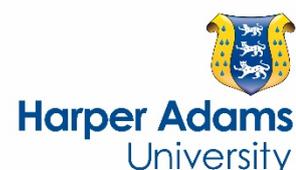


# Natural evolution of alkaline characteristics in bauxite residue

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27 **Keywords:** Bauxite residue; Alkaline characteristics; Natural evolution; Exchangeable  
28 sodium; Acid neutralizing capacity; Environmental management

## 29 **1. Introduction**

30 As a result of the high demand for aluminum, the global alumina industry has  
31 developed rapidly. However, these rapid developments have triggered numerous  
32 environmental issues (Gelencser et al., 2011; Mayes et al., 2016; Ruyters et al., 2011)  
33 that severely restrict the sustainable development of the alumina industry. Bauxite  
34 residue (red mud) is an alkaline solid waste generated by extraction of alumina from  
35 bauxite in refineries. The volume of bauxite residue generated while producing one ton  
36 of alumina is typically about 0.5-2 tons. With increasing demand for alumina worldwide,  
37 the global inventory of bauxite residue has reached an estimated 4 billion tons based on  
38 its current rate of production, and is still rapidly increasing (Kinnarinen et al., 2015;  
39 Liu and Naidu, 2014; Power et al., 2011). China is the largest producer of alumina in  
40 the world (Liu et al., 2014; Si et al., 2013). Its accumulative inventory of bauxite residue  
41 has reached over an estimated 0.6 billion tons with an annual increase of more than 70  
42 million tons (Xue et al., 2016). Currently, almost all bauxite residue is stored  
43 indefinitely in land-based bauxite residue disposal areas (BRDAs) (Burke et al., 2013;  
44 Santini et al., 2015; Zhu et al., 2016a), which require continuous resources to manage  
45 and transform the waste and reduce its potential to contaminate water and land, as well  
46 as the surrounding ecology (Banning et al., 2014; Lockwood et al., 2015; Santini and  
47 Fey, 2015). Leaching of alkaline waste is a further potential problem (Buckley et al.,  
48 2016; Pulford et al., 2012; Samal et al., 2015). The adverse alkalinity means that bauxite  
49 residue is listed as a contaminated waste, which limits its disposal, applications and  
50 options for its sustainable reuse.

51 Many amelioration techniques have been developed in an attempt to reduce the  
52 alkalinity of bauxite residue. For example, seawater neutralization is used by some  
53 coastal refineries (e.g. Shandong Aluminium Industry Co., Ltd; Queensland Alumina),  
54 which involves the addition of excess seawater to convert soluble hydroxides,  
55 aluminates and carbonates into insoluble solids as calcite ( $\text{CaCO}_3$ ), hydrocalumite

56  $(\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot\text{CO}_3)$ , aluminohydrocalcite  $(\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O})$ , brucite  
57  $(\text{Mg}_3(\text{OH})_6)$  and hydrotalcite  $(\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O})$  (Clark et al., 2015; Johnston  
58 et al., 2010; Menzies et al., 2004). Seawater neutralization lowers pH and alkalinity, but  
59 the generated colloidal particles are difficult to deal with. Carbon dioxide ( $\text{CO}_2$ )  
60 sequestration utilizes the reaction of  $\text{CO}_2$  with  $\text{OH}^-$  to form  $\text{HCO}_3^-$ , and the reversibility  
61 of key alkalinity reactions between  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  (Renforth et al., 2012; Wang  
62 et al., 2009; Yadav et al., 2010). The innovative nature of this technique is the  
63 consumption of  $\text{CO}_2$  to reduce atmospheric and industrial carbon dioxide emissions via  
64 sequestration (Cooling et al., 2002; Guilfoyle et al., 2005; Rai et al., 2013; Sahu et al.,  
65 2010). Interaction of waste acid can react with and transform hydroxides, oxides and  
66 sodalite (Freire et al., 2012; Lu et al., 2010), but the leached liquor and residue becomes  
67 a complex problem to manage, generating additional pollution issues (Burke et al., 2013;  
68 Goloran et al., 2015; Zhu et al., 2015a). Furthermore, the physical properties of  
69 bauxite residue present a problem, being a hostile environment for plant establishment  
70 (Borra et al., 2015; Kopittke, 2004; Zhu et al., 2015b). Gypsum transformation of  
71 bauxite residue lowers the pH by precipitating  $\text{OH}^-$ ,  $\text{Al}(\text{OH})_4^-$ , and  $\text{CO}_3^{2-}$  as calcium  
72 hydroxide ( $\text{Ca}(\text{OH})_2$ ), tri-calcium aluminate (TCA,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ), hydrocalumite  
73  $(\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot\text{CO}_3)$  and calcite ( $\text{CaCO}_3$ ) (Babu and Reddy, 2011; Courtney and  
74 Kirwan, 2012). The efficacy of gypsum in transforming the alkalinity is limited to  
75 gypsum's ability to readily dissolve (Courtney et al., 2009; Courtney and Harrington,  
76 2012).

77 These amelioration strategies may temporarily contribute to reduce the alkalinity of  
78 bauxite residue, but nevertheless there remains insufficient long-term success due to  
79 side effects and economic issues. Many of the current research techniques have focused  
80 on artificial amelioration of alkaline substances with less attention being paid to the  
81 natural evolution of alkalinity and its occurrence in bauxite residue.

82 There is limited mechanistic understanding of bauxite residue alkalinity  
83 characteristics following its long term disposal. Indeed, lack of understanding of  
84 evolution chemistry and alkalinity behavior has been highlighted as a significant  
85 knowledge gap in relation to the safe management and revegetation of bauxite residue

86 in BRDAs. This study therefore had the following specific objectives: (1) Discuss the  
87 changes in overall alkalinity of bauxite residue during its disposal history. (2) Identify  
88 the quantitative relationships between EC, Na<sup>+</sup> and OH<sup>-</sup>. (3) Investigate the  
89 transformations in exchangeable cation and sodium percentages. (4) Understand the  
90 neutralization behavior following long term natural evolution of the residue.

## 91 **2. Materials and methods**

### 92 *2.1 Field sampling and sample handling*

93 The raw bauxite residue sample used in this study was collected at the BRDA of the  
94 Zhongzhou refinery, Aluminum Corporation of China, Henan province, China.  
95 Samples were collected from 5 locations as follows; freshly deposited residue (0 years)  
96 (Lat 35°24'3.76" N, Long 113°25'38.18" E), 5 year old residue (5) (Lat 35°24'3.03" N,  
97 Long 113°25'38.82" E), 10 year old residue (10) (Lat 35°24'2.43" N, Long  
98 113°25'38.26" E), 15 year old residue (15) (Lat 35°24'1.86" N, Long 113°25'40.39" E)  
99 and 20 year old residue (20) (Lat 35°24'28.11" N, Long 113°25'47.33" E). Residue  
100 age differences are approximate but were determined due to a change in zonation which  
101 was clearly visible within the stacks. At each location, three sub-samples were collected  
102 with a distance of 5 meters from each other to form a representative sample. Samples  
103 were stored in polyethylene bags, returned to the laboratory and subsequently air-dried  
104 for 1 week, disaggregated using a mortar and pestle, and sieved to retain the <2 mm  
105 fraction. Subsequently, X-ray powder diffraction (XRD) analysis was conducted on the  
106 samples using a Bruker D8 discover 2500 with a Cu K $\alpha_1$  tube using a Sol-X detector.  
107 X-ray diffraction patterns were collected from 10 to 80° at a scan rate of 1° 2 $\theta$ /min and  
108 a step size of 0.04° 2 $\theta$ . XRD data analysis used the PANalytical analysis package to  
109 identify and quantify phases.

### 110 *2.2 Analytical methods*

111 Bauxite residue : water (1:5) extracts were prepared to determine pH, electrical  
112 conductivity (EC), and alkaline anions, and a bauxite residue : 1mol/L ammonium  
113 acetate (1:5) extract was prepared to analyze exchangeable cations. Supernatant liquors

114 from the water extraction were mixed at 150 rpm (1 h) then centrifuged at 3000 rpm  
115 (10 min) and analyzed for pH and EC (Clark et al., 2015). Sodium, K, Ca and Mg in  
116 ammonium acetate (pH=7) extracts were analyzed by inductively coupled plasma  
117 atomic emission spectroscopy (ICP-AES). Since no exchangeable acidic cations are  
118 expected to exist in alkaline conditions, the sum of exchangeable Na, K, Ca and Mg  
119 can be used as an estimate of cation exchange capacity (CEC).

120 Prepared supernatants from the water extraction were analyzed for alkaline anions  
121 (carbonate, bicarbonate and aluminate) by titration using a 0.02 mol/L H<sub>2</sub>SO<sub>4</sub>  
122 standardized solution. The supernatant (5 mL) was diluted with Milli-Q water to 30 ml.  
123 For solutions that were initially at a pH above 10.5, the solution was titrated to pH 10.3  
124 (first titration), and then a 250 g/L sodium gluconate solution was added until pH no  
125 longer increased. The solution was then titrated from pH 10.3 (second titration) to pH  
126 4.5 (third titration) (Kirwan et al., 2013). For solutions that were initially at a pH  
127 between 8.3 and 10.3, the solution was directly titrated to pH 4.5 (third titration). From  
128 the first titration, the free hydroxide concentration (OH<sup>-</sup>) was determined. From the  
129 second titration, the aluminate concentration (Al(OH<sub>4</sub>)<sup>-</sup>) was determined, and from the  
130 third titration, the carbonate concentration (CO<sub>3</sub><sup>2-</sup>) was measured.

### 131 *2.3 Batch neutralization experiments*

132 Acid neutralizing capacity (ANC) from each of the 5 locations was determined by  
133 repeatedly titrating the supernatants. Samples (10 g) were weighed into conical flasks  
134 (100 ml). Hydrochloric acid (HCl) (0.5 mol/L) was subsequently added at 0.8 ml  
135 increments, and made up to volume (50 ml) with Milli-Q water. The supernatant liquors  
136 were then shaken by hand and pH determined immediately. Samples were then placed  
137 on a shaker operating at 120 rpm (25°C). Supernatant pH was determined after 1 min,  
138 then on day 1, 5, 15, 30 and 60 of shaking. Measurements were conducted on  
139 supernatants in the conical flasks without removal of any sample. All samples (each in  
140 duplicate) from the different disposal dates were used for ANC determinations.

141 **3. Result and discussion**

142 *3.1 Transformation of basic alkalinity*

143 Basic alkalinity of the residue from the five locations are presented in Table 1.  
144 Following disposal, alkalinity decreased. For fresh residue, initial alkalinity was  
145 28349.69 mg/L Na<sub>2</sub>CO<sub>3</sub>, compared to 21857.02 mg/L Na<sub>2</sub>CO<sub>3</sub> from the 20 year old  
146 disposal area. Alkalinity is a result of the caustic solution from the Bayer process, and  
147 because of incomplete washing prior to disposal, alkaline substances (sodium  
148 hydroxide, NaOH; sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>; sodium aluminate, NaAl(OH)<sub>4</sub>) remain  
149 in the bauxite residue. During disposal, compounds such as OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and Al(OH)<sub>4</sub><sup>-</sup>,  
150 will undergo a chemical transformation. These reactions are expressed as Eqs. (1), (2)  
151 and (3). Notably, the concentration of OH<sup>-</sup> was greatly reduced after 15 years following  
152 disposal.

153

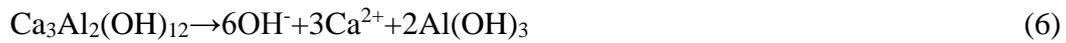


154

155 Slaked lime (Ca(OH)<sub>2</sub>) is commonly added within the Bayer process to improve  
156 digestion of alumina from the ore. This can lead to the formation of many solid phase  
157 calcium hydroxides, carbonates and aluminates, such as hydrogarnet  
158 (Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>x</sub>(OH)<sub>12-4x</sub>), calcite (CaCO<sub>3</sub>) and tri-calcium aluminate (TCA,  
159 Ca<sub>3</sub>Al<sub>2</sub>(OH)<sub>12</sub>) (Fig. 1). These insoluble solids act as an alkali store and their dissolution  
160 (hydrogarnet, Eq. (4); calcite, Eq. (5); tri-calcium aluminate, Eq. (6)) can provide a  
161 continuous source of alkaline compounds OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and Al(OH)<sub>4</sub><sup>-</sup> (Gomes et al., 2015).  
162 These alkaline anions are continuously consumed (Fig. 1), but even after 20 years, the  
163 alkalinity of the residue remained at a relatively high level; this may be attributed to  
164 these insoluble solid substances.

165





166

167 The de-silication products (DSPs) are a sub-set of more general Bayer process  
 168 characteristic solids (BPCSs) generated by the reaction of reactive silica with sodium  
 169 hydroxide and which impart significant alkalinity to the residues. The main DSPs  
 170 formed are Bayer sodalite ( $[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot [2\text{NaOH} \text{ or } \text{Na}_2\text{CO}_3]$ ) and cancrinite  
 171 ( $[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2[\text{CaCO}_3]$ ) (Fig. 1); they have a zeolite-type caged construction which  
 172 can attach sodium. These anions tend to be dominated by  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{Al}(\text{OH})_4^-$ .  
 173 With natural disposal, it is difficult for these attached anions to be released and  
 174 transformed. Hence in this way, DSPs can be a source of alkalinity. The natural  
 175 transformation of these anions associated with the dissolution of DSP results in  
 176 relatively stable alkalinity. However, with increasing duration following disposal,  
 177 concentration of sodalite, hydrogarnet and calcite (Fig. 1) gradually reduced, whilst free  
 178 hydroxides, carbonates and aluminates changed and the alkaline nature of the residue  
 179 decreased.

### 180 3.2 Transformation of electrical conductivity

181 During disposal, EC decreased with increasing duration following disposal (Fig. 2).  
 182 For fresh residue, the initial EC was 3.73 mS/cm, compared to 0.36 in the 20 year old  
 183 residue. During disposal, electrical conductivity affected the evolution of the residues  
 184 alkaline characteristics. To elucidate the relationships between EC and alkaline sodium  
 185 ions ( $\text{Na}^+$ ) and EC and hydroxide ions ( $\text{OH}^-$ ) linear curves were plotted (Fig. 3 and  
 186 Fig. 4). High EC values present high concentrations of alkaline  $\text{Na}^+$  and is replenished  
 187 from Na-bearing solids. With increasing time from initial disposal, Na-bearing solids  
 188 decreased with a corresponding decrease in EC (Fig. 2).

189 Electrical conductivity is also related to hydroxide ions ( $\text{OH}^-$ ), and it is important to  
 190 note that the linear relationship is approximately a factor of 1/3. The linear curve was a  
 191 good fit and showed  $\text{EC (mS/cm)} \sim 1/3 \text{ OH}^- \text{ (mmol/L)}$  (Fig. 4). High EC values also

192 demonstrate high concentrations of  $\text{OH}^-$ . The dissolution reactions are the main source  
193 of  $\text{OH}^-$ , which result in bauxite residue becoming weakly alkaline with increasing  
194 duration following disposal.

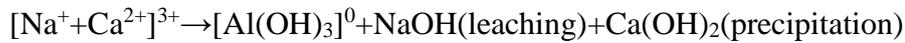
195 In the absence of detailed supernatant compositional data, EC is the most feasible  
196 quantity to estimate ionic strength. In natural aqueous solutions, Griffin and Jurinak  
197 (1973) determined the equation of  $\text{EC} \sim 78 \text{ IS}$ . The double-layer thickness of charged  
198 particles of bauxite residue becomes weak. Residue particles become dispersed, and the  
199 osmotic potential becomes more favorable. These transformed properties are beneficial  
200 to the disposal of bauxite residue and to stabilize the BRDA over the long term.

### 201 *3.3 Transformation of exchangeable cations*

202 The natural evolution of exchangeable cations (Na, K, Ca, Mg) are presented in Fig.  
203 5. Exchangeable Na decreased with increasing disposal time whilst exchangeable K,  
204 Ca and Mg increased with increasing time following disposal. For fresh bauxite residue,  
205 the molar concentrations of various exchangeable cations were in the following  
206 decreasing order:  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ . Exchangeable Na accounted for approximately  
207 72 % of the total exchangeable cations (mean molar concentration). This revealed that  
208 exchangeable Na dominated the basic cations in fresh bauxite residue. However, the  
209 concentration of exchangeable Na decreased from 20.28  $\text{cmol}_c/\text{kg}$  in fresh residue to  
210 9.81  $\text{cmol}_c/\text{kg}$  in 20 year old residue. The concentration of exchangeable Ca increased  
211 from 6.96  $\text{cmol}_c/\text{kg}$  in fresh residue to 17.40  $\text{cmol}_c/\text{kg}$  in 20 year old residue. The  
212 increase in K and Mg was however not obvious, indicating that a large concentration  
213 of exchangeable Na was replaced with exchangeable Ca during the disposal process.

214 It should also be noted that the cation exchange capacity (CEC) of the residue  
215 decreased with increasing duration following disposal (Fig. 6). This may be attributed  
216 to a reduction in pH over time (Eq.(7), resulting in precipitation of  $\text{Ca}(\text{OH})_2$  but also  
217 leaching of NaOH. The original negatively charged  $[\text{Al}(\text{OH})_6]^{3-}$  lost three  $\text{OH}^-$  which  
218 resulted in zero-charged  $[\text{Al}(\text{OH})_3]^0$  (Eq. (8)). Similar exchange reactions are available  
219 at edge sites of other alkaline compounds. The charged state of the colloids is therefore  
220 a significant regulator for cation exchange. During the time from disposal, with a

221 reduction in CEC, the negatively charged sites became increasingly positive.

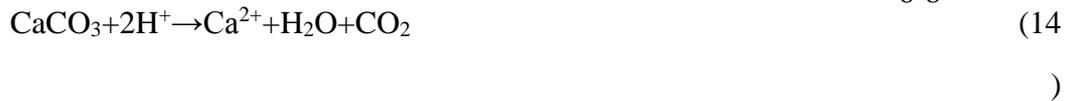
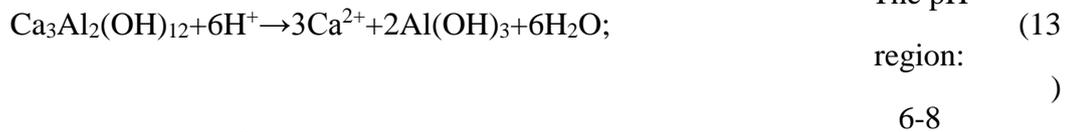
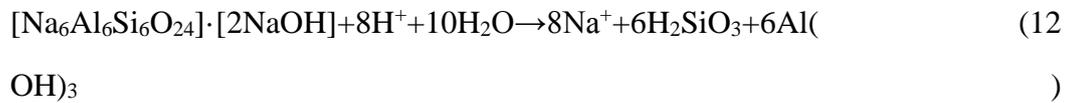
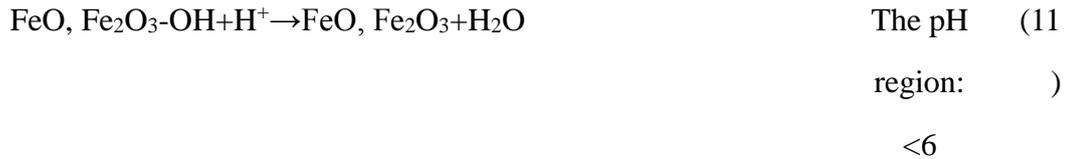
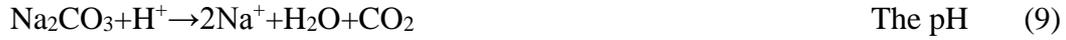


222 The exchangeable sodium percentage (ESP) (Fig. 7) decreased with increasing  
223 duration following disposal. The ESP approximates to the composition of cation  
224 exchange sites on the residue surface as a result of the composition of exchangeable Na,  
225 Ca and Mg (Gräfe and Klauber, 2011). Sodium ions can't be dehydrated as readily as  
226 Ca and Mg, which is indicative of stable hydration layers in bauxite residue particles.  
227 Additionally, Na ions can't be coordinated with negatively charged surfaces. The effect  
228 is that particles of fresh bauxite residue do not aggregate well and usually tend to be  
229 crusted and eroded in the dry state as Na eventually precipitates out as soda ash (trona  
230 and nahcolite), which simultaneously leads to the formation of alkaline dust and  
231 efflorescence at the surface of BRDAs (Klauber et al., 2008). The poor structural  
232 conditions at the surface of BRDAs are ultimately dependent on revegetation. With  
233 increasing time following disposal, the poor structural conditions may gradually be  
234 ameliorated (Zhu et al., 2016b).

### 235 *3.4 Transformation of Acid neutralizing capacity*

236 Acid neutralization of fresh residue shows changes in pH created by addition of  
237 hydrochloric acid (Fig. 8). Acid neutralizing capacity (ANC, final pH 7) of 1 min, 1, 5,  
238 15, 30 and 60 days were 0.091 mol H<sup>+</sup>/kg, 0.27 H<sup>+</sup>/kg, 0.36 H<sup>+</sup>/kg, 0.57 H<sup>+</sup>/kg, 0.68  
239 H<sup>+</sup>/kg and 0.78 H<sup>+</sup>/kg solids, respectively. Fig. 8 shows that the moles of H<sup>+</sup> taken to  
240 reach pH 7 increase as neutralizing time elapses, and most of the increase occurs at day  
241 1 and 5. The curve at day 60 reveals an extensive horizontal section. Some of this  
242 neutralizing behavior can be attributed to soluble free Na<sub>2</sub>CO<sub>3</sub> and NaOH (Eqs. (9) and  
243 (10)) occurring at the region of pH>8. Much of this neutralizing behavior is associated  
244 with hydroxyls on the surfaces of iron oxides (FeO, Fe<sub>2</sub>O<sub>3</sub>-OH, its reaction (Eq. (11)  
245 occurs at the region of pH<6) in the bauxite residue and dissolution of sodalite,  
246 tricalcium aluminate and calcite ([Na<sub>6</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>]·[2NaOH], Ca<sub>3</sub>Al<sub>2</sub>(OH)<sub>12</sub> and CaCO<sub>3</sub>

247 (Eqs. (12), (13) and (14) (Snars and Gilkes, 2009; Wissmeier et al., 2011; Xue et al.,  
 248 2016). The length of the neutralizing region reflects the contents of these components  
 249 in the bauxite residue.



250 The natural evolution of acid neutralizing capacity (ANC) (Fig. 9) was examined due  
 251 to the characteristics of the fresh bauxite residue (Fig. 8). During disposal, ANC  
 252 demonstrated some inconsistencies with increasing duration following disposal. For  
 253 fresh residue, the initial ANC recorded (at pH 7) was 0.78 mol H<sup>+</sup>/kg solid, which  
 254 presents a strong ANC compared to 0.25 mol H<sup>+</sup>/kg solid from the 20 year old residue.  
 255 The ANC of fresh residue was higher than that of the residue disposed over the long  
 256 term, which may be attributed to partial removal of NaOH and Na<sub>2</sub>CO<sub>3</sub> by leaching  
 257 during rainfall and alkali compound transformations. Furthermore, the curves for fresh  
 258 and 5 year old residue (Fig. 9) present a broad horizontal section; the curves for 10, 15  
 259 and 20 year old residue (Fig. 9) only exhibit a narrow section. This neutralizing  
 260 behavior is associated with the dissolution of sodalite, tricalcium aluminate, calcite and  
 261 other alkaline compounds (Snars and Gilkes, 2009; Wissmeier et al., 2011). This  
 262 tendency may demonstrate that fresh bauxite residue contains a larger concentration of  
 263 sodalite, tricalcium aluminate and calcite, compared to aged residues (consistent with  
 264 Fig.1 results). Further, the acid neutralizing behavior may enhance the natural evolution

265 of alkaline substances in bauxite residue following disposal.

### 266 3.5 Environmental management for long-term disposal

267 Historically, the management practices of BRDAs have focused on containment,  
268 with little attention given to long term changes in the chemical and physical properties  
269 of the residues. Currently, management plans are moving towards remediation and  
270 revegetation and/or further soil-formation of BRDAs to reduce environmental risks  
271 associated with long term disposal. Subsequently this will establish a stable  
272 ecosystem in the residue disposal areas, finally returning occupied land areas to an  
273 alternative option. In this work, alkalinity of bauxite residue was reduced with  
274 increasing duration following disposal. In addition, aged residue particles (10 to 20  
275 years) had favorable osmotic potential that can't be considered dangerous to the  
276 surrounding environment and may be safely disposed. Furthermore, the long-term  
277 disposal of bauxite residue allows a significant decrease in exchangeable Na, EC, and  
278 pH values, which can increase the rate of revegetation. The ecological restoration of  
279 bauxite residue has many challenges due to its high alkalinity, salinity and sodium  
280 content, deficiencies in organic matter and nutrient concentrations. Recent research has  
281 indicated the possibility for surface revegetation by Bermuda grass (*Cynodon dactylon*)  
282 together with arbuscular mycorrhizal fungi (Babu and Reddy, 2011) and giant reed  
283 (*Arundo donax L.*) (Alshaal et al., 2013). Revegetation of bauxite residue following  
284 disposal in combination with phytoremediation may be a feasible option in the future.

285 Recently disposed bauxite residue presents potential threats to the environment  
286 such as leakage of alkaline compounds into groundwater, risk of caustic exposure to  
287 organisms, overflow of alkaline substances during storm events and the loss of alkaline  
288 dust and efflorescence forming at the surface of BRDAs, which require sustained and  
289 intensive resources to manage and transform their alkalinity. Several methods have  
290 been considered for safe disposal, including washing, dewatering, covering with  
291 vegetation, neutralization and wetland construction (Burke et al., 2013; Liu et al., 2014;  
292 Santini and Banning, 2016). It is critical that residues are washed and dewatered for  
293 separation of caustic liquors prior to disposal into BRDAs. Following this, the residue

294 particles may aggregate well and be stable rather than crusted and become eroded.  
295 Furthermore, the formation of alkaline dust and efflorescence at the residue surface may  
296 be ameliorated and the residue may be safely stored for long-term natural regeneration.

#### 297 **4. Conclusion**

298 This work provides evidence for the natural evolution of alkaline characteristics of  
299 bauxite residue in BRDAs following long term disposal. Bauxite residue has highly  
300 alkaline characteristics which decrease with increasing duration following disposal.  
301 High EC is related to  $\text{Na}^+$  and  $\text{OH}^-$  which appear to decrease with increasing disposal  
302 time. Cation exchange capacity and exchangeable sodium percentage decrease with  
303 increasing duration following disposal. Furthermore, Na was the predominant  
304 exchangeable cation in fresh residue but decreased over the long term being replaced  
305 with Ca. Acid neutralizing capacity curves changed with disposal history and bauxite  
306 residue demonstrated a characteristic buffering behavior that further confirms the  
307 natural evolution of alkalinity. More importantly, these findings are applicable to  
308 surface revegetation and improved soil-formation because they demonstrate that  
309 decreasing alkalinity and increasing structural formation have a positive influence on  
310 the residues physical and chemical properties.

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