

Development of alkaline electrochemical characteristics demonstrates soil formation in bauxite residue undergoing natural rehabilitation

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Development of alkaline electrochemical characteristics improves land degraded by bauxite Residue

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ABSTRACT

Bauxite residue (BR) is a highly alkaline hazardous waste produced from alumina extraction processing, and has a complex mineralogy, which gives rise to soil basification and land degradation. Current management practices have mainly focused on containment, with less attention given to long-term natural evolution of its physical and chemical properties, particularly surface electrochemical characteristics. Weathering appears to reduce its environmental impact and alleviate its effect on land degradation whilst potentially providing opportunities for surface revegetation, improved soil-formation and hence land development of bauxite residue disposal areas (BRDAs). Natural evolution of mineralogy, zeta potential, isoelectric point (IEP), surface protonation and active alkaline groups are investigated here. Alkaline minerals of calcite, hydrogarnet and sodalite were slowly transformed or dissolved and their concentrations reduced with increasing duration following disposal. Amorphous and semi-amorphous minerals also decreased with a corresponding decrease in BET surface area and sorption sites. Zeta potential curves of the fresh residue had more slope during potentiometric titration, whilst for aged residue these became shallower with disposal duration. The IEP of fresh residue was significantly higher ($P < 0.05$), and the IEPs of aged residues were significantly lower ($P < 0.05$) with a significant decrease of IEP with increasing disposal time. Transformation of alkaline minerals, improvement of the poorly crystalline structure, and precipitation of amorphous and semi-amorphous minerals, decreased surface protonation and surface active alkaline groups with disposal duration, benefiting decision making with regards to soil formation and further land development of BRDAs.

KEYWORDS: Bauxite residue; natural evolution; alkalinity; isoelectric point; alkaline groups

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37 Land degradation is costly to human progress as a result of mismanagement of natural capital (Costanza
38 *et al.*, 2014; Sutton *et al.*, 2016). Increasing demand for accessible productive land therefore requires the
39 remediation and improvement of degraded land. Bauxite mining is well-known for its aggressive mining
40 activities, producing large tailings, particularly of bauxite processing residues, which degrade large tracts
41 of land and cause multiple environmental problems that currently restrict the sustainable development of
42 the alumina industry (Gelencser *et al.*, 2011; Mayes *et al.*, 2016; Goloran *et al.*, 2017; Kong *et al.*, 2017a).
43 Bauxite residue (BR), or red mud, is an alkaline solid waste produced during alumina extraction from
44 bauxite, with approximately 0.5-2 tons of residue generated per ton of alumina product (Grafe *et al.*,
45 2011; Evans *et al.*, 2016). Currently, the accumulative inventory of bauxite residue has reached over 4
46 billion tons, and is still increasing rapidly (Liu & Naidu, 2014; Ye *et al.*, 2014; Kinnarinen *et al.*, 2015).
47 The management of bauxite residue is a seriously challenging waste problem that is a major concern to
48 alumina refineries. Globally, there is no economic alternative to landfill, therefore almost all bauxite
49 residue continues to be stored indefinitely in land-based BRDAs (Burke *et al.*, 2013; Xue *et al.*, 2016a;
50 Zhu *et al.*, 2016a). The liabilities and environmental risks including freshly formed alkaline dust and
51 efflorescence, leaching of caustic liquor, degradation of surrounding land and trace metal and remediation
52 costs (Liu *et al.*, 2014; Samal *et al.*, 2015; Buckley *et al.*, 2016; Santini & Banning, 2016; Higgins *et al.*,
53 2016; Xue *et al.*, 2016b; Higgins *et al.*, 2017) have all afforded incentives to find selectable management
54 and treatment options.

55 The majority of the residues mineralogy is derived from weathering of bauxite and parent rock, but the
56 bauxite digestion process also produces secondary minerals, especially desilication products of
57 aluminosilicates such as cancrinite, sodalite and hydrogarnet, but also oxides, carbonates, and hydroxides
58 (Grafe *et al.*, 2011; Palmer & Frost, 2011). The majority of calcium (Ca) and all the sodium (Na) present
59 are introduced from the caustic soda (NaOH) and lime (CaO) added during alumina extraction and NaOH
60 regeneration. Formations of cancrinite ($[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2[\text{CaCO}_3]$), sodalite ($[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot [2\text{NaX}$ or
61 $\text{Na}_2\text{X}]$), and other aluminosilicates are generated predominately during digestion (Freire *et al.*, 2012; Pan
62 *et al.*, 2015). These are fine grain sized and structurally complex combined with high sodicity and soluble
63 alkalinity. Furthermore, Ca minerals are commonly produced during caustic regeneration with calcium
64 hydroxide precipitating carbonate alkalinity (Pan *et al.*, 2015; Xue *et al.*, 2016a). Subsequently these
65 minerals appear as alkaline minerals in bauxite residue.

66 Currently, research has focused on conversion of the high alkalinity of bauxite residue prior to disposal
67 and as an amelioration technique for encouraging revegetation and further land development (Xue *et al.*,
68 2016a; Kong *et al.*, 2017b). Seawater neutralization, waste acid dosing, gypsum transformation and
69 carbon dioxide sequestration are often used to ameliorate its alkalinity, but nevertheless, there still
70 remains insufficient long-term success as a result of economics and side effects (Wong & Ho, 1993;
71 Wong & Ho, 1994; Tuazon & Corder, 2008; Sushil & Batra, 2012; Couperthwaite *et al.*, 2013; Rai *et al.*,
72 2013; Clark *et al.*, 2015; Jones *et al.*, 2015; Kishida *et al.*, 2016). Furthermore, such methods have only
73 concentrated on artificial amelioration of alkaline substances with less attention being given to natural
74 development of alkalinity and its occurrence in bauxite residue disposal areas (BRDAs).

75 The natural change in behavior of alkalinity in the residue is primarily governed by electric charge;
76 positively charged cations are attracted to negatively charged surfaces, and negatively charged anions are
77 attracted to positively charged surfaces. This opposite attraction could be determined by the zeta potential

78 (ζ), and is dependent on pH (Castaldi *et al.*, 2010; Liu *et al.*, 2013; Kosmulski, 2014). The pH in which
79 surface charge is efficiently balanced, is the surface charge density and the electroacoustic isoelectric
80 point (IEP), and is influenced by the electro and/or surface chemistry of the complexity of mineralogy and
81 the various hydrolysable surface groups (Kairies *et al.*, 2005; Wang *et al.*, 2008; Freire *et al.*, 2012).

82 There is limited mechanistic understanding of bauxite residue surface electrochemical characteristics
83 following its long term disposal. Certainly, a lack of understanding of development of electrochemical
84 chemistry and its effects on alkalinity behavior, has been highlighted as a significant knowledge gap with
85 special reference to the safe management, revegetation, soil formation and inhibition of land degradation
86 in BRDAs (Grafe *et al.*, 2011; Liu *et al.*, 2013; Kong *et al.*, 2017b). This study therefore had the
87 following specific objectives: (1) to discuss the transformation in alkaline mineralogy within bauxite
88 residue following long term natural disposal, and (2) to investigate the zeta potential, isoelectric point,
89 surface protonation and alkaline groups of bauxite residue, and to characterize the natural evolution of
90 surface chemical characteristics.

91 MATERIALS AND METHODS

92 *Field sampling and sample preparation*

93 The bauxite residue sample used in this study was collected at the bauxite residue disposal area (BRDA)
94 of the Zhongzhou refinery, Aluminum Corporation of China, Jiaozuo city, Henan province, China.
95 Samples were collected from 5 locations as follows; freshly deposited residue (0 years) (Lat 35°24'3.76"
96 N, Long 113°25'38.18" E), 5 year old residue (5) (Lat 35°24'3.03" N, Long 113°25'38.82" E), 10 year old
97 residue (10) (Lat 35°24'2.43" N, Long 113°25'38.26" E), 15 year old residue (15) (Lat 35°24'1.86" N,
98 Long 113°25'40.39" E) and 20 year old residue (20) (Lat 35°24'28.11" N, Long 113°25'47.33" E).
99 Residue age differences are approximate, but were determined due to a change in zonation which was
100 clearly visible within the stacks. At each location, three sub-samples (0-30 cm sampling depths) were
101 collected having a distance of 5 meters from each other to form a representative sample. Samples were
102 respectively deposited in polyethylene bags, returned to the laboratory and subsequently air-dried for 5
103 days, slightly disaggregated using a mortar and pestle, and sieved to retain the <2 mm fraction. Two
104 stages of water washing were conducted to remove soluble alkalinity and/or salt. Samples were mixed
105 with ultrapure water with a vortex mixer (adequate mixing) for two stages of 5 min to insure dissolution
106 of the maximum soluble alkaline minerals and/or salts. Subsequently the suspension was centrifuged at a
107 low speed (4000 rpm for 15 min), and residual solids were naturally dried for 2 days, afterwards dried at
108 60 °C for 96 h. The fully dried solids were slightly crushed in a mortar to disaggregate, and sieved to
109 retain the <48 μ m fraction.

110 *Sample characterization*

111 Bauxite residue samples for X-ray powder diffraction (XRD) analysis were conducted on a Bruker D8
112 discover 2500 with a Cu $K\alpha_1$ tube using a Sol-X detector. X-ray diffraction patterns were collected from
113 10 to 80° at a 0.04° 2θ step size and a 1° 2θ min⁻¹ scan rate. The PANalytical analysis package was
114 applied to identify and quantify phases from XRD data. The relative intensity of the method was used to
115 quantitatively calculate mineral phases. The value of the reference intensity ratio (RIR_i) of the reference
116 code corresponding to phase i is directly determined, and the area I_i of maximum intensity peak of the
117 phase i is calculated. Then, the weight fraction W_i is calculated from $W_i = (I_i/RIR_i) / (\sum_i^n I_i/RIR_i)$.

118 Amorphous and semi-amorphous minerals of each sample was estimated with the aid of Jade v.7
119 software. The BG-Offset parameter shifts was used to fit an appropriate background, where the peaks
120 above this were integrated, then the whole integrated area provides a proportion of crystalline material.
121 Semi-amorphous materials were evaluated by identifying the area between the complex higher-order
122 background (BG) and a simple first-order BG for peak fitting by means of weighted integration.
123 Subsequently, the whole weighted area was subtracted from this determined area. The simple first-order
124 background, and the diffraction pattern profile were deleted, then diffraction pattern was divided on a 5
125 decimal equal place. This area between the simple first-order BG and the complex peak fitting BG was
126 cut off, and the two regions were respectively weighed, finally quantifying the semi-amorphous minerals.

127 Specific surface area (BET) of dried residues were performed on a Quantachrome Quadrasorb S1-3MP
128 auto-adsorption analyzer (employing liquid nitrogen adsorption) with the static volumetric technique
129 (using t method). Liquid nitrogen was equilibrated with solid powder samples for 20 seconds, followed
130 by degassing 20 min. Subsequently, samples were sequentially degassed at 150 °C for 1 h at 0.02 - 0.2
131 atm pressures (P/P_0). Qswin analysis software was used to analyze adsorption isotherm to determine the
132 BET.

133 Scanning electron microscopy (SEM) of bauxite residue samples were observed on a Netherlands FET
134 Quanta-200. Samples were paved on a Cu support plate filmed with Au (conductive coating), then
135 deposited by low vacuum sputter coating, and subsequently examined by a GSED field emission probe.

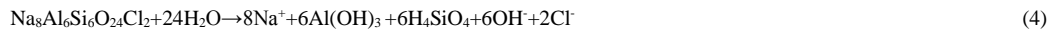
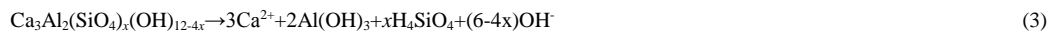
136 *Isoelectric point determination*

137 The isoelectric point (IEP) of bauxite residue was measured by potentiometric titration using ultrasonic
138 attenuation and electro-sonic acoustics in a Colloid Dynamics Acoustizer II. All three replicates of the 5
139 different aged residues were respectively dispersed at 2.5 % (mass fraction) in a 0.001 mol L⁻¹ NaCl
140 electrolyte (Freire *et al.*, 2012). Then, samples were dispersed in an ultrasonic cell crusher noise-isolating
141 chamber for 30 min, then rested for 10 min. The electrolyte pH was normalized to pH 10 from its initially
142 resting pH (approximately 11-9) prior to introduction into the Acoustizer II. Immediately, samples were
143 stirred at 150 rpm for 3 min, forming a homogeneous suspension. Subsequently, a potentiometric titration
144 was proceeded from pH 10 to 5 with 0.1 mol L⁻¹ HCl at 0.5 pH unit decrements.

145 RESULTS AND DISCUSSION

146 *Mineralogy*

147 The quantitative phases of bauxite residue obtained by PANalytical analysis from XRD data reveal phase
148 transformations during the residues long-term disposal (Table I). The alkaline phases from the freshly
149 stored bauxite residue were calcite (CaCO₃), cancrinite (Na₈Al₆Si₆O₂₄(CO₃)(H₂O)₂), hydrogarnet
150 (Ca₃Al₂(SiO₄)_x(OH)_{12-4x}), sodalite (Na₈Al₆Si₆O₂₄Cl₂) and tri-calcium aluminate (Ca₃Al₂(OH)₁₂), whilst a
151 range of Al hydroxide (α -AlOOH), Fe oxide (α -Fe₂O₃), a Ti mineral (Ca(TiO₃)) and Si oxide (SiO₂) were
152 also identified (Figure 1). The quantitative XRD results (Table I) indicate that the freshly stored residue
153 contained 49.1 % alkaline minerals, originating from alumina extraction processes (Bayer, sinter and
154 combined process), the bauxite source (gibbsite, diaspore and boehmite), digestion conditions and CaO
155 addition (Liao *et al.*, 2015). The mineral characteristics of calcite, cancrinite, hydrogarnet, sodalite and
156 tri-calcium aluminate are fundamental to the residues high alkalinity, and the following dissolution
157 reactions of these buffering alkaline solids are summarized as Eqs. 1-5.



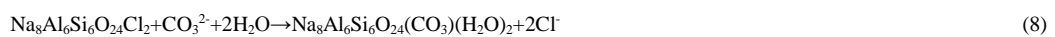
159

160 Hydrogarnet is the primary alkaline mineral (Table I) and quantification reveals that this mineral was
 161 gradually dissolved and converted to stable gibbsite (Eq. 3) due to its persistent dissolution characteristics
 162 (Santini *et al.*, 2015b). For fresh bauxite residue, the calcite concentration was 10.0 %, compared to 8.2 %
 163 in the 20 year old residue. Transformation of calcite was relatively slow compared to those of acid, CO₂
 164 and heat treated bauxite residues (Genç-Fuhrman *et al.*, 2004; Sharif *et al.*, 2011; Yang *et al.*, 2012; Zhu
 165 *et al.*, 2015). Results here suggest that during time from disposal, calcite minerals were partly dissolved
 166 (approximately 2 %). The dissolved calcite was more than 2 % due to formation and precipitation of fresh
 167 calcite (Eqs. 6 and 7). Sodalite concentration also decreased with increasing time from disposal whilst its
 168 concentration in the 20 year old disposed residue reduced by 20 %. During disposal, sodalite was slowly
 169 transformed to cancrinite (Eq. 8) (Barnes *et al.*, 1999; Gatta *et al.*, 2016), slightly increasing the cancrinite
 170 concentration in the 20 year old residue. However, there was no obvious change to cancrinite until this
 171 period (Table I), and may be attributed to its dissolution (Eq. 2) during time from disposal. Tri-calcium
 172 aluminate dissolved more slowly than other buffering alkaline minerals. The majority of tri-calcium
 173 aluminate was stable (its concentration maintained at about 3.3 %) during disposal, which is consistent
 174 with the transformation mechanisms described elsewhere (Hawkins & Roy, 1963; Tsuchida, 2000; Gong
 175 *et al.*, 2003). Transformations of hydrogarnet, cancrinite and sodalite resulted in an increasing
 176 concentration of gibbsite (Table I). The gibbsite to diaspore transformation is well-known (Murray *et al.*,
 177 2009; Santini *et al.*, 2015b), naturally increasing diaspore concentrations in the aged residues. Results
 178 indicate that the concentration of diaspore was maintained at approximately 6.0 %, suggesting that the
 179 transformation of gibbsite to diaspore was not activated through natural conditions (Table I).

180



Where present, Ca²⁺ and OH⁻ mainly come from the dissolution reactions of hydrogarnet and tri- calcium
 aluminate (Eqs. 3 and 5).



181

182 Furthermore, XRD results (Table I and Figure 1) reveal a large quantity of hematite (approximately
 183 26 %) in the different aged residues. Hematite concentrations had no obvious change. Hematite remained
 184 constant in the aged residues because its transformation required acidic conditions (pH 4 to 5) (Snars &
 185 Gilkes, 2009; Jones *et al.*, 2015;), and was therefore limited by the buffering action of the alkaline solids.
 186 Perovskite and quartz minerals were also stable (Table I). Results indicate that perovskite and quartz are
 187 not affected by weathering even after 20 years.

188

189 XRD results also show a large proportion of amorphous and semi-amorphous minerals in the different
 190 aged residues. Following disposal, concentrations of these minerals decreased with a corresponding
 decrease in BET surface area (Table I). A similar trend was attributed to reduced metal and oxyanion

191 binding on sorption sites of hematite (Genc-Fuhrman *et al.*, 2004; Smičiklas *et al.*, 2014). Additionally,
192 these minerals with structural defects further influence sorption behavior, since mineral porosity and
193 structural defects determine intraparticle diffusion which allow the surface adsorbed ions to re-distribute
194 (Davis & Kent, 1990; Axe & Trivedi, 2002; Castaldi *et al.*, 2008; Clark *et al.*, 2009; Clark *et al.*, 2011).
195 With increasing time from disposal, sorption sites decreased (Table I) whilst intraparticle diffusion
196 decreased ion binding, filling in the surface charge to release ions.

197 *Zeta potential curves and isoelectric point*

198 Zeta potential curves from the different aged residues (Figure 2) reveal that for fresh residue more slope
199 exists during the potentiometric titration (zeta potential changed from 27.7 mV to -27.9 mV at pH range
200 of 5-10). For the older residue (20 years) the zeta potential curve has a shallower slope, changing from 17
201 mV to -17.8 mV at the same pH range. The trends of the 5, 10 and 15 year old residues were between that
202 of the fresh and 20 year old residue. Before titration, the soluble alkalinity may have been removed during
203 the two stages of water washing. Changes to the curves suggest that concentrations of alkaline minerals
204 (hydrogarnet, calcite, sodalite) (Table I) may contribute to control the sloped tendency of the curve. The
205 fresh residue that contained a higher concentration of alkaline materials (49.1 %, Table I), had a higher
206 zeta potential (Figure 2). The alkaline concentrations of the aged residues decreased post disposal, and the
207 zeta potentials were also considerably lower (Figure 2), further reflecting that transformations of
208 hydrogarnet, calcite and sodalite over time. Following disposal, concentrations of amorphous and
209 semi-amorphous minerals decreased (Table I), as did the zeta potentials (Figure 2), suggesting that these
210 materials may be responsible for the slope of the curves. In addition, the fresh residue that was composed
211 of 0.1-0.5 μm particles in 5-10 μm aggregates was poorly-crystallized, relatively dispersed and disordered
212 (Figure 3 A). During disposal, small particles were partly removed (Figure 3 B-C), which may have been
213 leached by rainwater, whilst others formed new aggregates. The macro-aggregate particles of the aged
214 residues increased and were regularly distributed (Figure 3 B-C). Particle results further suggest that fine
215 grains decreased and macro-aggregates formed, providing a much shallower zeta potential curve, whilst a
216 corresponding decrease in BET surface area occurred after disposal (Table I).

217 The isoelectric points of the different aged residues were calculated from the mean zeta potential
218 curves (Figure 2) and statistical analysis (Figure 4). They indicate significant differences between the
219 fresh and aged residues. A significant decrease in the IEP was clear with increasing time from disposal;
220 the IEP of fresh residue was significantly higher ($P \leq 0.05$), whilst the IEP of aged residues was
221 significantly lower ($P \leq 0.05$).

222 The fresh residue had a higher concentration of alkaline materials (hydrogarnet, calcite and sodalite)
223 (Table I), which had a higher IEP (Figure 4), whilst the aged residues that contained a lower concentration
224 of alkaline minerals, had a lower IEP (Figure 4). The difference in mineralogy between the fresh and aged
225 residues was only in their concentrations (Table I), suggesting that the IEP is directly related to the
226 content of alkaline minerals within residues. Transformation of calcite results showed that the dissolved
227 products were Ca^{2+} and CO_3^{2-} (Eq. 1), where calcite appears to only weakly influence the IEP (similar to
228 previous findings (Freire *et al.*, 2012)). Hydrogarnet and sodalite dissolved and formed orthosilicic acid
229 polymers, which are unstable and slowly hydrolyzed, resulting in the precipitation of SiO_2 . The newly
230 formed SiO_2 lowers the IEPs in the aged residues due to its lower IEP (approximately 2)
231 (Jimenez-Angeles, 2012; Kosmulski, 2014). Additionally, the lower IEP in the aged residues may also be
232 attributed to the changes of particle size distribution due to the decrease of fine grains and the formation

233 of macro-aggregates (Figure 3), which further verify the corresponding decrease of BET surface area post
234 disposal.

235 *Surface protonation and alkaline group*

236 The acid-base titration curves (Figure 5) reflect the clear distinction of acid adsorption to the surface of
237 minerals within the residues following long-term disposal. The titration curve of the fresh residue
238 provides a relatively shallower exchange curve, suggesting that the fresh residue produced increased
239 protonation, particularly at low pH. The curves of the aged residues provide a steep exchange curve,
240 indicating that the aged residues have limited adsorption of acid to their surfaces. In particular, the proton
241 exchange curve of 20 year old residue is the steepest, reflecting that surface adsorption of H⁺ may be a
242 primary buffering agent. It appears that a reduction in alkaline mineral concentrations (Table I), together
243 with the improvement of the crystalline structure (fine grains reduced and macro-aggregates formed,
244 Figure 3) (Axe & Trivedi, 2002; Freire *et al.*, 2012), and precipitation of amorphous and semi-amorphous
245 minerals (sorption sites reduced, Table I) during long-term disposal, may provide decreased surface
246 protonation and acid neutralizing capacity.

247 The acid-base titration curves reveal a clear distinction of the extensively horizontal section (the
248 distance between beginning location and end location) (Figure 5), which is governed by the proton's
249 adsorption/desorption of the surface active alkaline groups of minerals within the residues following
250 long-term disposal. The length of the horizontal region may reflect the concentration of these groups on
251 the surface of minerals, and the natural evolution of the surface active alkaline groups (-OH) may be
252 calculated and examined (Figure 6).

253 The surface active alkaline groups from the different disposal ages (Figure 6) indicate that alkaline
254 groups exist on the surface of residue particles. During disposal, development of surface active alkaline
255 groups provided some inconsistencies with increasing duration following disposal. For fresh residue, the
256 initial alkaline group recorded was 1.02 mol H⁺ kg⁻¹ solid and was significantly greater ($P \leq 0.05$) (Figure
257 6), which continuously consumed H⁺ to some extent (a broad horizontal region shown in Figure 5) whilst
258 maintaining a relatively constant pH. Fresh residue presents relatively abundant alkaline groups, but these
259 significantly decrease in the aged residues, especially the 20 year old bauxite residue (0.54 mol H⁺ kg⁻¹
260 solid). The alkaline groups decreased slowly over time, which may be attributed to the transformation or
261 dissolution of alkaline minerals (hydrogarnet, calcite, sodalite) during weathering. In addition, disposal
262 promotes a decrease in fine grains and the formation of macro-aggregates (Figure 3), whilst resulting in
263 reduction of the specific surface area; these changes affect the distribution of alkaline groups on particle
264 surfaces. Furthermore, precipitation of amorphous and semi-amorphous minerals accelerates this behavior,
265 and improvement of these minerals with structural defects determine the intraparticle diffusion that allow
266 the surface adsorbed alkaline groups to re-distribute (Castaldi *et al.*, 2008; Wu *et al.*, 2009; Clark *et al.*,
267 2011). Further to this, the alkaline group behavior may enhance the development of alkaline minerals in
268 bauxite residue following disposal.

269 *Potential implications for soil formation and land development at BRDAs*

270 Bauxite residues have multiple chemical and physical limitations that require amelioration prior to
271 forming a stable soil structure and land substrate to support plant growth. High alkalinity and complex
272 alkaline minerals appear to mainly restrain land development and rehabilitation on BRDAs.
273 Environmental management of BRDAs have commonly focused on containment and alkalinity

274 neutralized or removed by artificial trials (Courtney *et al.*, 2009; Smart *et al.*, 2016; Goloran *et al.*, 2017),
275 with less attention given to long term evolution of the electrochemical properties of alkalinity following
276 disposal, particularly soil formation and further land development. Currently, almost all BRDAs in China
277 are left to natural weathering processes (Zhu *et al.*, 2016b; Zhu *et al.*, 2016c). Environmental plans are
278 gradually moving to amelioration and soil formation to reduce environmental risks and occupied land
279 degradation, and subsequently establish a stable ecosystem. This study has demonstrated that reduction of
280 alkalinity within bauxite residue is closely related to changes in mineralogy, zeta potential, bulk IEP,
281 surface protonation and alkaline groups. With increasing duration following disposal, transformations or
282 dissolution of hydrogarnet, cancrinite, sodalite and calcite, and a decrease in IEP and alkaline groups, the
283 alkalinity of residue decreases.

284 Understanding the influences of bauxite residue mineralogy on the proton adsorption behavior is
285 important in relation to environmental issues of BRDAs. Complex mineralogy often dominates residue
286 disposal areas, leading to long term leakage of alkaline compounds, alkalization and/or degradation of
287 occupied land, and diffusion and/or overflow of alkaline dust and efflorescence substances formed at the
288 surface of BRDAs during storm events (Courtney & Harrington, 2012; Santini & Fey, 2015; Higgins *et al.*,
289 2016; Higgins *et al.*, 2017; Zhu *et al.*, 2017). Therefore, understanding the effects of different disposal
290 years on bauxite residue mineralogy, and the influences of mineralogy on proton adsorption behavior of
291 bauxite residue, highlight the requirement for effective environmental management of BRDAs.
292 Furthermore, surface electrochemical characteristics following disposal are an important step in the
293 transformation of alkaline substances and a reduction in the alkaline properties, especially surface
294 alkaline groups, which may further increase the rate of soil formation and land development (Xue *et al.*
295 2016b).

296 Disposal duration significantly improves surface alkaline electrochemical characteristics of bauxite
297 residue whilst ameliorating some physical properties (fine grains reduced and macro-aggregates formed)
298 in respect to soil formation at the surface of BRDAs'. A decrease in IEP and alkaline groups have a
299 positive effect on improving physical properties, releasing a novel signal that soil formation and
300 rehabilitation of BRDAs may achieve with disposal duration, but the evidences are insufficient only
301 concentrating on macro-aggregate formations. Future investigations should focus on the increasing
302 physical limitations (aggregate structural formation, resistance to erosion, water holding characteristics),
303 whilst questioning the interactions between electrochemistry and soil development of bauxite residue
304 following long-term natural weathering, finally forming a land surface and achieving rehabilitation on
305 BRDAs.

306

CONCLUSION

307 This paper presents evidence of changes in surface electrochemical characteristics of alkalinity within
308 bauxite residue following long term disposal. Transformation of alkaline minerals of calcite, hydrogarnet
309 and sodalite occur over time and their concentrations decrease by approximately 20 % after a 20 year
310 duration following disposal. Some amorphous and semi-amorphous minerals in the 20 year old residue
311 decreased by 10 % with a corresponding decrease in BET surface area and sorption sites. Alkaline
312 minerals and amorphous minerals are responsible for the magnitude and range of zeta potential curves.
313 Dissolution of hydrogarnet and sodalite appear to greatly affect IEP shifts, significantly reducing the IEP.
314 Over time (20 years) there was a reduction in alkaline mineral concentrations but also the improvement of

315 the poorly electrostatic and crystalline structures of amorphous and semi-amorphous minerals, reduced
316 surface protonation and a 47 % reduction in surface active alkaline groups. These findings are significant
317 as they help to understand the effects of mineralogy on adsorption behavior in bauxite residue, and benefit
318 decision making with regards to degradation of occupied land, soil formation and land development of
319 BRDAs.

320

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491 Table I. Mineral composition of bauxite residue following its long-term disposal.

Mineral phase			Disposal years				
Name	Formula	units	Fresh	5	10	15	20
Calcite	CaCO ₃	%	10.0	10.2	9.7	8.9	8.2
Cancrinite	Na ₈ Al ₆ Si ₆ O ₂₄ (CO ₃)(H ₂ O) ₂	%	3.6	3.6	3.5	3.6	3.8
Diaspore	α-AlOOH	%	5.9	6.1	6.0	5.8	5.9
Gibbsite	Al(OH) ₃	%	- ^a	2.4	4.7	7.1	8.9
Hydrogarnet	Ca ₃ Al ₂ (SiO ₄) _x (OH) _{12-4x}	%	20.2	19.8	18.1	17.5	16.2
Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ Cl ₂	%	12.2	11.7	10.9	10.1	9.5
TCA ^b	Ca ₃ Al ₂ (OH) ₁₂	%	5.5	5.4	5.2	5.3	5.2
Hematite	α-Fe ₂ O ₃	%	26.3	26.4	26.2	25.8	26.0
Perovskite	Ca(TiO ₃)	%	12.6	12.3	12.4	12.2	12.2
Quartz	SiO ₂	%	2.5	2.9	3.3	3.7	4.1
Amorphous mineral		%	62.8±1	60.9±1	59.1±1	57.7±1	56.3±1
Semi-amorphous mineral		%	22.4±0.6	21.9±0.5	21.6±0.5	21.0±0.4	20.3±0.5
BET surface area		m ² /g	8.84	8.16	7.78	7.09	6.32
Estimated sorption site ^c		μmol/g	33.95	31.33	29.88	27.23	26.27

^aGibbsite may exist in the fresh bauxite residue, but the mineral content lowers the detection limit of X-ray powder diffraction.

^bTCA: Tri-calcium aluminate.

^cEstimation of sorption site is calculated by the standard value of 3.84 μmol/m² derived from Davis and Kent (Davis & Kent, 1990).

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