9	9
SAR ^d	307.2	233.1	673	31.5	10
ESP ^e	68.9	19.6	91	32.1	10
ANC, 7.0 ^f	0.94	0.3	1.64	0.68	13
ANC, 5.5 ^g	4.56	-	-	-	1
PZC ^h	6.9	1.0	8.25	5.1	11
BD	2.5	0.7	3.5	1.6	13
SSA ⁱ	32.7	12.2	58.0	15.0	30

2.2 Mineral, chemical and physical inputs from the Bayer process.

In order to understand the nature of bauxite residues, it is useful to briefly summarise the Bayer process including its mineral, chemical and physical inputs (Figure 1). The Bayer process is a high temperature, high-pressure dissolution process extracting gibbsite (Al(OH)₃) and/or boehmite (γ-AlOOH) from bauxite by dissolving these constituents in concentrated NaOH solution. This process takes advantage of the solubility of Al³⁺ as aluminate (Al(OH)₄⁻) relative to other constituents in bauxite. The reaction temperature, pressure and concentration of NaOH (Table 2) depend on the mineralogical composition of the bauxite (Table 3). Due to the solubility of phyllosilicate clays such as kaolinite, a pre-desilication step is often necessary to minimise contamination of the green liquor by silica (Si). Pre-desilication is associated with significant losses of Na⁺ and Al³⁺, due to the formation of sodium-aluminium silicates such as sodalite. In order to minimise costly Na⁺ losses, slaked lime (Ca(OH)₂) may be added to the digestion process to form cancrinite instead of

^a std = standard deviation of the population (n)

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

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

^d SAR = sodium adsorption ratio

^e ESP = exchangeable sodium percentage

^f ANC, 7.0 = acid neutralisation capacity normalised to the weight of the residue to a pH endpoint of 7.0 using a strong acid

^g ANC, 5.5 = 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, 5.5 was estimated from graphs.

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

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

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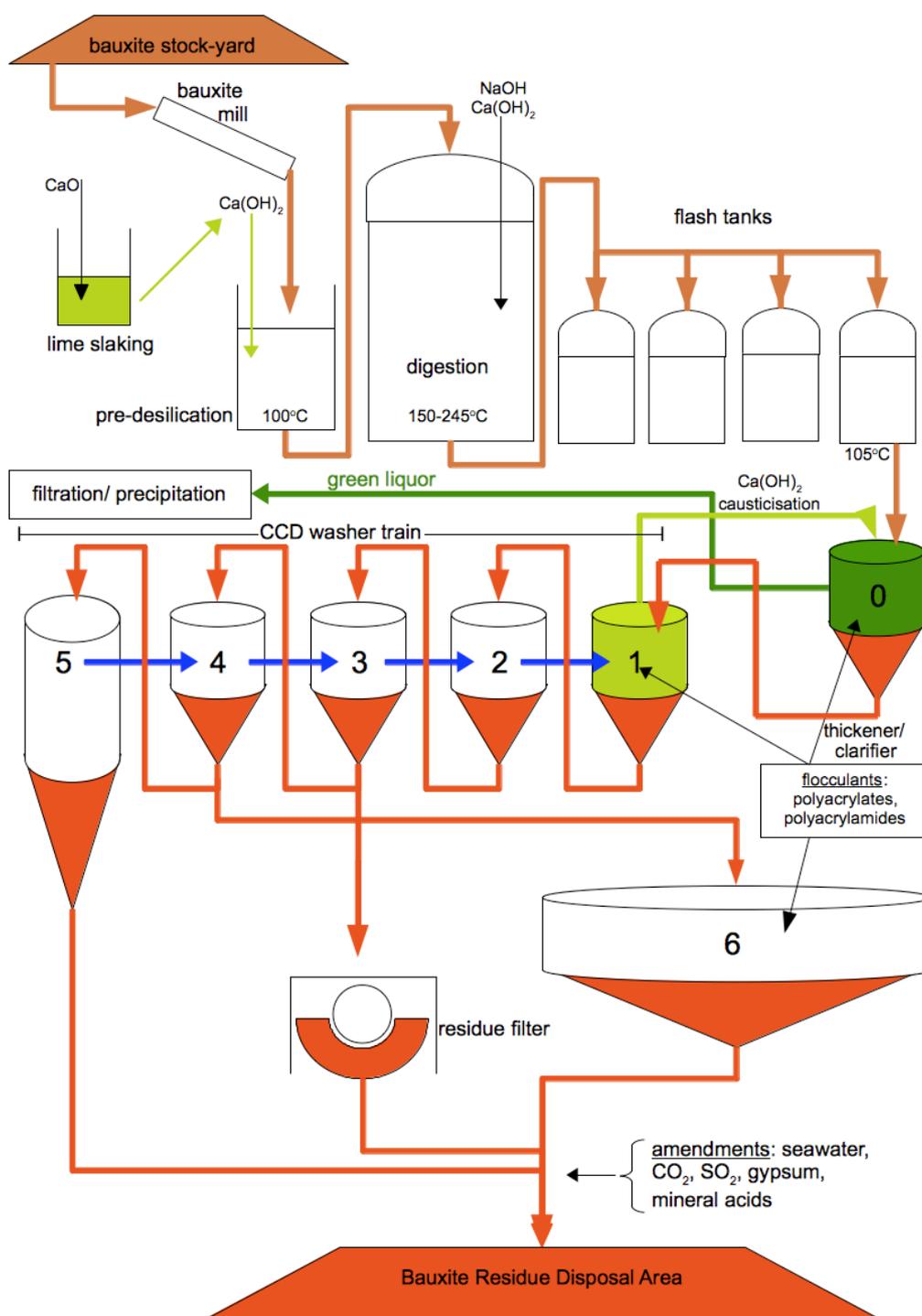


Figure 1: Bauxite residue flow chart indicating places of NaOH , Ca(OH)_2 and flocculant inputs. The blue arrows indicate the direction of the wash water counter-current to the flow of bauxite residues. Adopted with modifications from [22]. For more detail and explanation of the bauxite residue production process, please see [4].

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sodalite. Sodalite and cancrinite are Bayer process characteristic solids (BPCSs) that are disposed with bauxite residues and impart significant acid neutralising capacity onto the residues as a whole, i.e. the residues are alkaline.

Table 2: Bayer Digest Variables [23].

	Gibbsite, Al(OH) ₃	Boehmite, γ-AlOOH
Temperature, °C	140-150	230-250
Pressure, atm	3.0	6.0
NaOH, M	2.4-2.75	3.5-3.75

Table 3: Main elemental and mineralogical composition of bauxites [8]. The minerals are listed in order of general abundance.

Element (as oxides)	content, wt. %			Main mineral phases	Unit cell formula
	Min	Avg	Max		
Al ₂ O ₃	20	26-60	70	Gibbsite	Al(OH) ₃
				Boehmite	γ-AlOOH
Fe ₂ O ₃	0.5	10-35	65	Goethite	α-FeOOH
				Hematite	α-Fe ₂ O ₃
TiO ₂	0.1	2-4	25	Anatase	TiO ₂
				Rutile	TiO ₂
				Ilmenite	TiFeO ₃
SiO ₂	0.1	4-8	15	Kaolinite	Si ₄ Al ₄ O ₁₀ (OH) ₈
				Quartz	SiO ₂

Following bauxite digestion, the NaAl(OH)₄ - rich solution (green or pregnant liquor) is separated (*clarification*) from the remaining solids, i.e., the bauxite residues. The separation process occurs in pressure-decanters [24] or settlers with the aid of flocculants [25-27]. Other additives such as iron oxides [28], slaked lime [29], MgSO₄ [29], and apatite solids [30] are added for specific purposes according to the refinery and bauxite; to minimize the contamination of the green liquor by soluble and colloidal iron, carbonate, organics including oxalate, phosphate and other unwanted impurities. The solids generated from these reactions, e.g. calcite, CaCO₃, tricalcium aluminate (Ca₃Al₂(OH)₁₂), whewellite (CaC₂O₄·H₂O) and/or apatite Ca₁₀[PO₄]₆(OH)₂ become part of the bulk bauxite residue mixture.

After separation from the green liquor, bauxite residues are washed sequentially in counter-current decantation washer trains employing high volume settler tanks to recover entrained NaOH and Al(OH)₄⁻, which are returned to the Bayer process. Flocculants such as polyacrylates and polyamides are used to optimise solid liquid separation. In the final washing step, bauxite residues are thickened to a paste with a specific solids concentration (wt. %) before being sent to bauxite residue disposal areas [4]. Even after repeated washing, bauxite residues remain strongly alkaline, because much of the alkalinity is in form of slowly dissolving solid phases.

In 2007, the majority (~65%) of alumina producers were dry-stacking bauxite residues in land-based disposal areas [4]. Most other refineries used wet lagooning (~20-30 wt. % solids) as their disposal method, but at least two (Gardanne and Alumine de Grece) disposed their residues to the off-shore marine environment [31, 32].

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Several alumina refiners apply a degree of amendment to their bauxite residues. For example, at Queensland Alumina Refinery (QAL, Gladstone, Queensland), bauxite residues are slurried with seawater for pumping the slurry to the BRDA, which has the beneficial side-effect of lowering the pH [33]. Neutralisation by seawater is also practiced at Eurallumina (Sardinia, Italy) and for supernatant liquor at Gove (Northern Territory, Australia) [34, 35]. At Alcoa's Kwinana refinery (Western Australia), bauxite residues are treated with CO₂ prior to disposal to reduce the pH [36], but notably also to improve settling characteristics and shear strength acquisition [37]. In other cases bauxite residues are disposed as dry filter cakes (e.g., Renukoot, 70% solids) [31, 32, 38].

In summary, bauxite residues are highly alkaline solid-liquid mixtures, whose properties are a result of the treatment of bauxite by the application of NaOH, heat and pressure, as well as lime and other chemical additives. Presently, well over 2 Bt of residue exists in land-based disposal areas. In some cases the residue is partly neutralised, but in all cases its overall chemical and physical characteristics inhibit the establishment of vegetation and pose a barrier to many possibilities for reuse.

3. ITEM 5: DETAILED LITERATURE REVIEW OF RESIDUE ALKALINITY AND ASSOCIATED CHEMISTRY

3.1 Characterization Of Bauxite Residues

3.1.1 Physical and mineralogical description of bauxite residues

The identity and quantity of mineral phases in bauxite residues is important to residue alkalinity because some of these minerals impart alkaline conditions in solution. Knowing which and how many of these minerals are present in bauxite residues provides information about the residues' buffering capacity as the minerals dissolve in acid. In addition, physical parameters such as particle size distribution, specific surface area and bulk density are relevant with respect to the reactivity of the solids. For example, specific surface area influences the rates of dissolution reactions, and bulk density relates to the packing density and hence to hydraulic conductivity.

3.1.2 Mineralogy of bauxite residues

Bauxite residues are solid-solution mixtures ranging in solids content from 20 to 80 % by weight depending on the disposal method of the refinery. The elemental abundance in bauxite residues is $Fe > Si \sim Ti > Al > Ca > Na$ (Table 3, Table A2).

Bauxite residues consist on average of approximately 70% (by weight) crystalline phases and 30% amorphous materials (Table B1). Hematite is present in all in bauxite residues with a concentration range of 7% to 29%. Goethite is particularly prevalent in bauxite residues generated from Jamaican and Darling Range bauxites that contain significant amounts of goethite [39, 40] (Figure 2). Magnetite occurs in bauxite residues generated from bauxite with higher levels of boehmite or diaspore that may require sintering with soda to solubilise the Al minerals. Boehmite (γ - $AlOOH$), gibbsite ($Al(OH)_3$), anatase, rutile (both TiO_2), ilmenite ($FeTiO_3$), perovskite ($CaTiO_3$), and SiO_2 are the other minerals commonly present in bauxite residues.

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

Table 4: Elemental and mineralogical composition of bauxite residues. Points of zero charge were taken from [41-44]. Bayer process characteristic solids (BPCSs) are identified by **bold** lettering.

Element (n ^a)	content			Minerals	Unit cell formula	PZC ^b
	Min	avg±std ^c	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	7.5-8.5
				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] ^d	n/d ^f
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] ^c	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
				Perovskite	CaTi ^{IV} O ₃	8.1
				Ilmenite	Ti ^{IV} Fe ^{II} O ₃	n/d
				Calcite	CaCO ₃	8.3
				Perovskite	CaTi ^{IV} O ₃	8.1
CaO (76)	0.6	8.6±9.4	47.2	Whewellite	CaC ₂ O ₄ ^g	n/d
				TCA	Ca ₃ Al ₂ (OH) ₁₂	n/d
				hydro-calumite	Ca ₄ Al ₂ (OH) ₁₂ ·CO ₃ ·6H ₂ O ^h	n/d
				Sodalite	Na ₆ [Al ₆ Si ₆ O ₂₄]·[2NaOH, Na ₂ SO ₄] ^a	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] ^b	n/d
				Dawsonite	NaAl(OH) ₂ ·CO ₃	n/d
LOI (46)	4.4	10.0±2.8	21.1			

^a n = number of samples

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

^c avg±std = average ± standard deviation of the population.

^d Sodalite has between 0 and 6 waters of hydration 22. Whittington, B., The chemistry of CaO and Ca(OH)(2) relating to the Bayer process. *Hydrometallurg.* **1996**, *43*, (1-3), 13-35, 45.

Whittington, B.; Fletcher, B.; Talbot, C., The effect of reaction conditions on the composition of desilication product (DSP) formed under simulated Bayer conditions. *Hydrometallurg.* **1998**, *49*, (1-2), 1-22..

^e Cancrinite has 0 to 2 waters of hydration depending on the ions in the cage 22. Whittington, B., The chemistry of CaO and Ca(OH)(2) relating to the Bayer process. *Hydrometallurg.* **1996**, *43*, (1-3), 13-35.: 0 for 2CaCO₃, 1 for 2NaOH, and 2 for Na₂SO₄.

^f The point of zero-charge for the desilication products sodalite and cancrinite has not been determined yet. As tectosilicates, their PZC may be similar to that of feldspar, ~ 2-2.4.

^g Whewellite is also known as calcium oxalate.

^h After Table 2 and 3 in 46. Vieillard, P.; Rassineux, F., Thermodynamic and geochemical modelling of the alteration of two cement matrices. *Appl. Geochem.* 1992, (**Supp. 1**), 125-136..

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

The Bayer process characteristic solids (BPCSs) contain primarily (in no particular order) Al^{3+} , Ca^{2+} , Na^+ , $\text{H}_3\text{SiO}_4^-/\text{H}_2\text{SiO}_4^{2-}$, OH^- and CO_3^{2-} . These metals (Al, Ca, Na) and ligands (OH , SiO_4 , and CO_3^a) are present in the form of minerals including sodalite, cancrinite, hydrated Ca-silicates, tri-calcium aluminates, hydrocalumites, calcite/aragonite, and sodium carbonates (Table 4). Sodalite is the most common desilication product forming during pre-desilication, while cancrinite may form in the presence of Ca in the elevated temperature regimes during the digestion of boehmitic bauxites. Sodalite concentrations of 16-24% [47] and up to 50% cancrinite [48] 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 due to the addition of lime during the Bayer process, for example as reported for Chinese refineries by Liu [49]. Hydrated Ca-silicates, tri-calcium aluminates, hydrocalumites form from adding slaked lime during digestion and causticisation (Figure 1). 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 . Other minor mineral constituents often found in bauxite residues are ilmenite (FeTiO_3), and kaolinite ($\text{Al}_4\text{Si}_4\text{O}_{10}[\text{OH}]_8$) and in one unusual case [49] imogolite ($\text{Al}_2\text{SiO}_3[\text{OH}]_4$). The presence of kaolinite and imogolite in bauxite residues is an indication of incomplete dissolution during pre-desilication and digestion.

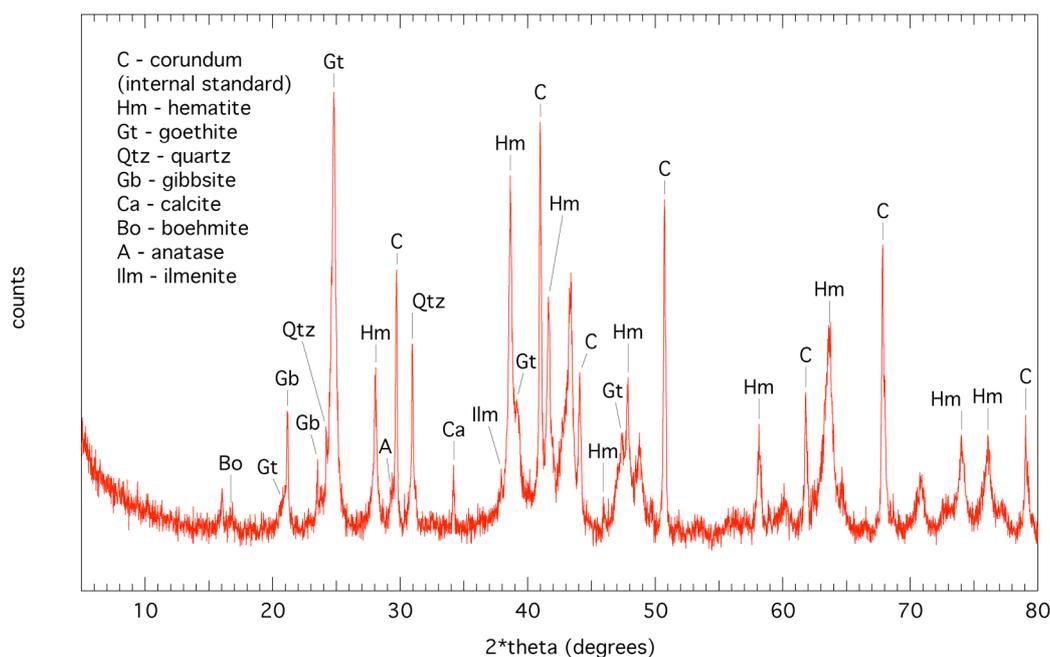
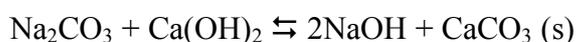


Figure 2: XRD pattern of Worsley bauxite residue. Corundum serves as an internal standard for calibration and determination of amorphous phase content. CSIRO Minerals internal data base. The unassigned peaks refer to sodalite.

^aWhen referring to polyprotic acids/ bases in general terms, we will not provide the pH dependent chemical species, but refer to them in more general terms, e.g., carbonates = CO_3 , silicate = SiO_4 , phosphate = PO_4 . Where speciation is relevant, we provide the appropriate chemical speciation, e.g.: At pH 13, $\text{H}_2\text{SiO}_4^{2-}$ dominates in solution.

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

The elemental abundance and mineralogical composition of bauxite residues in comparison to bauxite (Tables 3 and 4) show that iron is the most abundant metal following the extraction of aluminium-bearing phases, and that the Ti and Si have approximately doubled in relation to the parent bauxite. Phyllosilicate minerals such as kaolinite have converted to desilication products (sodalite and cancrinite), and ferrihydrite and goethite may have either fully or partially converted to hematite. In addition, Na and Ca are two significant components of bauxite residue because they are added during the Bayer process and are only partially removed by the counter-current washing process. The addition of Ca as slaked lime during pre-desilication, digestion and/or causticization and to filters as a filter aid causes the formation of Ca-bearing minerals which report to the residue, including: CaCO_3 , TCA, cancrinite, hydrocalumite and perovskite. One result of this is that less Na^+ is consumed either by minerals (e.g., sodalite vs cancrinite) or as Na_2CO_3 in solution. For example, the causticisation reaction replaces carbonate ions with hydroxyl ions in solution by precipitating the former as calcium carbonate (calcite):



Calcite reports to the bauxite residue, while NaOH is effectively recycled into the Bayer process to digest bauxite. These reactions contribute mineral products in bauxite residues, which are unrelated to the original mineralogy of the bauxite, but which are specific to the chemical inputs to the refinery process.

3.1.3 Physical characteristics of bauxite residues

The particle size of bauxite residues averages 2 to 100 μm with a typical range of 100 nm to 200 μm [50, 51]. It is therefore on average in the *silt* to *fine sand* textural class [52]. Newson et al. [53] reported a particle size range for bauxite residues from the UK (likely Burntisland, Scotland) between 1 and 300 μm with 50% of the particles being larger than 5 μm . Fuller et al. [54] have shown that the texture of the residues can be dependent on the location within the disposal area (Figure 3).

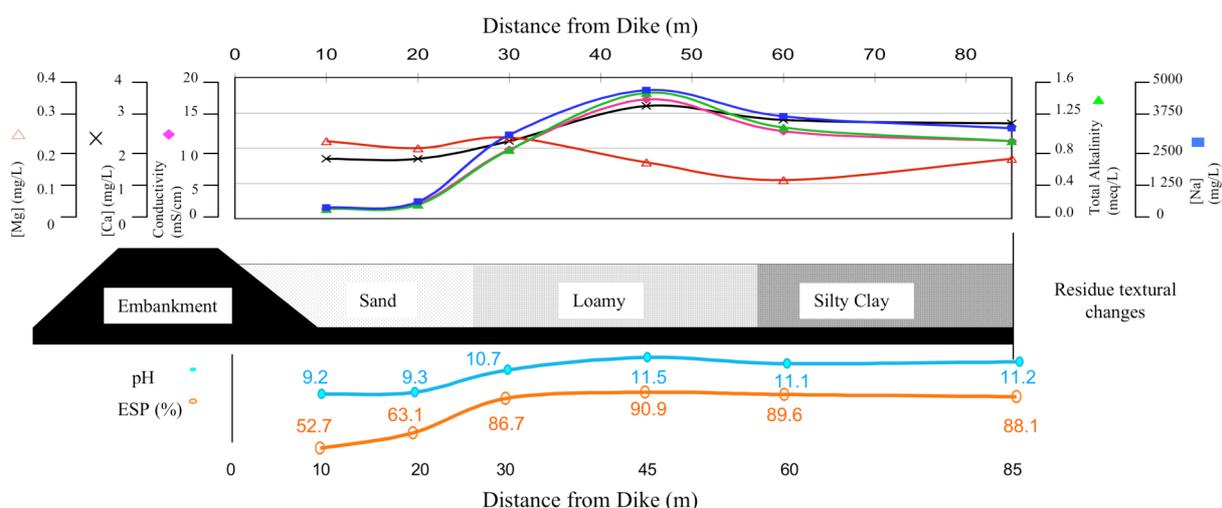


Figure 3: Graphical display of the Mobile refinery's BRDA according to data in [54].

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

In the residue area of the decommissioned Alcoa refinery at Mobile (Alabama, USA), the residues become increasingly finer with increasing distance from the embankment. Ten to twenty metres from the embankment, the residues are sandy (sand, silt, clay % = 76-90, 4-16, 4-8, respectively); 30-40 metres away, they are loamy (sand, silt, clay % = 19-43, 30-43, 26-38, respectively); and at > 50 metres, the residues are silty-clayey (sand, silt, clay % = 5-7, 41-43, 53-54, respectively). The size fractionation with distance from embankment shows that the residues began to separate immediately from the point of discharge near the embankment, suggesting that the residues were disposed of as wet slurries in lagoons rather than as thickened pastes discharged for dry-stacking.

The average bulk density of bauxite residues are reported as $2.5 \pm 0.7 \text{ g cm}^{-3}$. Bulk densities exceeding 1.5 g cm^{-3} impede root penetration and therefore the establishment of plants, and at bulk densities above 1.6 g cm^{-3} healthy plant growth is unlikely. Nikraz et al. [37] 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} . On the other hand, bitters lowered the bulk density to 1.62 g cm^{-3} , at which level root penetration would be possible.

The average specific surface area (SSA) of bauxite residues is $32.7 \pm 12.2 \text{ m}^2 \text{ g}^{-1}$ and ranges between 15 and $58 \text{ m}^2 \text{ g}^{-1}$, which is consistent with the approximate size/distribution and textural class of the residue. This SSA is small in comparison with many soils, particularly with soils that have high amorphous mineral content and/or 2:1 type clays, which have high internal surface areas. Both of these types of minerals are absent in bauxite residues because they are unstable under the digestion conditions in the Bayer process (i.e. they dissolve in digestion).

3.2 Chemicophysical characteristics of bauxite residues

3.2.2 pH: The master variable

Many geochemists call pH the master variable, because most reactions are a partial function of pH and therefore changing the pH can either drive a reaction forward or backward. For example, $\text{Al}(\text{OH})_3 (\text{s})$ is quite stable at pH 7.5, however at pH 4.0 and at pH 13, it will readily dissolve.

The pH in bauxite residue solutions is 11.3 ± 1.0 and ranges between 9.7 and 12.85 (Table A1). The alkaline anions in bauxite residue solution are OH^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, $\text{Al}(\text{OH})_4^-/\text{Al}(\text{OH})_3 (\text{aq})$ and $\text{H}_2\text{SiO}_4^{2-}/\text{H}_3\text{SiO}_4^-$. These anions are the dissolution products of most BPCSs. Thornber and Binet [55] conducted an experiment in which they sequentially exchanged bauxite residues with H_2O . The authors determined that the weight of the solids decreased with sequential washings, but neither the pH, Na^+ , $\text{Al}(\text{OH})_4^-$, CO_3^{2-} nor the OH^- concentration changed in solution. This simple experiment demonstrated that the solution pH of the residues was buffered by alkaline solids, and that the pH did not change until these solids were completely dissolved and their reaction products removed.

3.2.3 Acid neutralising capacity (ANC)

The experiment by Thornber and Binet [55] and that of others [15, 54] also demonstrated that bauxite residues have the ability to neutralise acid. How much acid bauxite residues can neutralise is expressed by their acid neutralisation capacity (ANC), which measures the amount of mineral acid required to reach a specific pH endpoint (Table 1) [49, 56-58]. Figure 4 shows a (redrawn) acid neutralisation capacity curve for bauxite residues from Pinjarra (Alcoa, Western Australia), desilication product (DSP) (probably sodalite) and calcite. The ANC to pH 7.0 of this bauxite residue is about 1.2 mol H⁺ kg⁻¹ of residue, while that of DSP is 2.6 mol H⁺ kg⁻¹. Calcite buffers the pH at 7.0 irrespective of how much acid added.

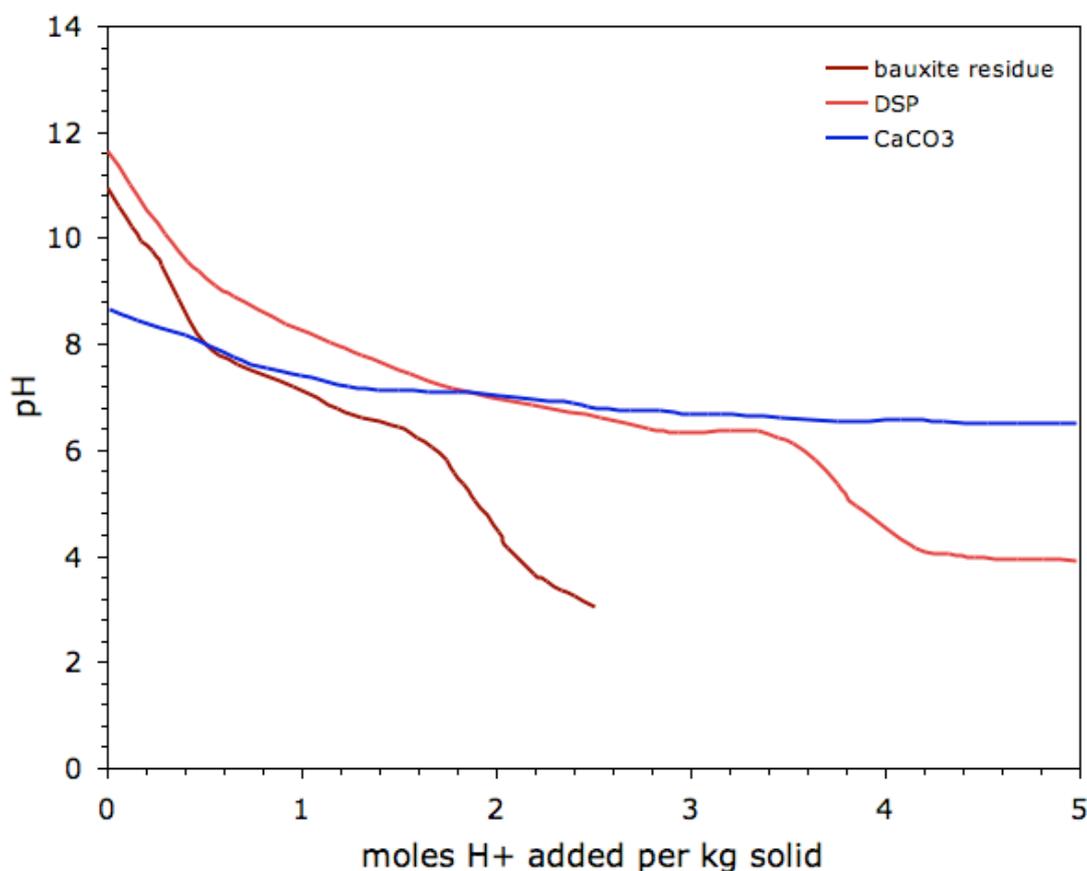


Figure 4: Acid neutralisation capacity curves of Pinjarra bauxite residues, DSP and calcite. Redrawn from [56].

Inflection points on ANC curves indicate complete mineral dissolution and a new phase assuming the buffering role. The length of the plateau is related to the amount of buffer present. DSP exhibits its greatest buffering capacity near pH 7 and an abrupt inflection point near pH 5 as the last of the DSP is dissolved. This result is similar to the findings of Wong and Ho [59] who showed the disappearance of XRD peaks of natrodavyne (a cancrinite group member) at pH 6.3 and its complete disappearance by pH 5.4.

Carter et al. [58] described the ANC of bauxite residues from nine different Alcoa

refineries. The buffering curves of untreated residues showed multiple inflection points suggesting that several solids were buffering the pH. The ANC of the residues to pH 7 ranged from 1 to 3.5 mol H⁺ kg⁻¹ residue, which is greater than the ANC (pH 7) measured previously by Snars et al. [56] for bauxite residues of similar origin. The explanation could be related to the dependency of ANC on the equilibration period used after each acid addition. Thornber and Hughes [60] showed that the change in pH increased significantly as the equilibration period was varied from 1 minute to 5 days, and that the shape of the buffering curve was also highly dependent on equilibration time. Under well-mixed conditions such that reactions are not diffusion limited, the results showed that the neutralisation reaction in solution was instantaneous, while the neutralisation reactions related to the solids were limited by the rates of dissolution of the solid phases. The ANC to pH 7 increased from about 0.2 mol H⁺ kg⁻¹ solids at a 1-minute equilibration period to 1 mol H⁺ kg⁻¹ solids at a 5 day equilibration period.

These results are consistent with the observations made by Liu et al. [49], who found also found that ANC values were higher at longer equilibration times. Using a residue that had not been pre-treated, the authors measured an ANC to pH 5.5 and allowed each acid aliquot to equilibrate initially over a 24-hour period and later in the experiment over several days, before adding additional acid. The experiment was terminated after 780 days and 367 titration steps and recorded an ANC (to pH 5.5) of 10 mol H⁺ kg⁻¹.

These results suggest that the acid neutralisation of bauxite residues is governed by a complex set of reactions that depend on the interplay between multiple solid and solution phases. Consequently, as many researchers have shown, the ANC curves of bauxite residues do not resemble the acid neutralisation behaviour of pure minerals (Figure 4). Unfortunately, data relating dissolution behaviour over time in a specific buffering pH region is absent from the literature, but is critical if a well-founded acid neutralisation model is to be realised to model ANC based on mineralogy.

3.2.4 Sodium (Na⁺)

In clay-water mixtures, Na⁺ is associated with clay dispersal, poor aggregate structure, cementation and dust formation upon drying at the surface [61, 62]. Its presence in significant quantities at alkaline pH is a significant inhibitor to the creation of aggregate structure and hydraulic conductivities 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 and denies plants the uptake of water.

Studies by Fuller et al. [54] on residues from the Alcoa-Mobile (AL, USA) refinery have shown that the concentrations of Na⁺ in solution range between 17 and 200 mmol L⁻¹, exceeding Ca²⁺ and Mg²⁺ concentrations by two to four orders of magnitude. Other studies by Liu et al [49] and Courtney and Timpson [63] showed Na⁺ concentration in solution of 10 and 9 mmol L⁻¹, respectively, exceeding Ca²⁺ and Mg²⁺ concentrations by two to three orders of magnitude. These concentrations are the result of the low solubility of Ca and Mg carbonates above pH 10.

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

The buffering capacity of the residue solids for Na^+ has not been studied in detail [55]. As noted above Thornber and Binet [55] conducted sequential washings of bauxite residues in water and showed that the release of Na^+ was related to the total alkalinity (TA, according to a modified method of Watts and Utley [64, 65]) of the solution extracted after washing. The authors argued that the main source of Na^+ was DSP, where Na^+ was exchanged from the cages of DSP particles. The authors did not mention, however, which cation(s) were substituting for Na^+ , whether DSP was dissolving or what general mechanism was responsible for enabling the “exchange” to occur.

3.2.5 Electrical conductivity (EC)

Electrical conductivity is related to cation and anion concentrations in solution and therefore to the ionic strength of a solution. In the absence of detailed solution data, it is the only feasible quantity to measure to investigate total cation and anion concentrations and to estimate ionic strength. The ionic strength is relevant as it determines the double-layer thickness of charged particles, a property that applies to bauxite residue particles (see next section on point of zero charge), and which in turn relates to physical behavior such as dispersion and coagulation. In bauxite residues, the high EC is due to high Na^+ concentrations in solution and in the solid phases. Calcium, magnesium and other cations do not contribute significantly to the EC as their concentrations are negligible in solution at pH above 10. Anions of relevance in solution are OH^- and SO_4^{2-} .

The 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 1). In amended residues, the EC varies from as low as 0.3 to as high as 60 mS cm^{-1} . Acid neutralised residues tend to have lower ECs, whereas seawater-neutralised residues have higher ECs [15, 47, 56]. Electrical conductivity is related to total cation and anion concentrations in solution, expressed as mmoles of charge per litre, by approximately a factor of 10 [61]:

$$\begin{aligned} \text{Total cations (mmol}_{(+)} \text{ L}^{-1}) &\sim \text{EC (mS cm}^{-1}) * 10 & [1] \\ \text{Total anions (mmol}_{(-)} \text{ L}^{-1}) &\sim \text{EC (mS cm}^{-1}) * 10 & [2] \end{aligned}$$

Marion and Babcock [66] established a similar relationship, which measured the ionic concentration (C, corrected for ion pairs) in solutions as a function of EC, which worked well up to 15 mS cm^{-1} :

$$\text{Log C} = 0.955 + 1.039 \log \text{EC} \quad [3]$$

Due to its relation to total cation and anion concentration, the EC can also be converted to an approximate ionic strength (IS). In natural aqueous solutions, Griffin and Jurinak [67] determined that:

$$\text{IS} \sim 0.0127 * \text{EC} \quad [4]$$

In addition, the EC is related to the quantity of total dissolved solids (TDS, [61]):

$$\text{TDS (mg L}^{-1}) \sim \text{EC (mS cm}^{-1}) * 640 \quad [5]$$

How applicable these relationships are for bauxite residues is not known, but they have worked well for soil solutions, which are similarly complex but not nearly so alkaline. In the absence of detailed solution analysis data, we can estimate that the ionic strength in solution is between 0.02 and 0.4 mol L⁻¹ and on average 0.1±0.08 mol L⁻¹ using equation 5. Taking data from Fuller et al. [54], EC values ranged from 1.4 to 16.9 mS cm⁻¹. Assuming that a quarter of the Na⁺ concentration is balanced by CO₃²⁻ and the remainder by OH⁻, the ionic strength indicated using Griffin and Jurinak's [67] equation is in reasonable agreement (86%) in the absence of a more accurate solution description.

3.2.6 Surface charge

Residue is a mixture of fine-sized heterogeneous solids. Inter- and intra-particle behaviour in the presence of water (and the inherent dissolved salts) is critically dependent on the surface charge of the constituent particles. This affects not only gross macroscopic physical behaviour such as rheology, aggregation and coagulation, but the entire range of particle chemistry including surface hydration, ion-exchange, and redox behaviour. Throughout the report, we have been making references to concepts of surface charge, e.g., point of zero charge (PZC), and double layer thickness. This subject is very complex both from an operational definition point of view (i.e. how it is measured) and how it affects the aggregation and repulsion behaviour of particles. Nevertheless, bauxite residue particles as a mineral mixture carry charge, because the individual mineral components carry charge in solution. In the following paragraph, we briefly explain origins and natures of charge in minerals and mineral assemblies. More detail on this subject may be found in the following references [42, 61, 68, 69].

Charge development in pH-sensitive mineral-solution phases regulates ion exchange and adsorption/desorption reactions of ions at the mineral-water interface. The charged state of the mineral assemblage is therefore a significant regulator for ions participating in the acid neutralisation reactions to either dissolve into or be removed from solution. The nature of the charge is strongly related to its origin: The mineral composition of bauxite residues reveals that *pH-dependent, variably-charged* surfaces exist (Fe-, Al- and Ti-oxides + SiO₂) alongside *permanently, negatively-charged* surfaces stemming from DSPs. Thus, two origins of mineral surface charge are recognised: 1) *variable* or *pH-dependent* charge and 2) *permanent* or *pH-independent* charge.

The origin of charge is either a local (surface) charge imbalance caused by a lack or abundance of H⁺ or a structural charge imbalance caused by the substitution of a host metal centre with a metal of different charge to that of the host metal, e.g. Al³⁺ occupying a Si⁴⁺ site in sodalite (DSP). Permanent charged minerals are either negatively charged (e.g., DSP) or positively charged (e.g., hydrocalumite, hydrotalcite). In un-neutralised bauxite residues, both permanently charged (DSPs) and pH-dependent charge minerals (e.g., metal oxides) are present. In seawater-neutralised bauxite residues, the precipitation of hydrotalcite adds a permanent, positively charged mineral to the residues [70].

DETAILED LITERATURE REVIEW OF RESIDUE CHEMISTRY

The charge stemming from a mineral surface or crystal structure is distributed throughout the oxygen-layer structure of the mineral and extends into solution, where it creates the electric or diffuse double layer. The thickness of this layer is dependent (amongst other things) on ionic strength and therefore on the concentration and charge of the cations and anions in solution.

The composition of the residue solution is hence not only important with respect to pH buffering, but also with respect to how surface charge and electric double layer thickness change [42]. The PZC of bauxite residues has been addressed by only a few studies [71-74] and varies significantly among them due to the different origin of the bauxites, variability in the Bayer process variables, the addition of different types of flocculants and the composition of the background electrolyte. Results by Zhang et al. [73] and Chevdoev et al. [71] suggest that polyacrylate is adsorbing specifically to the surface of red mud particles and thereby decreases the PZC from 8.3 to 7.6 and 7.8 to 6.0, respectively. In contrast, polyacrylamide had little or no effect on the PZC [73]. Even lower PZC (6.0 and 5.3, respectively) values for red mud have been reported by Lopez et al. [74] and Castaldi et al. [47].

For refineries that are lagooning slurries knowledge over where the point of zero charge lies in their bauxite residues can be exploited to help settle bauxite residue particles by promoting coagulation by surface charge neutralisation in high ionic strength solutions. Coagulation operates on a different mechanism from flocculation, because a flocculant requires the cation concentration in solution to bridge the negative charge stemming from the mineral surfaces and the negatively charged polymer [75, 76]. In bauxite residue solutions, which are strongly pH buffered and have high Na^+ concentrations in solution, flocculation is the preferred option of thickening residues as approaching the PZC of the mineral assembly would require permanent neutralisation of the alkaline constituents to maintain the PZC.

Developing an understanding of how surface charge develops, distributes and abates in the residue mineral assemblage as a function of acid input will be paramount to understanding neutralisation reactions overall, to successfully model them, and ultimately to implement the most effective neutralisation measures that create conditions at the surface conducive to plant growth.

4 DISCUSSION

4.1 Alkalinity and buffering

The main contribution to pH buffering is the ability of the solids to maintain the concentration of the alkaline anions in solution. This is known as the *buffering capacity* of the residue and entails alkaline anions that are present in both soluble and solid forms. In order to buffer, the solids need to be soluble to some degree, and some degree of H⁺-acceptance (Brønsted base behaviour with distinct acid dissociation constant, pKa) by the alkaline anion in solution (Table 5) is required. Above pH 10.2 and in the absence of excess Ca²⁺, Na₂CO₃ controls the concentration of HCO₃⁻/CO₃²⁻ in solution, because calcite (CaCO₃) is virtually insoluble. Hence, Na₂CO₃ and other alkaline solids which are more soluble at pH > 10 buffer the solution pH.

In bauxite residues, the main alkaline anions buffering the solution are HCO₃⁻/CO₃²⁻, Al(OH)₄⁻ and OH⁻. Other, less concentrated anions, which may help to buffer the solution pH as well, are H₂SiO₄²⁻/H₃SiO₄⁻/H₄SiO₄, VO₄³⁻/HVO₄²⁻ and PO₄³⁻/HPO₄²⁻/H₂PO₄⁻. Their reactions in solution are summarised in Table 5. The pH region between two pKa values is the buffering region for the Brønsted acid-base pair, e.g., the buffering regime of HCO₃⁻ is around pH 8.3 (the average of 10.2 and 6.35). Al(OH)₄⁻ precipitates rapidly below pH 10 to form gibbsite.

Table 5: Buffering reactions of common weak bases in aqueous solution of bauxite residues [77, 78].

Reaction	Acidity constants
$\text{OH}^- + \text{H}_3\text{O}^+ \rightleftharpoons 2\text{H}_2\text{O}$	$\text{pK}_w = 14.0$
$\text{Al}(\text{OH})_4^- + 2\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightleftharpoons \text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O} (\text{s}) + 2\text{H}_2\text{O}$	$\text{pK}_{a4} \sim 10.2$
$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$	$\text{pK}_{a2} = 10.2$
$\text{HCO}_3^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{CO}_3^* + \text{OH}^-$	$\text{pK}_{a1} = 6.35$
$\text{H}_2\text{SiO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{SiO}_4^-$	$\text{pK}_{a2} = 12.95$
$\text{H}_3\text{SiO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$	$\text{pK}_{a1} = 9.85$
$\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$	$\text{pK}_{a3} = 12.35$
$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^-$	$\text{pK}_{a2} = 7.2$
$\text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_3\text{PO}_4 + \text{OH}^-$	$\text{pK}_{a1} = 2.25$

To enhance the performance of the overall extraction of gibbsite and/or boehmite from bauxite, Ca in the form of slaked lime (Ca(OH)₂) may be introduced at various stages prior to, during and after digestion [22]. This leads to the formation of a number of BPCSs, which impart significant buffering capacity to bauxite residue solutions. The abundance of these solids in bauxite residues is dependent on the exact conditions of the bauxite processing. In the case of boehmitic bauxites, Ca(OH)₂

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increases the dissolution of boehmite at temperatures above 240°C due to the presence of titanium. In the presence of kaolins (kaolinite and or halloysite), which are always present in bauxites, Ca(OH)₂ helps reduce the formation of (hydroxy)sodalite (which constitutes a significant loss of Na⁺ from the digestion liquor) by instead transforming some to cancrinite (Table 6) which reduces the SiO₄ content in solution, thereby producing a pregnant liquor with lower SiO₄ (impurity) content [22]. The addition of Ca(OH)₂ furthermore favours the formation of tri-calcium aluminate, which is a hydrogarnet, which in the presence of SiO₄ transforms to hydro-grossular by the exchange of 4OH⁻ for one SiO₄⁴⁻. The extent of this substitution reaction appears however limited: $n \leq 0.6$ [22]. The lack of reliable dissolution constants and or solubility products in the literature makes it impossible to assess the buffering capacity of most of the BPCSs listed in Table 6. Only from the certain knowledge that the oxide minerals of Fe, Al, Ti and Si are not the solid buffering agents do we know that the BPCSs must be responsible for the buffering. The lack dissolution constants and overall understanding of the dissolution mechanism of BPCSs is a significant knowledge gap.

The solubility product of the BPCSs is particularly important in context of dissolution in water and the contact that this alkaline solution makes with the vertical and horizontal sealants in the residue disposal area. Many of the sealants used are clay based and therefore have the potential to leak in alkaline pH conditions as has been witnessed at the Kwinana (Western Australia) refinery [79]. The safeguarding of the sealants is paramount to maintain the alkaline water within the confines of the disposal area embankments. Therefore a review of the sealants and their stability is warranted to assess the risks posed by alkaline water in contact with them.

The mechanisms and factors controlling the rates of the dissolution reactions are critical, because they determine the rates of replenishment of ions into solution and therefore the timeframes over which neutralisation reactions need to be evaluated. When comparing ANCs of bauxite residues from the literature, it becomes rapidly apparent that the dissolution reactions of the minerals vary considerably. Wong and Ho [59] conducted dissolution experiments of red mud from Kwinana (Alcoa, Western Australia) and showed that the XRD signature of natrodavyne (Na₅Ca₂[Al₆Si₆O₂₄]Cl₂(OH)), a desilication product similar to cancrinite, began disappearing for samples treated to a pH beyond 6.3. This suggests that desilication products are sparingly soluble in water and need to be treated with mineral acids in order to completely dissolve, consistent with Thornber and Binet's [55] theory of Na⁺ exchange, possibly from DSPs, as a source of Na⁺ in solution. In contrast, recent work by Khaitan et al. [80] suggests that DSPs begin dissolving at pH just below 9. The variability of these results confirms the need to understand the mechanisms and factors responsible for the dissolution of alkaline solids present in bauxite residues if effective neutralisation measures are to be devised.

DISCUSSION

Table 6: Dissolution reactions of common buffering solids present in bauxite residues [46, 78, 81, 82].

Dissolution reaction	solubility products ^a
natron-decahydrate	
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} (\text{s}) + \text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+ + \text{HCO}_3^- + \text{OH}^- + 10\text{H}_2\text{O}$	$\text{pK}_{\text{sp}} = 1.31$
calcite	
$\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	$\text{pK}_{\text{sp}} = 8.42 (6.2)^{\text{b}}$
hydrocalumite	
$\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot \text{CO}_3 \cdot 6\text{H}_2\text{O} + 7\text{H}_2\text{O} \rightleftharpoons 4\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 (\text{aq}) + \text{HCO}_3^- + 7\text{OH}^- + 6\text{H}_2\text{O}$	$\text{pK}_{\text{sp}} = \text{n/d}$
tri-calcium aluminate (TCA or hydrogarnet, n = 0)	
$\text{Ca}_3\text{Al}_2[(\text{OH})_{12-4n}](\text{SiO}_4)_n (\text{s}) + \text{H}_2\text{O} \rightleftharpoons 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 + 6\text{OH}^-$	$\text{pK}_{\text{sp}} = \text{n/d}$
hydrogrossular ($0 < n \leq 0.6$ in Bayer process)	
$\text{Ca}_3\text{Al}_2[(\text{OH})_{12-4n}](\text{SiO}_4)_n (\text{s}) + 6\text{H}_2\text{O} \rightleftharpoons 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 + n\text{H}_4\text{SiO}_4 + 6-4\text{OH}^-$	$\text{pK}_{\text{sp}} = \text{n/d}$
hydroxysodalite^c	
$\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{NaOH} + 24\text{H}_2\text{O} \rightleftharpoons 8\text{Na}^+ + 8\text{OH}^- + 6\text{Al}(\text{OH})_3 + 6\text{H}_4\text{SiO}_4$	$\text{pK}_{\text{sp}} = \text{n/d}$
cancrinite^d	
$\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{CaCO}_3 + 26\text{H}_2\text{O} \rightleftharpoons 6\text{Na}^+ + 2\text{Ca}^{2+} + 8\text{OH}^- + 2\text{HCO}_3^- + 6\text{Al}(\text{OH})_3 + 6\text{H}_4\text{SiO}_4$	$\text{pK}_{\text{sp}} = \text{n/d}$

^a $\text{pK}_{\text{sp}} = -\log K_{\text{sp}}$

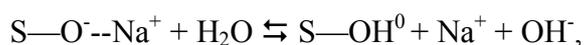
^b Value in parentheses corresponds to dissolution constants in seawater.

^c In *sodalite* 2OH^- are replaced by 2Cl^- ; in *noselite*, 2OH^- are replaced by 1SO_4^{2-} .

^d In *vishnevite*, 2CaCO_3 are replaced by $2\text{Na}_2\text{SO}_4$ and $2\text{H}_2\text{O}$; in *hydroxycancrinite*, 2CaCO_3 are replaced by 2NaOH and $1\text{H}_2\text{O}$.

DISCUSSION

In addition to the dissolution of minerals bearing alkaline anions, exchange reactions occurring at the mineral surface of the metal oxides need to be taken into account [71]. Chevdoev et al. [71] argued that part of the buffering capacity of bauxite residues between pH 9 and 6 can be attributed to the titration of surface hydroxyl (OH^-) groups and that their buffering capacity was significantly enhanced by specifically sorbing polyacrylate flocculants. Hematite, the most abundant of all minerals, has the highest point of zero charge at approximately 9.8 (Table 2). Hence at $\text{pH} > 10$, all mineral surfaces are negatively charged and therefore will repel anions and attract cations to their surfaces. In the absence of alternative cations in solution, hematite may exchange electrostatically bound Na^+ at its surface for a proton and thereby contribute to the buffering capacity of the residues:



where S—O^- is a deprotonated, and hence negatively charged surface site on hematite, whose charge is compensated by an Na^+ ion.

Similar exchange reactions are possible at edge sites of other minerals. As the pH drops below 9.8 (PZC) during acid neutralisation and declines further, the negative surface charge of the residues overall becomes increasingly smaller, and OH^- and other anions in solution become attracted to the surface as the surface charge becomes increasingly positive.

The positions of the point of zero charge reported above for bauxite residues are questionable, because point-of-zero-charge determinations made by point of zero salt effect titrations rely on the assumption that the charging surfaces dissolve only minimally [68]. Bauxite residues have a number of distinctly soluble mineral species as evident from their ANC, which dissolve and re-precipitate over the course of a neutralisation reaction and therefore cannot meet the conditions required for a point of zero salt effect. Charge development in pH-sensitive mineral-solution phases regulates ion exchange and adsorption/desorption reactions of ions at the mineral-water interface. The charged state of the mineral assemblage is therefore a significant regulator for ions participating in the acid neutralisation reactions to either dissolve into or be removed from solution.

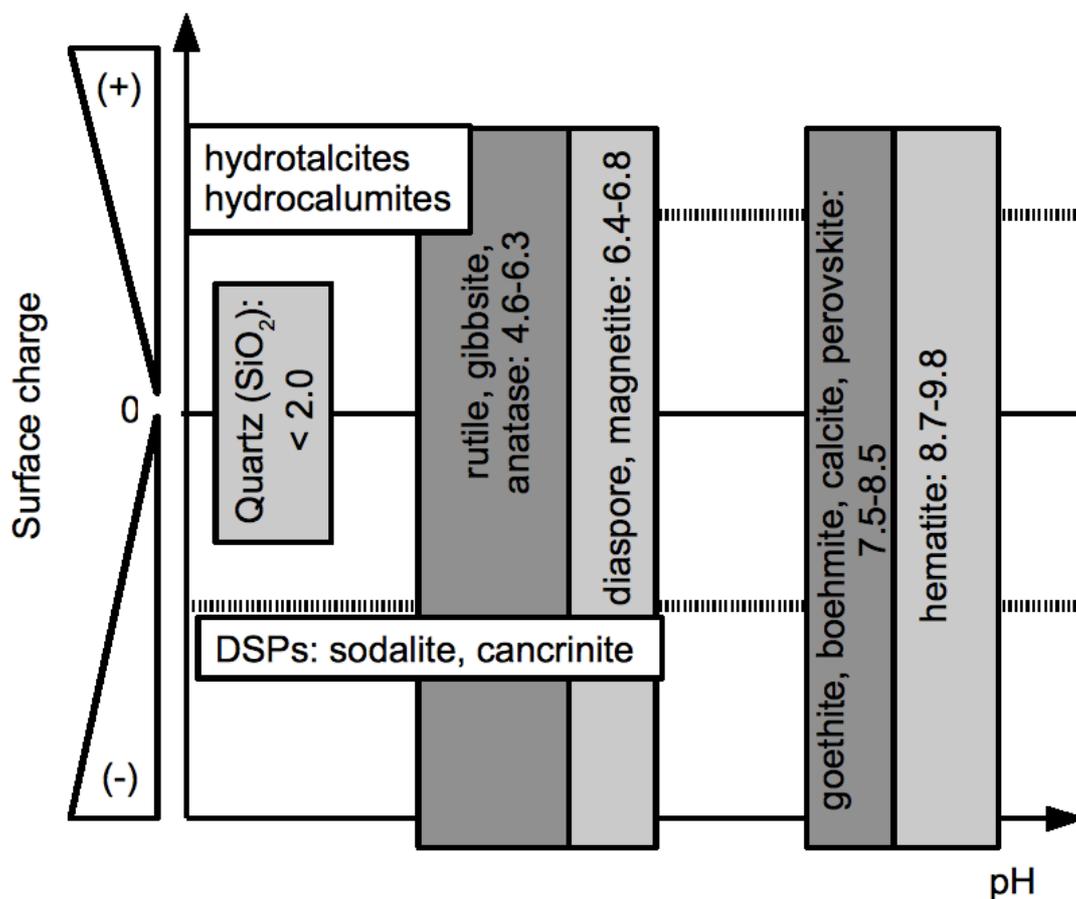


Figure 5: Approximate regions of zero surface charge for individual minerals commonly present in bauxite residues. Hydrotalcites and hydrocalumites, and DSPs have permanent-positive and permanent-negative charge, respectively. The metal oxides (Fe, Al, Ti and Si) have pH dependent charge. pH-dependent charge may also occur at edge sites of DSPs and other permanently charged minerals. A fundamental question is whether surface charge retains an individual mineral character or if it a single value exists for the mineral assembly.

4.2 Alternative means of neutralising bauxite residues

4.2.2 Seawater

Even though Ca^{2+} , Mg^{2+} and HCO_3^- are not the most abundant ions in seawater (Table 5), the addition of seawater to residue lowers the concentration of OH^- and $\text{Al}(\text{OH})_4^-$ in solution due to the precipitation of brucite ($\text{Mg}_3(\text{OH})_6$), calcite/ aragonite (CaCO_3), hydrotalcites ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), aluminohydrocalcite ($\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O}$), hydrocalumite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot \text{CO}_3$), pyroaurite ($\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) among others [83, 84]. Depending to on the solid-to-seawater ratio, the neutralisation proceeds through two to three buffering stages before reaching a pH of 8.2 to 9.0 [84]. This pH regime is further stabilised by the increased solubility of carbonate phases (calcite and aragonite) in seawater [78].

pH neutralisation by seawater operates differently from mineral acid neutralisation in that Ca^{2+} and Mg^{2+} remove alkaline anions from solution as precipitates in place of

DISCUSSION

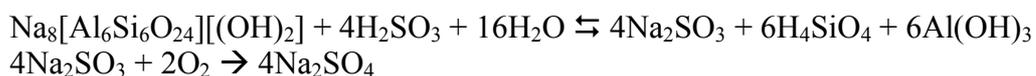
the simple reactions of hydroxide and other alkaline anions that occur with acid. The minerals that are formed (brucite, calcite/ aragonite, hydrotalcites, aluminohydrocalcite, hydrocalumite, and others) exhibit their own buffering capacities according to their solubility products. Effectively, buffering capacity of soluble, alkali species is shifted to the less soluble alkaline species. Therefore the buffering capacity and ANC to pH 5.5 is enhanced through the addition of seawater, in part due to the formation of calcite/aragonite.

Table 7: Composition of seawater for a total salinity of 3.5 wt% [78].

Ion	Concentration (g kg ⁻¹)
Na ⁺	10.77
Mg ²⁺	1.29
Ca ²⁺	0.4121
K ⁺	0.399
Sr ²⁺	0.0079
Cl ⁻	19.354
SO ₄ ²⁻	2.712
HCO ₃ ⁻	0.1424
Br ⁻	0.0673
F ⁻	0.0013
B	0.0045
TOTAL	35

3.2.2 CO₂ and SO₂

Large scale neutralisation of bauxite residues with CO₂ began in 2000 at Alcoa's Kwinana refinery (Western Australia) [36, 85] reaching full capacity to treat all Kwinana residue by 2007 with the construction of a CO₂ pipeline from a nearby ammonia plant [86]. Refineries in Japan (Sumitomo) and Italy (Eurallumina) have been using residue to scrub SO₂ from flue gases, thus neutralising small quantities of residue, since the mid 1970s and early 2000 respectively [35, 36, 87-89]. The neutralisation reactions by either gas phase are based on the diffusion of the gases into solution. In the presence of O₂, Na₂SO₃ oxidizes further to Na₂SO₄ [87, 90]. Prolonged treatment of bauxite residues with SO₂ (g) depletes (free) Na⁺ in solution and increases the H⁺ concentration and thereby contributes to the dissolution of Na-bearing minerals, including the desilication products [35]:



H₂CO₃* is a much weaker acid than H₂SO₃*, with its first dissociation constant at pH 6.35 and the second at 10.2. Khaitan et al. [91] have shown that the pH of bauxite residue slurries treated with CO₂ decreases within 1 day to an apparently stable value, but that it will subsequently increase over time. A 30 day exposure to 1 atm of CO₂ was required to stabilise the pH of the bauxite residue slurries at 7.5. This is explained on the basis that the initial neutralization reaction occurs primarily in the liquid phase, and that the rebounding of the pH is caused by the continuous dissolution of buffering solids, primarily tri-calcium aluminate [36, 91]. The kinetics

DISCUSSION

of these dissolution reactions in the HCO_3^- and H_2CO_3^* stability regions have not been studied in detail. Khaitan et al. [91] and Cooling et al. [36] have suggested that any TCA present in bauxite residue will dissolve during CO_2 treatment and re-precipitate as CaCO_3 and gibbsite, based on results of pure TCA neutralisation by CO_2 [92]. A further observed reaction is the formation of dawsonite ($\text{NaAl}(\text{CO}_3)(\text{OH})_2$), which is stable between pH 4.1 and 7.8 [93]. In addition, HCO_3^- may form inner-sphere surface complexes on amorphous gibbsite, which would contribute to an overall lowering of the point of zero charge of the mineral-solution assemblage. The extent of CO_2 sequestration by a residue body is therefore limited by its soluble Ca-bearing solids, the ability to precipitate with Al and Na, and by additional external inputs, e.g., gypsum, bitterns, to promote the formation of CaCO_3 .

4.2.3 Gypsum

Gypsum (CaSO_4) lowers the pH of bauxite residues by precipitating excess OH^- , $\text{Al}(\text{OH})_4^-$ and CO_3^{2-} as $\text{Ca}(\text{OH})_2$, TCA, hydrocalumite, and CaCO_3 . The pH of a 5 and 8 wt. % gypsum amended bauxite residue is about 8.6 suggesting that the pH of the residue solution is buffered by CaCO_3 as either calcite or aragonite [11, 19]. The soluble product of the reaction is Na_2SO_4 which increases the EC of the residue solution considerably, but which can be leached from the system with water having a lower salinity under adequate drainage conditions.

The efficacy of gypsum in lowering the pH is related to the ability of gypsum to dissolve and release Ca^{2+} into the solution to react with OH^- , $\text{Al}(\text{OH})_4^-$ and CO_3^{2-} . Polcaro et al [94] and Xenidis et al [95] observed that gypsum solubility limited the extent of the pH reaction and only upon activation with H_2SO_4 did the desired pH reductions take place. This limitation may have occurred due to the precipitation of CaCO_3 on gypsum particles as has recently been observed by other researchers [96]. In addition, common ion effects, particle-size and specific surface area control the dissolution rate of gypsum.

4.2.4 Microbial neutralisation

Bauxite residue neutralisation by microbial means has been investigated by a only a small number of researchers despite early results showing significant promise [97-100]. Column studies conducted on bauxite residues from Alcoa's Mobile (AL, USA) plant demonstrated that the pH could be lowered from 13 to 6-7 provided that the bacterial cultures received adequate nutrients, for example in the form of hay or sterile nutrient solutions [100]. Similar results were achieved several years later by Krishna et al. [98] using *Aspergillus tubingensis*. While the exact mechanism of the neutralisation reactions is not fully understood, it is assumed to be a combination of organic acids released by the microbes and the diffusion of the respiratory gases into solution [97]. Bauxite residues incubated at 24°C for 34 days with alfalfa hay showed the presence of lactic, acetic, propanoic and butyric acid ranging from 0.6-1.0 (butyric acid) to 10-14 (acetic acid) g L^{-1} [97] originating from more than 150 cultures of bacteria including *Bacillus*, *Lactobacillus*, *Leuconostoc*, *Micricoccus*, *Staphylococcus*, *Pseudomonas*, *Flavobacterium* and *Endobacter*.

In contrast to the mineral acids, H_2SO_3^* and H_2CO_3^* , weaker organic acids are

DISCUSSION

known to operate in a twofold manner concerning the dissolution of minerals. Proton promoted dissolution can be enhanced by the chelation of the released metal with excess organic acids in solution thereby lowering the activity of the free metal in solution. Alternatively, specific adsorption of the organic acid to the surface of the solid can destabilise bonds between the surface metal and the bulk mineral by either ligand-to-metal or metal-to-ligand charge transfers and ultimately promotes the dissolution of metals at the surface [42].

The neutralisation of bauxite residues using micro-organisms is significant in four ways:

- 1) The neutralisation is continuously controlled by a biological entity rather than the application of an acid;
- 2) The pH is buffered by microbes as long as they are provided with nutrients rather than buffering being controlled by the dissolution of alkaline bearing solids;
- 3) The bulk structure of the solids is improved due to the presence of microbes, which improves drainage, nutrient exchange, and the chances for establishing a plant cover;
- 4) Microbes are an integral component of functioning rhizospheres of plants covering mine and residue spoils.

Bauxite residues treated with alfalfa hay showed survival of red wigglers and night crawlers for up to 300 days in addition to various plants including poplar, monkey and pampas grass [97]. Based on these results, there is considerable potential to optimise bauxite residue neutralisation by micro-organisms and combine it with a revegetation program.

4.3 Na⁺ and its effect on structure

The high concentration of exchangeable sodium (Na⁺) relative to divalent cations, in particular Mg²⁺ and Ca²⁺, is of major concern given the strong association to colloidal dispersion, which gives rise to poor structural characteristics including swelling, surface crusting/sealing, and erosion [61]. Because of the single positive charge on Na⁺ and its high solubility in water, Na⁺ ions do not dehydrate as readily as divalent cations, indicative of very stable hydration layers. In addition, sodium ions do not coordinate readily among themselves (e.g., sharing water or OH⁻ molecules among Na⁺ ions) or with negatively charged surfaces. The effect is that particles do not aggregate well and usually tend to be massive and crusted in the dry state as Na⁺ eventually precipitates out as nahcolite or trona (Na₂CO₃ species), which concurrently leads to the formation of dust at the surfaces of residues disposal areas [62]. Poor structural conditions at the surface are ultimately also detrimental to the revegetation of bauxite residues [54, 63, 101, 102]. The sodium adsorption ratio (SAR) is frequently used in agriculture to delineate whether a soil is sodic or non-sodic.

$$\text{SAR} = [\text{Na}^+]/([\text{Ca}^{2+} + \text{Mg}^{2+}] * 0.5)^{0.5}; \quad [6]$$

Where the [concentration] values are in mmol L⁻¹. A SAR of > 15 is indicative of the soil to be sodic. The SAR is related to the exchangeable sodium percentage by:

$$0.015\text{SAR} = \text{ESP}/(100-\text{ESP}) \quad [7]$$

DISCUSSION

Soils with an ESP > 30 are impermeable and would restrict plant growth and root penetration considerably. Studies by Fuller et al. [54] on residues from Mobile (LA, USA) have shown that the concentration of Na⁺ in solution can exceed that of Ca²⁺ and Mg²⁺ by two to four orders of magnitude. An SAR of 76 in the sandy layers near the embankment and SAR values of 673, 45 metres away from the embankment in the silty clayey layers have been measured. The corresponding ESP values range from 53 to 91. Other researchers [63, 102] have also shown SAR/ESP values significantly exceeding 30.

Poor hydraulic conductivity is one of the main consequences of high ESP values. Hydraulic conductivity measurements of unamended bauxite residues range between 0.2 and 0.3 mm hr⁻¹ with an average void ratio, *e*, of 1.6-1.7 [21, 37]. Neutralisation measures have mostly had limited success in improving hydraulic conductivity, however bitterns treated residues seem to have higher hydraulic conductivities (0.4 mm hr⁻¹) than untreated residues and higher void ratios (*e* = 2.3-2.9) [37].

In addition to lowering the pH, seawater and gypsum lower the SAR due to an increase in exchangeable Ca²⁺ and Mg²⁺ in solution and a decrease of exchangeable Na⁺ [63, 103]. The latter reflects on the one hand the greater preference for Mg²⁺, Ca²⁺ and K⁺ on the exchange complex than for Na⁺ (Helfferich's series [104-107]), on the other hand it is also possibly a coating effect of neo-precipitates blocking DSPs and other exchangeable Na⁺ sources [83, 84]. The net effect of such reactions should be a marked improvement in residue structure and the creation of viable pore networks, which improve the hydraulic conductivity of the residues [11, 18].

5 SUMMARY AND CONCLUSIONS

5.1 Summary

The chemistry of bauxite residues is dominated by the presence of multiple alkaline solids, which impart significant acid neutralising capacity. The pH in BR solutions is 11.3 ± 1.0 and ranges between 9.7 and 12.85. Thus BRs are highly alkaline, hazardous, and will not support plant life. The alkaline pH of BRs is strongly buffered by the presence of alkaline solids (hydroxides, carbonates and aluminates) that are formed by the action of caustic soda on bauxite in the Bayer process refinery, leading, among other, to the formation of Bayer process characteristic solids (BPCSs). The buffering action of multiple BPCSs causes the acid neutralisation behaviour of BRs to be highly complex. It is impractical to remove the alkalinity from BR by washing with water or mineral acids. Ultimately, however, the alkalinity of BRs needs to be abated because it has profound implications for all aspects of BR, including: storage requirements, raw materials usages and recoveries, neutralisation, sedimentation rates, bulk density, compaction, hydraulic conductivity, drying rates, dusting behaviour, and physical strength after drying.

5.2 Knowledge Gaps

Future progress on improved storage practices, remediation, rehabilitation and reuse will be dependent upon the development of better understanding of the complex buffering and neutralisation chemistry of BR. Developing an understanding of how surface charge develops, distributes and abates in the residue mineral assemblage as a function of acid input will be paramount in order to understand neutralisation reactions overall, to successfully model them, and ultimately to implement the most effective neutralisation measures that create conditions at the surface conducive to plant growth. Support for fundamental research to develop of a model for the neutralisation behaviour of bauxite residue based on an understanding of the underlying mineralogy and its relationship to surface charge is warranted. Data relating dissolution behaviour over time in specific buffering pH regions is absent from the literature, but is critical if a well-founded, mineralogy-based acid neutralisation model is to be realised. Support for the establishment of a comprehensive data set relating to the dissolution behaviour of bauxite residue specific solids is warranted.

The reactivity and longevity of the naturally-occurring and synthetic sealants that are used to improve the security of bauxite residue storage areas in relation to leaching of alkaline waters to ground and surface waters are not well documented in the literature. Support for a review of the sealants and research on their reactivities under accelerated test conditions would be appropriate.

The establishment of techniques for creating self-managing, sustainable ecosystems from bauxite residue impoundments is the most realistic solution to the large and increasing inventory (currently 2.7 Bt increasing to 4 Bt by 2015) of bauxite residue globally. Applied research to support implementation in the following areas is

SUMMARY AND CONCLUSIONS

required as a matter of priority:

- Microbiologically assisted bio-remediation of bauxite residues;
- Hydrological modelling of liquid flow in bauxite residues impoundments;
- Optimised amendments for the development BR structure conducive to plant growth;
- Effective vegetative covers in bauxite residue disposal areas; and
- Best agronomic practices for managing vegetative covers overlying bauxite residue disposal areas.

Bauxite residues are known to contain a range of trace metals and NORMs, but little is known of their mineralogy, chemical speciation or leaching behaviour, especially in relation to neutralisation. A significant research effort is needed to provide the basic information about the speciation of these constituents for evaluation of long-term storage practices, remediation and rehabilitation strategies, and reuse options. Support for research in this area is warranted.

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APPENDIX A

Physical and Mineralogical Characteristics of Bauxite Residues

Table A1: Physical characteristics of bauxite residues.

Reference	Bauxite Origin	Refinery	neutralisation or treatment	BD, G_s ¹ g/cm ³	void ratio (e)	SSA ² m ² /g	PZC ³ pH, σ_0
[1, 2]	Darling Range	Kwinana	10 wt % gypsum			23	
[1, 2]	Darling Range	Kwinana	10 wt % gypsum, 4 years age			24	
[1, 2]	Darling Range	Pinjarra	5 wt % gypsum + leaching			26	
[3]	Weipa	Eurallumia	acid			25.2	5.3
[4]	Ghana	Burntisland	acid		1.75		
[5]	Darling Range	Pinjarra	acid			29.9	
[1, 2]	Darling Range	Kwinana	bitterns			27	
[6]	Darling Range	Kwinana	bitterns, winter	1.62	2.84		
[1, 2]	Darling Range	Kwinana	CO ₂			19	
[6]	Darling Range	Kwinana	CO ₂ , summer	1.8	1.97		
[6]	Darling Range	Kwinana	CO ₂ , winter	1.75	1.78		
[1, 2]	Darling Range	Pinjarra	dilute acid			30	
[5]	Darling Range	Pinjarra	gypsum + leaching			26.2	
[7]	China	Chalco	hot water, acid, DDI ⁴			14.34	8.25
[7]	China	Chalco	hot water, acid, DDI, Na-polyacrylate			10.1	7.6
[7]	China	Chalco	hot water, acid, DDI, polyacrylamide			11.88	8.24
[8]	Guinea, South Africa	Aughinish	none	2.75			
[9]	ex Yugoslavia	Birac Alumina	none	3.05			
[3]	Weipa	Eurallumia	none				5.1
[10]	Weipa	laboratory	none	2.9			6.5
[10]	Claremont, Jamaica	laboratory	none	3.5			7.8
[10]	Boke+Brazil	laboratory	none	3			
[11]	unknown	Mobile	none			48.7	
[11]	unknown	Corpus Christi	none			18.9	
[12]	unknown	unknown	none	3.47		22.2	

1 BD = bulk density, G_s = specific gravity

2 SSA = specific surface area

3 PZC = point of zero charge

4 DDI = double deionised water

APPENDIX A

Reference	Bauxite Origin	Refinery	neutralisation or treatment	BD, G _s g/cm ³	void ratio (e)	SSA m ² /g	PZC pH, σ ₀
[13]	unknown	unknown	none	2.9			
[14]	unknown	San Ciprian	none			14.3	6.9
[4]	Ghana	Burntisland	none	1.75 3.05	1.78		
[15]	Greece	Alumine de Grece	none	2.9		34	
[16]	unknown	S. Korean refinery	none	0.7			
[17]	Weipa	Eurallumia	none			58	
[5]	Darling Range	Pinjarra	none			29	
[1, 2]	Weipa	Eurallumia	none			27	
[1, 2]	Weipa	QAL	none			25	
[1, 2]	unknown	Corpus Christi	none			24	
[1, 2]	unknown	San Ciprian	none			25	
[1, 2]	unknown	VAW Stade	none			15	
[18]	unknown	Arkansas, USA	none			27	
[18]	unknown	Suriname	none			21	
[18]	Darling Range	Pinjarra	none			23	
[19]	unknown	Arvida	none			29	
[20]	Darling Range	Kwinana	none			25	
[21, 22]	Darling Range	Kwinana	none			25.5	
[10]	Claremont, Jamaica	laboratory	none, 190 ppm Nalco 9779 & Alclar 665	3.2		26.8	6
[23]	unknown	Mobile	none, 20 m from dike				
[10]	Boke+Brazil	laboratory	none, 200 ppm Alclar 665 & 663	3		20	6
[10]	Weipa	laboratory	none, 50 ppm Nalco 9779	3		21.9	6
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM1	3.99			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM2	3.87			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM3	3.74			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM4	3.69			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM5	3.66			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM6	3.7			
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM7	3.83		33	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM1	3.67		50.4	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM2	4.17		40	

APPENDIX A

Reference	Bauxite Origin	Refinery	neutralisation or treatment	BD, G _s	void ratio (e)	SSA	PZC
				g/cm ³		m ² /g	pH, σ ₀
[25]	Jamaica	laboratory	none, Nalco 7879, JHM3	3.75		46.6	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM4	4.22		47.4	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM5	2.92		46.7	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM6	3.94		41.6	
[6]	Darling Range	Kwinana	none, summer	1.87	1.72	51.7	
[6]	Darling Range	Kwinana	none, winter	1.82	1.57	19.2	
[26]	China	Pingguo	normal Bayer Process			44.8	
[27]	Weipa	QAL	partly-neutralised			22	
[28]	Weipa, Bintan	Tomakomai Works	red mud			44.5	
[29, 30]	Weipa	QAL	red mud			32.65	
[28]	Weipa, Bintan	Tomakomai Works	red sand			12.2	
[31]	China	Shanxi	unknown			73	

APPENDIX A

Table A2: Elemental composition of bauxite residues determined by XRF.

Reference	Bauxite		neutralisation or treatment	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	CaO	Na ₂ O	LOI ⁵
	Origin	Refinery								
[32]	unknown	unknown	acid	17.58	37.26	16.94	5.55	4.38	8.31	7.17
[4]	Ghana	Burntisland	acid	17.04	51.75	21.02	8.36	0.19	0.67	
[26]	China	Zhengzhou	Bayer Process + limestone		12.5	19.9	6.7	41.6	2.4	
[7]	China	Chalco	hot water, acid, DDI-H ₂ O	18.36	6.81	14.49	10.45	25.22	5.53	
[33]	Turkey	Seydisehir	none	20.24	39.84	15.27	4.15	1.8	9.43	8.79
[8]	Guinea, South Africa	Aughinish	none	23.6	30.6	9.65	17.85	6.4	5.3	10.1
[34]	Turkey	Seydisehir	none	20.24	39.84	15.24	4.15	1.8	9.43	
[34]	Guinea	Aughinish	none	23.6	30.4	9.65	17.85	6.4	5.3	
[9]	ex Yugoslavia	Birac Alumina	none	14.14	48.5	11.53	5.42	3.96	7.5	7.25
[11]	unknown	Point Comfort	none	17.8	40	9.59	8.48	7.57	2.69	10.3
[11]	unknown	Mobile	none	19.4	26.4	10.2	9.4	n/a	5.4	
[11]	unknown	Gramercy	none	15	51.5	1.7	6.7	7	0.97	9.3
[11]	unknown	Corpus Christi	none	8.89	52.5	4.48	6.64	10.85	3.17	8.46
[12]	unknown	unknown	none	19.2	47.3	7.5	8.3	3.8	4.3	8.7
[13]	unknown	unknown	none	15	30	8	18	10	4	12
[14]	unknown	San Ciprian	none	20.1	31.8	6.1	22.6	4.8	4.7	8.7
[4]	Ghana	Burntisland	none	23.43	36.31	18.25	5.97	4.38	12.36	
[15]	Greece	Alumine de Grece	none	15.6	42.5	9.2	5.9	19.7	2.4	
[16]	unknown	S. Korean refinery	none	23.7	16.6	22.9	6.7	6.7	11.6	
[35]	Weipa	Eurallumia	none	18	41.8	9.98	8.87	5.57	6.47	8.7
[36]	Turkey	Seydisehir	none	17.27	37.72	17.1	4.81	4.54	7.13	10.22
[17]	Weipa	Eurallumia	none	20	35.2	11.6	9.2	6.7	7.5	7.3
[18]	Darling Range	Pinjarra	none	17.1	36.2	23.8	3.9	3.9	1.6	10.4
[18]	unknown	Arkansas	none	23.1	10.1	23.1	3.6	47.2	3.6	4.4
[18]	unknown	Suriname	none	24.3	33.4	16	3.6	5	8	14
[19]	unknown	Arvida	none	20.6	31.6	8.9	6.2	1.7	10.3	21.1
[37]	Greece	Alumine de Grece	none	15.85	48	6.96	7.06	14.84	3.26	
[38]	Greece	none	none	16.94	39.34	6.95	4.79	13.2		
[23]	Southern Brazil	laboratory	none, Nalco 7879, BM1	6.8	71.9	1.35	7.8	3.2	0.4	10.4
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM2	7.9	65.3	0.6	10.9	5	0	12.8
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM3	10.8	64.6	0.8	8	2.9	0.1	10.5
[24]	Southern	laboratory	none, Nalco 7879, BM4	12	62.2	2.3	9.1	3.2	0.7	9.5

5 LOI = loss on ignition measured between 900 and 1100°C.

APPENDIX A

Reference	Bauxite Origin	Refinery	neutralisation or treatment	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	CaO	Na ₂ O	LOI	
	Brazil										
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM5	9.4	61.7	3.4	10.4	4.2	1.5	12.5	
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM6	13.5	60.4	0.8	9.3	3.2	0.4	8.1	
[24]	Southern Brazil	laboratory	none, Nalco 7879, BM7	7.8	65.7	3.8	9.7	3.6	1.4		
[24]	Jamaica	laboratory	none, Nalco 7879, JHM1	8.16	53.5	0.8	10.9	14.8	0.3	11.6	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM2	2.34	62.1	1.3	12.9	15.9	0.8	4.6	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM3	7.46	57.8	0.6	11.9	11.3	0.3	10.7	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM4	2.12	64.2	0.7	13.3	14.2	0.6	5	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM5	6.13	59.1	0.6	12.1	13.4	0.4	8.3	
[25]	Jamaica	laboratory	none, Nalco 7879, JHM6	5.98	59.4	0.6	12.9	13.2	0.4	7.6	
[26]	China	Pingguo	normal Bayer Process	26.8	26.9	13.1	7.3	23.5			
[28]	Weipa, Bintan	Tomakomai Works	red mud	17.9	45.3	12.4			6.9		
[28]	Weipa, Bintan	Tomakomai Works	red sand	19.6	53.9	12.8			2.0		
[35]	Weipa	Eurallumia	seawater	17.9	30.5	9.58	8.61	7.77	12.1	12.4	
[39]	Turkey	Seydischir	unknown	19.1	37.6	15.7	4.9	2.4	9.5	7.8	
[40]	China	Shandong	unknown	6.9	12.8	19.1	3.43	46.0	2.37	5.73	
[41]	India	Renukoot	unknown	21.9	28.1	7.5	15.6	10.2	4.5	12.2	
[41]	Hungary	Ajka	unknown	14.8	42.1	13.5	5.2	6.1	8.9	8.2	
[41]	Darling Range	Pinjarra	unknown	17.1	36.2	23.8	3.9	3.9	1.6	10.4	
[41]	India	Muri	unknown	24.3	24.5	6.2	18.0		5.3		
[41]	India	Korba	unknown	19.4	27.9	7.3	16.4	11.8	3.3	12.6	
[41]	India	Damanjodi	unknown	14.8	54.8	6.4	3.7	2.5	4.8	9.5	
[41]	India	Belgaum	unknown	19.2	44.5	7.0	13.5	0.8	4.0	10.0	
[41]	unknown	Gramercy	unknown	15.0	51.5	1.7	6.7	7.0	1.0	9.3	
[41]	unknown	Pocos de Caldas	unknown	21.9	29.6	17.5	4.4	2.9	8.3	11.5	
[41]	Virgin Islands	St. Croix	unknown	33.0	22.9	8.5	12.9	3.5	6.0	12.4	
[41]	unknown	Arvida	unknown	28.4	27.4	14.3	9.8	1.3	8.8	9.9	
[41]	Jamaica	Kirkvine	unknown	13.2	49.4	3.0	7.3	9.4	4.0	12.5	
[42]	unknown	Gramercy	unknown	14.6	48.9	2.7	6.9	9.1	1.5	11.6	
[42]	unknown	Corpus Christi	unknown	11.7	47.8	5.4	6.4	8.7	2.7	12.8	
[42]	unknown	Point Comfort	unknown	20.3	32.7	9.3	8.9	6.8	7.4	13.0	
[31]	China	Shanxi	unknown	7.3	6.8	13.9	2.5	33.9	2.7		

APPENDIX A

Appendix A References:

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APPENDIX B

Mineralogical Composition of bauxite residues

Table B1: Mineralogical composition of bauxite residues.

Reference	Bauxite Origin	Refinery	neutralisation or treatment	hematite	goethite	magnetite	diaspore	boehmite	gibbsite	quartz	rutile	anatase	sodalite	cancrinite	calcite	kaolinite	imogolite	perovskite	ilmenite	TCA	hydrocalumite	other	amorphous
				$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-FeOOH}$	Fe_3O_4	$\alpha\text{-AlOOH}$	$\gamma\text{-AlOOH}$	$\text{Al}(\text{OH})_3$	SiO_2	TiO_2	TiO_2	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{OH})_2]$	$\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{CaCO}_3$	CaCO_3	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	$\text{Al}_2\text{SiO}_3(\text{OH})_4$	CaTiO_3	FeTiO_3	$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	$\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot \text{CO}_3$		
[1]	China	Zhengzhou	aged 10 yr.	7.6	no	0	no	no	no	no	no	no	no	no	yes	no	no	11.5	no	no	no	illite	20.7
[1]	China	Zhengzhou	aged 5 yr.	8.2	no	7.8	no	no	no	no	no	no	no	no	yes	no	no	10.9	no	no	no	illite	24.6
[1]	China	Zhengzhou	Bayer Process + limestone	7	no	5	no	no	no	no	no	no	no	no	yes	no	no	11	no	no	no	illite	22
[1]	China	Zhengzhou	normal Bayer	7.4	no	8	no	no	no	no	no	no	no	no	yes	no	no	10.2	no	no	no	illite	20.8
[1]	China	Pingguo	Process	19	no	no	no	no	no	no	3	no	no	no	no	no	32	no	10	no	no		22
[2]	Darling Range	Kwinana	none	yes	yes	no	no	yes	yes	yes	no	yes	yes	no	yes	no	no	no	no	yes	no	muscovite	n/d
[3]	Darling Range	Kwinana	none	8.7	24.3	no	no	1.3	no	4.9	no	0.3	2.7	no	11.2	no	no	no	no	no	no	muscovite (5.8)	48.3
[4]	Ghana	Burntisland	acid	16.1	23.8	no	no	no	no	1.3	5.4	no	no	no	no	no	no	no	no	no	no	n/d	51
[4]	Ghana	Burntisland Alumine de	none	13.5	21.8	no	no	no	no	1.2	4.6	no	17.5	no	no	no	no	no	no	no	no	muscovite	38.2
[5]	Greece	Grece	none	yes	no	yes	yes	no	no	no	yes	no	yes	no	yes	no	no	yes	no	no	no	calcium silicate	n/d
[6]	Guinea, South	Aughinish	none	yes	yes	no	no	yes	yes	yes	yes	no	yes	yes	no	no	no	yes	no	yes	no	n/d	n/d
[7]	Africa	Aughinish	none	yes	yes	no	no	yes	yes	yes	yes	no	yes	no	no	no	no	yes	no	yes	no	n/d	n/d
[8]	India (Bihar)	Renukoot	causticised	13.8	7.3	no	0.5	9.6	1	no	1.1	11	2.3	0	1	no	no	0	no	no	no	hydrogrossular	n/d
[8]	India (Bihar)	Renukoot	none	22.2	10.9	no	0.6	1	3	no	1.8	3.8	3.7	4.7	1	no	no	1.1	no	no	no	NaTiO ₃	n/d
[9]	Jamaica	Arvida	none	yes	yes	no	no	yes	yes	no	no	yes	yes	no	yes	no	no	no	no	no	no	no	

APPENDIX B

Reference	Bauxite Origin	Refinery	neutralisation or treatment	hematite	goethite	magnetite	diaspore	boehmite	gibbsite	quartz	rutile	anatase	sodalite	cancrinite	calcite	kaolinite	imogolite	perovskite	ilmenite	TCA	hydrocalumite	other	amorphous
				$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-FeOOH}$	Fe_3O_4	$\alpha\text{-AlOOH}$	$\gamma\text{-AlOOH}$	$\text{Al}(\text{OH})_3$	SiO_2	TiO_2	TiO_2	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{OH})_2]$	$\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{CaCO}_3$	CaCO_3	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	$\text{Al}_2\text{SiO}_3(\text{OH})_4$	CaTiO_3	FeTiO_3	$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	$\text{Ca}_x\text{Al}_2(\text{OH})_{12} \cdot \text{CO}_3$		
[9]	Jamaica	Kirkvine	none	yes	yes	no	no	yes	no	no	no	yes	no	no	yes	no	no	no	no	no	no	bayerite	n/d
[6]	Turkey	Seydisehir	none	yes	yes	no	no	yes	yes	yes	yes	no	yes	yes	no	no	no	no	no	no	no	calcium silicate	n/d
[10, 11]	Turkey	Seydisehir	none	yes	no	no	yes	yes	yes	no	no	no	no	yes	yes	no	no	no	no	no	no	n/d	n/d
[12]	Weipa	Eurallumia	acid	27	no	no	no	5	4	no	no	5	24	29	no	no	no	no	no	no	no	n/d	n/d
[13]	Weipa	Eurallumia	none	yes	no	no	no	yes	yes	yes	yes	yes	no	yes	no	no	no	no	no	no	no	bayerite, chantalite	n/d
[14]	Weipa	Eurallumia	none	27	no	no	no	9	3	2		3		51	no		no	no	no	no	no	5	n/d
[12]	Weipa	Eurallumia	none	29	no	no	no	6	5	no	no	5	16	33	no	no	no	no	no	no	no	n/d	n/d
[15]	Weipa	QAL	seawater	yes	no	no	no	yes	yes	yes	no	no	yes	yes	yes	no	no	no	no	yes	yes	brucite, whewellite	n/d

APPENDIX B

References for Appendix B:

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Chemical Characteristics of bauxite residues

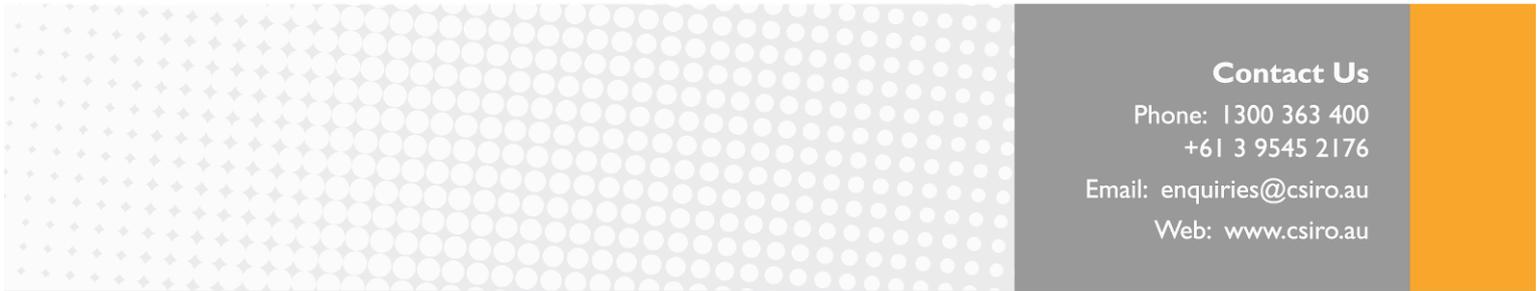
Table C1: Chemical characteristics of bauxite residues

Reference	Bauxite Origin	Refinery	neutralisation or treatment	pH	EC	mmol ₍₊₎ /L				SAR	ESP	CEC	ANC pH 7.0	ANC pH 5.5
						Na	Ca	Mg						
[1]	Darling Range	Kwinana	10 wt % gypsum	11.4	8.5								1.04	
[1]	Darling Range	Kwinana	10 wt % gypsum, 4 years age	10.7	0.72								0.52	
[1]	Darling Range	Pinjarra	5 wt % gypsum + leaching	9.2	2.4								0.88	
[2]	Weipa	Eurallumia	acid	7	0.3						98.2			
[3]	Darling Range Jamaica,	Pinjarra	acid	7.5	0.74								0.45	
[4]	Africa Jamaica,	Corpus Christi	acidic gypsum	8.1					2.0	4.0				
[4]	Africa	Corpus Christi	acidic gypsum + wood waste	8					2.0	5.0				
[5]	China	Aluminium Ltd Zhengzhou Changcheng	aged 10 years	9.6	15.4	2.8	0.39	0.06	5.9	8.1		496.6		
[5]	China	Aluminium Ltd	aged 5 years	10.6	17.2	5.2	0.25	0.03	13.9	17.3		514.6		
[1]	Darling Range	Kwinana	bitterns	9.9	6.7									1.3
[1]	Darling Range	Kwinana	CO ₂	10.9	6.3									1.05
[6]	Australia	unknown	CO ₂ , 5 min	10.2										
[6]	Australia	unknown	CO ₂ , 10 min	8.5										
[6]	Australia	unknown	CO ₂ , 20 min	7										
[6]	Australia	unknown	CO ₂ , 24 min	7.3										
[7]	unknown	Point Comfort	DDI-H ₂ O	12.5										
[1]	Darling Range Jamaica,	Pinjarra	dilute acid	8.4	0.67									0.45
[4]	Africa Jamaica,	Corpus Christi	elemental S	7.8					10.0	4.0				
[4]	Africa	Corpus Christi	elemental S + wood waste	8.7					11.0	5.0				
[8]	Guinea Jamaica,	Aughinish	gypsum	7.9		3	14.8	0.04	1.1	1.6				
[4]	Africa	Corpus Christi	gypsum	8.6					7	4				
[3]	Darling Range Jamaica,	Pinjarra	gypsum + leaching	8.7	1.04									0.88
[4]	Africa Jamaica,	Corpus Christi	gypsum + wood waste	8.5					7.0	5.0				
[4]	Africa Jamaica,	Corpus Christi	H ₂ SO ₄	8.6					3.0	6.0				
[4]	Africa Guinea, South	Corpus Christi	H ₂ SO ₄ + wood waste	7.8					5.0	5.0				
[9]	Africa	Aughinish	none	12.7										
[10]	ex Yugoslavia	Birac Alumina	none	12.2		226								
[2]	Weipa	Eurallumia	none	11.5	2.1							106.5		
[11]	Guinea	Aughinish	none	9.7		9.7	0.04	0.02	56.0	45.7				
[12]	Weipa	Eurallumia	none	11.5	2.1							107		
[13]	not specified Jamaica,	not specified	none	12.7	12									
[4]	Africa	Corpus Christi	none	10	3.77				360	66.0		30.1		
[6]	Australia	unknown	none	12.6										
[14]	India	Damanjodi	none	11.1	4.9									
[15]	China	Pingguo Zhengzhou Changcheng	none	10.5										4.56
[5]	China	Aluminium Ltd	none	11.58	28.4	8.9	0.15	0.01	31.5	32.1		883.6		
[16]	unknown	San Ciprian	none	10.2								10.8		
[17]	Ghana	Burntisland	none	11.6										
[18]	Greece	Alumine de Grece	none	10										

Reference	Bauxite Origin	Refinery	neutralisation or treatment	pH	EC	mmol ₍₊₎ /L				SAR	ESP	CEC	ANC pH 7.0	ANC pH 5.5
						Na	Ca	Mg						
[19]	Weipa	Eurallumia	none	12.5	8									
[1]	Darling Range	Kwinana	none	11.5	3								0.75	
[1]	Darling Range	Pinjarra	none	11.6	6.1								1.08	
[1]	Darling Range	Wagerup	none	12	2.7								0.68	
[1]	Darling Range	Worsley	none	12.6	6.3								0.88	
[1]	Gove	Gove	none	12.4	10.8								1.64	
[1]	Weipa	QAL	none	10.2	8.2								0.92	
[1]	Brazil	Alunorte	none	12.2	3.3								1.25	
[1]	unknown	VAW Stade	none	12.1	2.6								0.61	
[1]	Weipa	Eurallumia	none	9.8	18.2								0.94	
[1]	unknown	San Ciprian	none	12.6	2.3								0.86	
[1]	unknown	Corpus Christi	none	11	3.6								0.77	
[3]	Darling Range	Pinjarra	none	11.7	5								1.08	
[20]	Darling Range	Pinjarra	none	10.5										
[20]	unknown	Suriname	none	10.6								12.5		
[21]	Darling Range	Kwinana	none	10.5	3.9				158.6	70.4				
[22, 23]	Darling Range	Kwinana	none	10.5	7.7							41.9		
[7]	unknown	Point Comfort	none		60.8									
[24]	Greece	Alumine de Grece	none	12.81	7.66							38	0.7	
[25]	Greece	none	none	12.1										
[26]	unknown	Mobile, AL - USA	none, 10 m from dike	9.2	1.4	17.4	0.08	0.02	76.4	53.4		17.53		
[26]	unknown	Mobile, AL - USA	none, 20 m from dike	9.3	2.2	26.4	0.08	0.02	117.0	63.7		26.52		
[26]	unknown	Mobile, AL - USA	none, 30 m from dike	10.7	9.8	129	0.11	0.02	510.0	88.4		129.89		
[26]	unknown	Mobile, AL - USA	none, 45 m from dike	11.5	16.9	198	0.16	0.01	673.1	91.0		198.57		
[26]	unknown	Mobile, AL - USA	none, 60 m from dike	11.1	12.4	158	0.14	0.01	578.2	89.7		158.16		
[26]	unknown	Mobile, AL - USA	none, 85 m from dike	11.2	11	139	0.13	0.01	511.2	88.5		139.88		
[27]	Jamaica	laboratory	none, JHM1	11.6										
[27]	Jamaica	laboratory	none, JHM2	10.9										
[27]	Jamaica	laboratory	none, JHM3	11.8										
[27]	Jamaica	laboratory	none, JHM4	11.2										
[27]	Jamaica	laboratory	none, JHM5	11.7										
[28]	Weipa	QAL	partly-neutralised	11	1.9							3.68		
[29, 30]	Weipa	QAL	red mud	11.1	37.7	546	5.9	1.6	283	81		13		
[29, 30]	Weipa	QAL	red sand	9.5	30.2	428	0.60	0.70	531	89		8.5		
[19]	Weipa	Eurallumia	seawater	9	16									
[28]	Weipa	QAL	seawater-neutralised	8.8	21.8							3.74		
[15]	Weipa Jamaica,	QAL	seawater-neutralised	10.5	3.44									2.39
[4]	Africa	Corpus Christi	wood-waste	8.6					14	6				

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