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## Natural evolution of alkaline characteristics in bauxite residue

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## ABSTRACT

Bauxite residue, a highly alkaline solid waste, is extremely hazardous to the surrounding environment and current research approaches have largely focused on the removal and separation of alkaline substances. Natural weathering processes may be a step forward in terms of their regeneration. In this study, natural evolution of basic alkalinity, electrical conductivity, exchangeable ions and acid neutralizing capacity of residue in the disposal areas was discussed. Minerals, exchangeable cations and alkaline anions were analyzed by X-ray powder diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and titration, respectively. Acid neutralizing capacity was carried out by batch neutralization experiments. Basic alkalinity, electrical conductivity, cation exchange capacity and exchangeable sodium percentage decreased with increasing disposal duration. Sodium was the predominant exchangeable cation in fresh residue but its concentration significantly decreased with increasing time from initial disposal. The acid neutralizing capacity of bauxite residue was investigated by incubation with hydrochloric acid. Acid neutralizing capacity curves changed with disposal duration and each revealed a characteristic buffering behavior that could be controlled by its alkaline components.

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## 1. Introduction

As a result of the high demand for aluminum, the global alumina industry has developed rapidly. However, these rapid developments have triggered numerous environmental issues (Gelencser et al., 2011; Ruyters et al., 2011; Mayes et al., 2016; Wu et al., 2016; Zheng et al., 2017) that severely restrict the sustainable development of the alumina industry. Bauxite residue (red mud) is an alkaline solid waste generated by extraction of alumina from bauxite in refineries. The volume of bauxite residue generated while producing one ton of alumina is typically about 0.5–2 tons. With increasing demand for alumina worldwide, the global inventory of bauxite residue has reached an estimated 4 billion tons based on its current rate of production, and is still rapidly increasing (Power et al., 2011; Liu and Naidu, 2014; Kinnarinen et al., 2015). China is the largest producer of alumina in the world (Si et al., 2013; Liu et al., 2014; Hua et al., 2016). Its accumulative

inventory of bauxite residue has reached over an estimated 0.6 billion tons with an annual increase of more than 70 million tons (Xue et al., 2016b; Kong et al., 2017). Currently, almost all bauxite residue is stored indefinitely in land-based bauxite residue disposal areas (BRDAs) (Burke et al., 2013; Santini et al., 2015; Zhu et al., 2016a), which require continuous resources to manage and transform the waste and reduce its potential to contaminate water and land, as well as the surrounding ecology (Banning et al., 2014; Lockwood et al., 2015; Santini and Fey, 2015; Higgins et al., 2016). Leaching of alkaline waste is a further potential problem (Pulford et al., 2012; Samal et al., 2015; Buckley et al., 2016). The adverse alkalinity means that bauxite residue is listed as a hazardous waste, which limits its disposal, applications and options for its sustainable reuse.

Many amelioration techniques have been developed in an attempt to reduce the alkalinity of bauxite residue. For example, seawater neutralization is used by some coastal refineries (e.g. Shandong Aluminium Industry Co., Ltd; Queensland Alumina), which involves the addition of excess seawater to convert soluble hydroxides, aluminates and carbonates into insoluble solids as calcite ( $\text{CaCO}_3$ ), hydrocalumite ( $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot\text{CO}_3$ ), aluminohydrocalcite ( $\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O}$ ), brucite ( $\text{Mg}_3(\text{OH})_6$ ) and

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

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

There is limited mechanistic understanding of bauxite residue alkalinity characteristics following its long term disposal. Indeed, lack of understanding of evolution chemistry and alkalinity behavior has been highlighted as a significant knowledge gap in relation to the safe management and revegetation of BRDAs. This study therefore had the following specific objectives: (1) Discuss the changes in overall alkalinity of bauxite residue during its disposal history. (2) Identify the quantitative relationships between EC,  $\text{Na}^+$  and  $\text{OH}^-$ . (3) Investigate the transformations in exchangeable cation and sodium percentages. (4) Understand the alkalinity behavior following long term natural evolution of the residue.

## 2. Materials and methods

### 2.1. Field sampling and sample handling

The raw bauxite residue sample used in this study was collected at the BRDA of the Zhongzhou refinery, Aluminum Corporation of China, Henan province, China. Samples were collected from 5 locations as follows; freshly deposited residue (0 years) (Lat  $35^\circ 24' 3.76''$  N, Long  $113^\circ 25' 38.18''$  E), 5 year old residue (5) (Lat  $35^\circ 24' 3.03''$  N, Long  $113^\circ 25' 38.82''$  E), 10 year old residue (10) (Lat  $35^\circ 24' 2.43''$  N, Long  $113^\circ 25' 38.26''$  E), 15 year old residue (15) (Lat  $35^\circ 24' 1.86''$  N, Long  $113^\circ 25' 40.39''$  E) and 20 year old residue (20) (Lat  $35^\circ 24' 28.11''$  N, Long  $113^\circ 25' 47.33''$  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 (the sampling depths maintained at 0–30 cm), three sub-samples were collected with a distance of 5 m from each other to form a representative sample. Samples were stored in polyethylene bags, returned to the laboratory and subsequently air-dried for 1 week,

disaggregated using a mortar and pestle, and sieved to retain the <2 mm fraction. Subsequently, samples for X-ray powder diffraction (XRD) analysis were conducted on a Bruker D8 discover 2500 with a Cu  $K\alpha_1$  tube using a Sol-X detector. X-ray diffraction patterns were collected from  $10$  to  $80^\circ$  at a scan rate of  $1^\circ 2\theta \text{ min}^{-1}$  and a step size of  $0.04^\circ 2\theta$ . XRD data analysis used the PANalytical analysis package to identify and quantify phases.

### 2.2. Analytical methods

Bauxite residue: water (1:5) extracts were prepared to determine pH, electrical conductivity (EC), and alkaline anions, and a bauxite residue: 1 mol  $\text{L}^{-1}$  ammonium acetate (1:5) extract was prepared to analyze exchangeable cations. Supernatant liquors from the water extraction were mixed at 150 rpm (1 h) then centrifuged at 3000 rpm (10 min) and analyzed for pH and EC (Clark et al., 2015). Sodium, K, Ca and Mg in ammonium acetate (pH = 7) extracts were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Since no exchangeable acidic cations are expected to exist in alkaline conditions, the sum of exchangeable Na, K, Ca and Mg can be used as an estimate of cation exchange capacity (CEC).

Prepared supernatants from the water extraction were analyzed for alkaline anions (carbonate, bicarbonate and aluminate) by titration using a 0.02 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  standardized solution. The supernatant (5 ml) was diluted with Milli-Q water to 30 ml. For solutions that were initially at a pH above 10.5, the solution was titrated to pH 10.3 (first titration), and then a 250 g  $\text{L}^{-1}$  sodium gluconate solution was added until the pH no longer increased. The solution was then titrated from pH 10.3 (second titration) to pH 4.5 (third titration) (Kirwan et al., 2013). For solutions that were initially at a pH between 8.3 and 10.3, the solution was directly titrated to pH 4.5 (third titration). From the first titration, the free hydroxide concentration ( $\text{OH}^-$ ) was determined. From the second titration, the aluminate concentration ( $\text{Al}(\text{OH}_4)^-$ ) was determined, and from the third titration, the carbonate concentration ( $\text{CO}_3^{2-}$ ) was measured.

### 2.3. Batch neutralization experiments

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

## 3. Result and discussion

### 3.1. Transformation of basic alkalinity

Basic alkalinity of the residue from the five locations are presented in Table 1. Following disposal, alkalinity decreased. For fresh residue, initial alkalinity was 28350 mg  $\text{L}^{-1}$   $\text{Na}_2\text{CO}_3$ , compared to 21860 mg  $\text{L}^{-1}$   $\text{Na}_2\text{CO}_3$  from the 20 year old disposal area. Alkalinity is a result of the caustic solution from the Bayer process, and because of incomplete washing prior to disposal, alkaline substances (sodium hydroxide, NaOH; sodium carbonate,  $\text{Na}_2\text{CO}_3$ ; sodium aluminate,  $\text{NaAl}(\text{OH})_4$ ) remain in the bauxite residue. During

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