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Phosphogypsum stabilization of bauxite residue: conversion of its alkaline characteristics

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Abstract: Reduction of the high alkalinity of bauxite residue is a key problem to solve to make it suitable for plant growth and comprehensive utilization. In this study, phosphogypsum, waste product from the phosphate fertilizer industry was used to probe the alkaline transformation of the bauxite residue. Under optimal water washing conditions (Liquid/Solid ratio of 2 mL/g, 30 °C, 24 h), the impact of quantity added, reaction time and reaction mechanism during phosphogypsum application were investigated. Phosphogypsum addition effectively lowered pH levels and reduced the soluble alkalinity by 92.2%. It was found that the concentration of soluble Na and Ca ions in the supernatant increased gradually, whilst the exchangeable Na and Ca in solid phase changed from 219.2 to 111.59 mg/kg, and 160.44 to 259.07 mg/kg, respectively. Ca became the dominant element in the solid phase (phosphogypsum addition of 2%, Liquid/Solid ratio of 2 mL/g, 30°C, 12 h). XRD data indicated that cancrinite and hydrogarnet were the primary alkaline minerals. SEM images suggested that phosphogypsum could promote the formation of stable macro-aggregates, whilst the content of Ca increased from 5.61 to 18.2% and Na reduced from 6.80 to 2.44%. Treatment with phosphogypsum could significantly promote the transformation of alkalinity cations by neutralization, precipitation and replacement reactions. This research provided a feasible method to promote soil formation of bauxite residue by phosphogypsum amendment.

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Keywords:

Bauxite residue; Phosphogypsum; Alkaline ions; Alkaline transformation; Soil formation

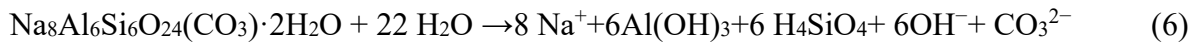
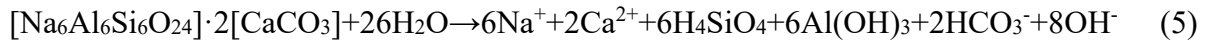
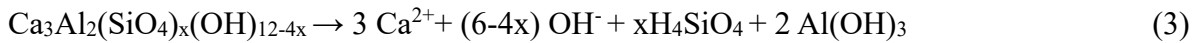
1. Introduction

The rapid development of the alumina industry in recent years has brought about a series of environmental problems (Chen et al., 2017; Wu et al., 2016), which have restricted sustainable development (Gelencsér et al., 2011; Mayes et al., 2016). Aluminium processing, results in a by-product described as bauxite residue which is separated into red mud (40% fine silt) and red sand (60% coarse fraction) according to particle size. These materials differ in terms of both physical and chemical properties (Xu et al., 2018). Approximately 150 million tons of bauxite residue are produced per year by the extraction of alumina using the Bayer process. Moreover, the global inventory of red mud was in excess of 4 billion tons in 2015 (Xue et al., 2016a; Zhu et al., 2015a). China is a major producer of alumina and about 61 million tons of BR was generated in 2016 (Zhu et al., 2016b).

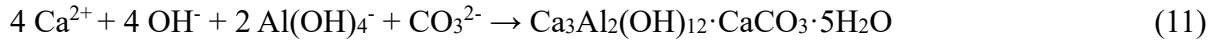
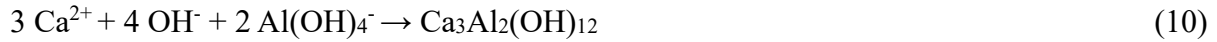
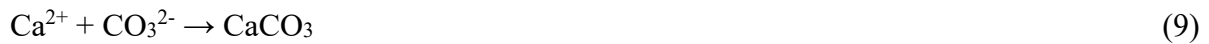
Therefore, the development of strategies to effectively manage BR and protect the environment has become more important (Lockwood et al., 2015). At present, BR is mainly large-scale stored on land adjacent to the alumina refineries to form the bauxite residue disposal area (BRDA) (Santini et al., 2015a; Zhu et al. 2016c). Due to the significant moisture content of bauxite residue, there are serious environmental safety risks in BRDA, such as tailings dam failure and landslide risks. High alkalinity leachates of bauxite residue present challenges for the management of BRDAs. For example, constructed wetlands used to grow *P.Australis* were one approach demonstrated to effectively treat alkaline bauxite-residue leachate (Higgins et al., 2016; Higgins et al., 2017). Trace metals are also present in BR which can cause hazardous environmental situations due to their mobility (Lockwood et al., 2015). Another major concern is fugitive dust which is generated from bauxite residue and potentially results in harm to surrounding communities (Xu et al., 2018). Collectively, these outlined problems make it difficult to remediate and establish a vegetation cover in a BRDA (Santini et al., 2015b). In order to effectively manage BRDA, strategies which could convert this material into a soil-like medium by revegetation, are regarded as the most promising prospect.

Extraction of alumina content from the Bayer process results in a highly alkaline by-product with inherently variable physical and chemical properties (Kong et al., 2017a; Santini et al., 2015b; Xue et al., 2016b; Zhu et al., 2016a). The alkali components of BR are complex and generally can be divided into two categories: soluble alkali and chemical bonded alkali

(Kong et al., 2017b). The soluble alkali component mainly includes sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium aluminate (NaAl(OH)₄), sodium silicate (Na₂SiO₃), potassium hydroxide (KOH), and potassium carbonate (K₂CO₃). These alkaline anions (OH⁻, Al(OH)₄⁻, CO₃²⁻, HCO₃⁻) were resolved by soluble alkali, which are the primary alkalinity anions in bauxite residue. Removing these anions can significantly reduce the pH of bauxite residue (Clark et al., 2015; Kinnarinen et al., 2015). In contrast, chemical bonded alkalis, such as calcite (CaCO₃), sodalite ([Na₆Al₆Si₆O₂₄]⁻·[2NaX or Na₂X]), cancrinite ([Na₆Al₆Si₆O₂₄]⁻·2[CaCO₃]), hydrogarnet (Ca₃Al₂(SiO₄)_x(OH)_{12-4x}) and tri-calcium aluminate (TCA, Ca₃Al₂(OH)₁₂) are relatively stable and exhibit low solubility. The dissolution reactions of these species can occur as shown in Equations 1 to 6 (Higgins et al., 2017; Paradis et al., 2007; Radomirovic et al., 2013; Santini et al., 2011; Whittington et al., 1998).



Therefore, a combination of high concentrations of alkali, significant salinity, low microbial activity, and reduced nutrient retention limit plant growth and thus comprehensive utilization with bauxite residue. To solve the aforementioned problems with BR stockpiling, considerable research effort has been devoted towards de-alkalization of bauxite residue. However, most of the suggested technical solutions cannot be implemented on a large scale. Use of inorganic acid neutralization, acidic gas neutralization, gypsum, seawater and brine have been popularized (Couperthwaite et al., 2014b; Courtney and Kirwan, 2012a; Dilmore et al., 2008; Kirwan et al., 2013; Lehoux et al., 2013; Menzies et al., 2004; Rai et al., 2013). Neutralization, precipitation and inhibition effects are observed in the process of ecological disposal and these reaction mechanisms are used to control the alkalinity in bauxite residue. The gypsum method produces less secondary pollutants, during in situ restoration of BRDA. Gypsum can continuously provide Ca²⁺ which reacts with CO₃²⁻, HCO₃⁻, OH⁻ and Al(OH)₄⁻ to generate calcite, calcium hydroxide and tri-calcium aluminate etc. (Equations 7-11).



Ideally, treatment of bauxite residue should best be conducted using a low cost approach due to the vast amount of material present. Therefore, application of a waste material to solve this issue is a potentially attractive strategy. Notably, during the processing of phosphate rocks by sulphuric acid to obtain fertilizer, a residue termed phosphogypsum is produced. This material has increasingly been considered as a resource in recent years and not simply as a waste (Cánovas et al., 2017a). For example, Cánovas et al. (Cánovas et al., 2017b) discussed the viability of recovering rare earth materials from phosphogypsum. Additionally, researchers have utilized phosphogypsum as an amendment to decrease pH in bauxite residue. Release of Ca^{2+} ions into solution is a key factor when amending bauxite residue with phosphogypsum, due to the ability of these species to neutralize and precipitate soluble alkali cations (Jone et al., 2012). However, the soluble alkalinity itself can leach under certain conditions. Thus these methods still have some shortcomings: for example, the effect of the leaching speed and time of bauxite residue alkaline was ignored under phosphogypsum treatment.

Therefore, the aim of this short-term study was to examine the control of alkalinity in bauxite residue using phosphogypsum addition. The hypothesis was that phosphogypsum would behave similarly to gypsum and allow an economic means of remediating bauxite residue. Specific research questions included: what is the impact of contact time when phosphogypsum is reacted with bauxite residue? how does the amount of phosphogypsum present influence the reaction with bauxite residue? and, what mineral phases and morphological changes occur in the bauxite residue upon reaction with phosphogypsum amendment. To answer the aforementioned research questions, bench scale tests were conducted with the bauxite residue and phosphogypsum generated in China.

2. Materials and Methods

2.1 Materials

The raw bauxite residue sample used in this study was collected from the Pingguo refinery operated by the Aluminum Corporation of China Limited, Guangxi province. Raw phosphogypsum was collected from Yunnan province. Samples were thoroughly homogenized and dried at 65 °C for 72 h. Subsequently, samples were ground into a fine powder using a mortar and pestle and sieved (100 mesh, mesh aperture is 150 μm).

2.2 Methods

The water leaching behavior of bauxite residue was firstly carried out to ascertain the optimum conditions (Liquid/Solid ratio was 2, temperature was 30 °C and time was 24 h) (Li et al., 2017). Under the optimum conditions of water leaching, the control of alkalinity in bauxite residue was carried out using phosphogypsum. In view of the economy and efficiency, a single-factor experiment was used to assess the stabilization effect of phosphogypsum including quantity added and reaction time. The ratio (w%) of added phosphogypsum was set as 0.5, 1, 1.5, 2, 3, 4, and 5% and reaction time was controlled at 1, 2, 4, 8, 12, 18, and 24 h (**Table 1**). Three replicates of each treatment were completed in order to effectively reduce the error. Weighed bauxite residue sample (20 g) was mixed with phosphogypsum and 40 ml deionized water in 250 ml bottles. Subsequently, the mixed slurry was stirred sufficiently for 30 s and sealed with a plastic membrane to prevent external interference. The experimental temperature was controlled by a water bath, and SHZ-D (III) vacuum suction filters were used to filter leachate. Filter residue was naturally dried and extracted supernatant with ammonium acetate.

2.3 Chemical Analysis

EC (electrical conductivity) and pH were measured by a PHS-3C pH meter and a DDS-307 conductivity meter, respectively (Johnston et al., 2010). The supernatant extracted by ammonium acetate (pH=7) was used to evaluate exchangeable Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Al^{3+} ions. These exchangeable and soluble cations in the supernatant were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Huang et al., 2016). Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were assessed by double indicator-neutralization titration using H_2SO_4 (0.005 mol/L).

2.4 Mineral Phase and Morphological Analysis

Raw bauxite residue sample and residue solids (0.04-0.05 mm) were characterized by X-ray powder diffraction (XRD). XRD was conducted with a 2θ scan range from 10 to 80° at a step size of 1°/sec. Patterns were indexed using Jade6. Sample morphology was of 0.1-0.05 mm grains was achieved with a scanning electron microscope equipped with energy dispersive X-ray spectroscopy (Newson et al., 2006).

2.5 Data Analysis

All data were analyzed in Microsoft Office Excel 2010 and IBM SPSS Statistics 20. All of the figures were constructed by Origin Pro8.0.

3 Results and Discussion

3.1 The Effect of Phosphogypsum Quantity on Bauxite Residue

The effect of phosphogypsum amendments on the alkalinity, pH, and concentration of soluble anions of the supernatant is presented in **Table 2** (L/S ratio of 2 mL/g, 30 °C, 24 hr). Due to the existence of a variety of alkali's (NaOH, Na₂CO₃, NaHCO₃, NaAl(OH)₄), the pH of the fresh samples was in the range 10 to 12, and the average pH was approximately 10.6. The pH of bauxite residue showed a significant reduction with the addition of phosphogypsum, and the final pH of the processed sample was approximately 8.1 (PBR is used to represent the treatment sample with phosphogypsum). Several researchers have examined application of phosphogypsum to alkaline materials (Singh and Garg, 2005) and noted pH was reduced after gypsum utilization to bauxite residues (Courtney and Timpson, 2005; Lee et al., 2007; Lehoux et al., 2013). It has been suggested that an excess of calcium in the form of gypsum can reduce pH to levels suited to plant growth by precipitating solution alkalinity and suppressing the solubility of solid phase alkalinity (Courtney et al., 2012a). The EC increased from 2.1 mS/cm to 6.4 mS/cm by the addition of phosphogypsum, which probably reflected changes in the Na⁺ and Ca²⁺ concentrations. In particular, the phosphogypsum released Ca²⁺ into solution and promoted precipitation of soluble alkaline anions; which caused significant increase in EC. Support for this conclusion was gained from the fact that gypsum amended residue had EC values ranging from 2.1-4.5 mS cm⁻¹ with higher levels recorded and Ca²⁺ was the major soluble ion in the gypsum amended process (Courtney and Mullen., 2009).

When 2% of phosphogypsum was added, the anion concentration of CO₃²⁻, HCO₃⁻ and Al(OH)₄⁻ reduced to the lowest value: 0.2, 3.9 and 0.02 mmol/L, respectively. This result suggested that soluble alkalinity of bauxite residue decreased to 92.2% and thus high soluble alkalinity concentration effects were mitigated. Application of gypsum (0, 40 and 90 t ha⁻¹) reduced sodicity and promoted nutrient uptake for P and Mn, which was indispensable for plant growth (Courtney and Harrington., 2012b). When the ratio of phosphogypsum continuously increased, the alkaline anion concentration began to decrease slowly and then remained steady for the duration of the exposure period. According to **Table 2**, among these alkaline anions, the concentration of CO₃²⁻ exhibited the greatest decrease and it was the dominant component of soluble alkali anion. The content of Al(OH)₄⁻ was minimal because most aluminum was

insoluble and crystallized. As Jones et al. reported, Ca^{2+} could react with soluble alkaline anions such as CO_3^{2-} , HCO_3^- , OH^- and $\text{Al}(\text{OH})_4^-$ (Jones et al. 2015). The mechanisms of both gypsum and phosphogypsum were similar, as both materials can provide excess calcium to precipitate soluble alkali (Kopittke et al., 2005; Jones et al., 2012). Notably, phosphogypsum dissolution not only released substantial divalent calcium but also some hydrogen ions, which consumed soluble alkalinity to precipitate calcium carbonate.

The measured concentration of cations indicated that most substances were insoluble and existed in crystalline form (**Table 3**). Initially there was an increase of soluble sodium concentration which gradually stabilized at 82 mmol/L when the addition of phosphogypsum was 2%. Soluble calcium had an original concentration of 0.04 mmol/L, and increased to approximately 10 mmol/L. On the contrary, the concentrations of soluble potassium and magnesium were almost impervious ($p>0.05$). Addition of phosphogypsum resulted in precipitation of CaCO_3 to release soluble sodium. Gobran et al. suggested that increasing salt concentration could promote gypsum dissolution, which was similar to the behavior of phosphogypsum dissolution (Gobran and Miyamoto, 1985). In a bauxite residue slurry, phosphogypsum dissolution observably increased and released abundant soluble calcium. The addition of a calcium source, most of them would react with the soluble alkalis and precipitate CaCO_3 to significantly drive the pH and some of them would remain in the supernatant to increase excess calcium. As calcium was released, alkaline carbonate in the bauxite residue was precipitated due to CaCO_3 formation (which was insoluble in alkaline solution).

The concentration of exchangeable Na reduced from 219.2 mg/kg to 111.6 mg/kg by addition of phosphogypsum, while the concentration of exchangeable Ca was concomitantly increased. When the addition of phosphogypsum was 2%, the amount of Na and Ca had significant differences ($P<0.05$) compared with other treatments (**Fig. 1**). Co-application of Spent Mushroom Compost and gypsum could reduce the values of exchangeable Na to below 10 % to increase plant growth (Courtney and Harrington., 2012b). However, concentrations of exchangeable K and Mg were mostly unaffected by addition of phosphogypsum ($P>0.05$). The abundance of exchangeable cations in initial bauxite residue slurry was in the order: $\text{Na}>\text{Ca}>\text{K}>\text{Mg}$. The initial content of Ca was 160 mg/kg and this increased to 259 mg/kg, which meant that calcium became the dominant element in the residue.

Concentrations of exchangeable Na were lowered during phosphogypsum treatment. The reason for this effect was that Na^+ was a monovalent cation and was as such not sorbed strongly on the cation exchange sites (Jones et al., 2015). The primary sodium salts (NaOH , Na_2CO_3 , NaHCO_3 , $\text{NaAl}(\text{OH})_4$) were able to leach soluble alkalinity ($\text{CO}_3^{2-}/\text{HCO}_3^-$) and promote alkaline reduction. Leaching of significant amounts of divalent Ca^{2+} indicated that soluble sodium ions in bauxite residue were replaced by calcium. Phosphogypsum amendment produced a lower exchangeable Na concentration and higher exchangeable Ca content with 2% phosphogypsum application in the solid residue.

From what has been discussed above, the amount of phosphogypsum present influenced the reaction with bauxite residue with 2% application preferred. In this case, the pH and soluble alkalinity were considerably lower, whilst the content of soluble sodium was increasing. This change indicated that the main soluble alkali species in bauxite residue (NaOH , Na_2CO_3 , NaHCO_3 and $\text{NaAl}(\text{OH})_4$) were continuously dissolved to release ions and reduce alkalinity.

3.2 Effect of Contact Time upon Interaction of Phosphogypsum and Bauxite Residue

The impact of reaction time upon the concentration of alkaline ions and pH of the supernatant was evaluated with phosphogypsum addition of 2%, L/S ratio of 2 mL/g, and temperature of 30°C.

The pH of supernatant was controlled in the range from 8.1 to 7.7 over a 12 h period. Whereas, the concentration of CO_3^{2-} (0.7 to 0.2 mmol/L) and HCO_3^- (5.2 to 3.3 mmol/L) were reduced and maintained for the duration of the exposure period. The range of pH was slightly only slightly changed by the reaction time ($P>0.05$). However, there was greater variance in the soluble cations (Na and Ca), which were released from 62 to 86 and 5.5 to 8.3 mmol/L, respectively (**Fig. 2**).

Kopittke et al. suggested that gypsum dissolution was an ionic transport-controlled process, which typically involved Ca^{2+} transfer into solution at a fast rate (Kopittke et al., 2005). With gypsum application, OH^- and CO_3^{2-} firstly took part in neutralization reaction and precipitated calcite within a relatively short time (12 h). The addition of calcium promoted the release of sodium ions, that potentially reduced salt stress to plant growth. (Grafe and Klauber, 2011; Grafe et al., 2011). High alkalinity and salinity are critical factors that can hinder soil

formation and seedling emergence. Excess salts inhibit seedling germination, which reduces the BR water potential (Courtney et al., 2012a). When increasing stabilization time, the concentration of calcium ions didn't increase substantially in the supernatant of PBR. An important aspect was the presence of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ in phosphogypsum, which had different solubility due to limitations associated with the surface solution concentrations of Ca^{2+} and SO_4^{2-} . During phosphogypsum amendment for different time periods, concentration of soluble potassium and magnesium was only marginally lower. The concentrations of soluble sodium and calcium were in a dynamic equilibrium state after 12 h.

Effect of reaction time on changes in exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) present in the transformation process is presented in **Fig. 3**. Concentrations of exchangeable Na and Ca both constantly decreased and reached minimum values after 12 h in the solid residue. After phosphogypsum treatment, a large significant amount of Ca in the solid phase was replaced by Na to get into supernatant, which was the main reason for the decrease of calcium concentration. Therefore, the exchange reaction between Na of BR and Ca in phosphogypsum was evidenced by both physical and chemical properties, particularly strong alkalinity in the short-term (Wong and Ho., 1991). But there were no significant difference around these treatment over 12 h ($P < 0.05$), which was different from the study of Wong and Ho who reported that Na and alkalinity increased over time. Concentrations of K and Mg by the ammonium acetate extracted were not influenced by reaction time ($P > 0.05$).

Ultimately, the alkalinity of bauxite residue (pH, total alkalinity, CO_3^{2-} and HCO_3^-) reduced to a minimum concentration after 12 h. The change of reaction time mainly affected the concentration of alkaline ions.

3.3 Evaluation of Bauxite Residue Dissolution

Lack of calcium in the leachate of bauxite residue is one of the reasons to limit reduction in the pH. Phosphogypsum, as a solid waste, is available from the by-product of phosphate fertilizer industry. It usually contains both a large amount of calcium sulfate dihydrate and some phosphoric acid. The application of phosphogypsum is an effective method for alkaline and hazard amelioration in the bauxite residue. In conclusion, the reduction in pH, alkalinity and alkaline ions concentration may include three reaction mechanisms. 1) Neutralization reaction:

the phosphoric acid creates acid environment to neutralize the alkalinity and then generates H₂O thus reducing the pH in the bauxite residue. 2) Precipitation reaction: OH⁻, Al(OH)₄⁻ and CO₃²⁻ in bauxite residue can precipitate calcium, which can generate Ca(OH)₂, CaCO₃ and Ca₃Al₂(OH)₁₂·CaCO₃·5H₂O. 3) Replacement reaction: using waste phosphogypsum as a raw material for Ca source can replace the dissociative Na, significantly reducing the alkalinity of bauxite residue. Due to the existence of the above three reactions, it is apparent that phosphogypsum may regulate and control alkaline conditions to promote soil formation of bauxite residue.

3.4 Mineral Phase and Morphology Characteristics

The mineral phases of the raw bauxite residue and PBR (phosphogypsum addition of 2%, L/S ratio of 2 mL/g, temperature of 30 °C and reaction time of 12 h) were analyzed by XRD (**Fig. 4**). The identified materials in the bauxite residue included hematite (Fe₂O₃), goethite (FeOOH), calcite (CaCO₃), hydrogarnet (Ca₃Al₂(SiO₄)(OH)₈), cancrinite (Na₆CaAl₆Si₆(CO₃)O₂₄·2H₂O), Al hydroxides (α -AlO(OH) and Al(OH)₃) and tri-calcium aluminate (TCA, Ca₃Al₂(OH)₁₂) (**Fig. 4a**). Similar minerals have been reported for various bauxite residues worldwide.

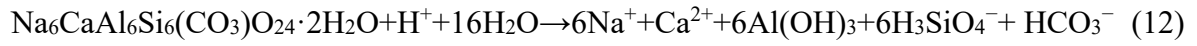
It is noted that different production processes and digestion conditions, coupled with bauxite resources of diverse composition means that the ratio of the mineral phases in the bauxite residue invariably exhibited significant variation in quantity (Liao et al., 2015).

Due to the high digestion temperature ($\geq 250^{\circ}\text{C}$) and higher level of CaO in the alumina production process, the chemical composition of bauxite residue from Pingguo alumina refinery contained a relatively high amount of ferrite. The ferrite mainly consisted of hematite (Fe₂O₃) and goethite (FeOOH), and the diffraction peak of Fe₂O₃ was the strongest among that of other minerals. Based on above results, the conversion of mineral phases was observed, which could offer a possibility to separate the goethitic alumina. For example aluminogoethite (Fe_(1-x)Al_xOOH(x=0-0.33)) may be converted to hematite (Suss et al., 2010) under such conditions. So, some suitable methods can be used to further recover iron and recycle the resources to reduce the hazard of bauxite residue.

Comparing with the phases in the original bauxite residue samples, the four mineral phases (hematite, calcite, hydrogarnet, cancrinite) existed in the residues after adding

phosphogypsum (PBR). The peaks of cancrinite and hydrogarnet were strongest in all the alkaline minerals, indicating cancrinite and hydrogarnet were primary alkaline minerals in the transformation process (Fig. 4b).

Cancrinite can be dissolved under phosphogypsum slurry (Eq. 3) and transformed into hydroxides (Zhang et al., 2011). The transformation mechanism for cancrinite is similar to acid condition (Eq. 12), but the dissolution reaction is controlled by acid concentration. There existed a decomposition reaction of the cancrinite phase in BR, and the quantity of cancrinite decreased to 4.5 wt.% (Liao et al., 2015). When using phosphogypsum to create acidic environment, the hydrogarnet can also be dissolved and precipitated to form gibbsite mineral phase (Couperthwaite et al., 2013a)(Eq. 13).



Using a soluble calcium source, the alkalinity of bauxite residue can be precipitated in similar reactions to those with gypsum. There existed two equilibrium reactions during the process, including precipitation and dissolution reactions. Under acid environment (Lin et al., 2004), the mineral phase of calcium can be transformed (Eq. s14). During acid transformation, calcite minerals are easy to be dissolved into the reaction solution (Kong et al., 2017b). Addition of phosphogypsum reduced the pH of mixed slurry to 8.05 and was conducive to form CaCO_3 (Eq. s15). Phosphogypsum addition could bring Ca^{2+} in solution, which precipitated excess soluble alkali to species such as tri-calcium aluminate, $\text{Ca}(\text{OH})_2$ and CaCO_3 (Jones et al., 2012). Since the concentration of soluble carbonate was larger than that of H^+ , the addition of phosphogypsum resulted in continually increasing calcite. It is possible that the calcium sources accelerated the precipitation of TCA (Eq. 10-11) to promote the alkaline reduction of bauxite residue. On the contrary, the calcium mineral (TCA) can be dissolved by acid transformation (Eq. 16). These alkaline minerals, such as cancrinite, hydrogarnet, calcite and TCA, acting as alkaline storage, can buffer solution to a pH around 8.



The SEM image of bauxite residue (0.1~0.5mm) illustrated particles were dispersed and

of variable shape (**Fig. 5A**). The raw sample included amorphous substances and these particles were of variable size. With the application of phosphogypsum, the loose particles disappeared and the aggregate particles were of uniform distribution (**Fig. 5B**). Adding phosphogypsum can promote the formation of stable macro-aggregates and these may form new particles (Zhu et al., 2016b). Similar studies mentioned dispersion and micro-aggregation of bauxite residue by gypsum amendment, which provided forming conditions for a soil-like medium (Courtney and Mullen., 2009). Calcium and sodium contents varied significantly together with the change of mineral morphology. The total calcium content increased from 5.61% to 18.02%, whilst the total sodium content decreased from 6.80% to 2.44%. This behaviour was consistent with the results of exchangeable calcium and sodium.

4. Conclusions

This study confirmed that phosphogypsum regulated the alkaline characteristics of bauxite residue under the optimal condition of: water washing (L/S ratio 2, temperature 30 °C and reaction time of 24 h); amount of phosphogypsum; and different reaction times which impacted the pH, EC, total alkalinity, soluble ions, exchange cation and the morphology. Hydrogarnet, cancrinite and tri-calcium aluminate were the main alkaline phases. These alkaline minerals were able to facilitate alkaline storage and their dissolution in appropriate conditions could buffer the solution to a pH around 8. The optimal condition for the study was the addition of 2 % phosphogypsum and a reaction time of 12 h. Phosphogypsum addition promoted hydrogarnet and cancrinite transformation, whilst also promoting the exchange of sodium and calcium. With phosphogypsum application, pH and total alkalinity continually reduced, especially CO_3^{2-} and HCO_3^- concentration. The total alkalinity and pH reduced from 50.82 to 4.10 mmol/L and 10.64 to 8.1, respectively; while the soluble Na and Ca increased from 54.1 to 79.9 mmol/L, and 0.04 to 8.5 mmol/L, respectively. The exchangeable Na and Ca in solid phase changed from 219 to 112 mg/kg, and 160.44 to 259.07 mg/kg, respectively; so Ca became the dominant element in the solid phase. The phosphogypsum can change the loose granular structure of the bauxite residue and make it into a large aggregate structure. The reaction mechanism of phosphogypsum involved neutralization reaction, precipitation reaction and calcium sodium replacement co-precipitation reaction. The phosphogypsum transformation of

BR is an important process and can be considered as a feasible way to treatment BRDAs. More importantly, it can achieve the purpose of “using waste treat waste” and reduce the risks of BRDAs, which is helpful to promote the soil formation’ process of bauxite residue.

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