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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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INTRODUCTION

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

The majority of the residues mineralogy is derived from weathering of bauxite and parent rock, but the bauxite digestion process also produces secondary minerals, especially desilication products of aluminosilicates such as cancrinite, sodalite and hydrogarnet, but also oxides, carbonates, and hydroxides (Grafe *et al.*, 2011; Palmer & Frost, 2011). The majority of calcium (Ca) and all the sodium (Na) present are introduced from the caustic soda (NaOH) and lime (CaO) added during alumina extraction and NaOH regeneration. Formations of cancrinite ($[Na_6Al_6Si_6O_{24}]\cdot 2[CaCO_3]$), sodalite ($[Na_6Al_6Si_6O_{24}]\cdot$[2NaX or Na_2X]), and other aluminosilicates are generated predominately during digestion (Freire *et al.*, 2012; Pan *et al.*, 2015). These are fine grain sized and structurally complex combined with high sodicity and soluble alkalinity. Furthermore, Ca minerals are commonly produced during caustic regeneration with calcium hydroxide precipitating carbonate alkalinity (Pan *et al.*, 2015; Xue *et al.*, 2016a). Subsequently these minerals appear as alkaline minerals in bauxite residue.

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

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

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

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

MATERIALS AND METHODS

Field sampling and sample preparation

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

Sample characterization

Bauxite residue samples for X-ray powder diffraction (XRD) analysis were conducted on a Bruker D8 discover 2500 with a Cu Ka_1 tube using a Sol-X detector. X-ray diffraction patterns were collected from 10 to 80° at a 0.04° 2θ step size and a 1° 2θ min^{-1} scan rate. The PANalytical analysis package was applied to identify and quantify phases from XRD data. The relative intensity of the method was used to quantitatively calculate mineral phases. The value of the reference intensity ratio (RIR_i) of the reference code corresponding to phase i is directly determined, and the area I_i of maximum intensity peak of the phase i is calculated. Then, the weight fraction W_i is calculated from $W_i = (I_i/RIR_i) / (\sum_i^n I_i/RIR_i)$.

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

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

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

Isoelectric point determination

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

RESULTS AND DISCUSSION

Mineralogy

The quantitative phases of bauxite residue obtained by PANalytical analysis from XRD data reveal phase transformations during the residues long-term disposal (Table I). The alkaline phases from the freshly stored bauxite residue were calcite ($CaCO_3$), cancrinite ($Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2$), hydrogarnet ($Ca_3Al_2(SiO_4)_x(OH)_{12-4x}$), sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) and tri-calcium aluminate ($Ca_3Al_2(OH)_{12}$), whilst a range of Al hydroxide (α-AlOOH), Fe oxide (α-Fe_2O_3), a Ti mineral ($Ca(TiO_3)$) and Si oxide (SiO_2) were also identified (Figure 1). The quantitative XRD results (Table I) indicate that the freshly stored residue contained 49.1 % alkaline minerals, originating from alumina extraction processes (Bayer, sinter and combined process), the bauxite source (gibbsite, diaspore and boehmite), digestion conditions and CaO addition (Liao *et al.*, 2015). The mineral characteristics of calcite, cancrinite, hydrogarnet, sodalite and tri-calcium aluminate are fundamental to the residues high alkalinity, and the following dissolution reactions of these buffering alkaline solids are summarized as Eqs. 1-5.

158

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \quad (1)$$

$$Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2 + 22H_2O \rightarrow 8Na^+ + 6Al(OH)_3 + 6H_4SiO_4 + 6OH^- + CO_3^{2-} \quad (2)$$

$$Ca_3Al_2(SiO_4)_x(OH)_{12-4x} \rightarrow 3Ca^{2+} + 2Al(OH)_3 + xH_4SiO_4 + (6-4x)OH^- \quad (3)$$

$$Na_8Al_6Si_6O_{24}Cl_2 + 24H_2O \rightarrow 8Na^+ + 6Al(OH)_3 + 6H_4SiO_4 + 6OH^- + 2Cl^- \quad (4)$$

$$Ca_3Al_2(OH)_{12} \rightarrow 3Ca^{2+} + 2Al(OH)_3 + 6OH^- \quad (5)$$

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, CO_2
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

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2, \quad (6)$$

Where present, Ca^{2+} and OH^- mainly come from the dissolution reactions of hydrogarnet and tri- calcium aluminate (Eqs. 3 and 5).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \quad (7)$$

$$Na_8Al_6Si_6O_{24}Cl_2 + CO_3^{2-} + 2H_2O \rightarrow Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2 + 2Cl^- \quad (8)$$

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

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

Zeta potential curves and isoelectric point

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

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

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

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

Surface protonation and alkaline group

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

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

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

Potential implications for soil formation and land development at BRDAs

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

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

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

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

CONCLUSION

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

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

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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	$Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2$	%	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	$Ca_3Al_2(SiO_4)_x(OH)_{12-4x}$	%	20.2	19.8	18.1	17.5	16.2
Sodalite	$Na_8Al_6Si_6O_{24}Cl_2$	%	12.2	11.7	10.9	10.1	9.5
TCA[b]	$Ca_3Al_2(OH)_{12}$	%	5.5	5.4	5.2	5.3	5.2
Hematite	α-Fe_2O_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

[a]Gibbsite may exist in the fresh bauxite residue, but the mineral content lowers the detection limit of X-ray powder diffraction.

[b]TCA:Tri-calcium aluminate.

[c]Estimation of sorption site is calculated by the standard value of 3.84 μmol/m^2 derived from Davis and Kent (Davis & Kent, 1990).