



Effect of integration of mechanical ball milling and flue gas desulfurization gypsum on dealkalization of bauxite residue

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Abstract: The synergistic impact of mechanical ball milling and flue gas desulfurization (FGD) gypsum on the dealkalization of bauxite residue was investigated through integrated analyses of solution chemistry, mineralogy, and microtopography. The results showed a significant decrease in Na₂O content (>30 wt.%) of FGD gypsum-treated bauxite residue after 30 min of mechanical ball milling. Mechanical ball milling resulted in differentiation of the elemental distribution, modification of the minerals in crystalline structure, and promotion in the dissolution of alkaline minerals, thus enhancing the acid neutralization capacity of bauxite residue. 5 wt.% FGD gypsum combined with 30 min mechanical ball milling was optimal for the dealkalization of bauxite residue.

Key words: bauxite residue; alkalinity regulation; flue gas desulfurization gypsum; mechanical activation; soil formation of bauxite residue

1 Introduction

Bauxite residue, a highly alkaline solid waste produced in the alumina industry [1–3], not only occupies a lot of valuable land but also causes potential pollution to the environment [4,5]. The high alkalinity is the major concern to bauxite residue in the risk management and ecological vegetation restoration of the disposal areas [6,7]. Alkaline substances in bauxite residue are mainly soluble alkali ions (CO₃²⁻, OH⁻, and Al(OH)₄⁻) [8] and insoluble alkaline solids (e.g. sodalite, cancrinite, hydrated garnet, calcite, and tricalcium aluminate) [9–11].

Alkaline regulation is the prerequisite for the large-scale treatment of bauxite residue. The

traditional dealkalization strategies mainly include water washing, seawater neutralization, acid leaching, acidic gas neutralization, and bio-remediation [12–15]. During the dealkalization process, the insoluble alkali could be converted into the soluble alkali by the dissolution of alkaline solids. Meanwhile, the soluble alkaline ions could be precipitated to form insoluble solids. These two processes are usually integrated to achieve the dealkalization of bauxite residue [16]. Considering the high costs, large consumption, and potential risks, salt precipitation and acid neutralization still remain huge challenges to realize the high efficient and eco-friendly dealkalization.

Gypsum, a slightly soluble calcium salt, can continuously provide calcium ions to neutralize the alkaline of bauxite residue [17], which has great

potential for applying to in-situ ecological restoration in bauxite residue disposal areas. However, the alkalinity is easy to rebound in bauxite residue after gypsum-driven neutralization, which is definitely an issue that should be further explored [2,5]. During the leaching process of bauxite residue, the main alkaline components of the leachate are OH^- , $\text{Al}(\text{OH})_4^-$, HCO_3^- , and CO_3^{2-} [18]. H^+ and Ca^{2+} released from flue gas desulfurization (FGD) gypsum could neutralize the alkaline ions, thereby reducing the alkalinity of bauxite residue [19–21]. However, bauxite residue contains a large amount of chemical-bonded alkaline substances, which could stabilize the alkaline ions at the liquid–solid interface, resulting in the recovery of the alkalinity. The solid phase reaction and alkaline mineral phase transformation are possible to improve the reduction of alkaline mineral contents and acid buffering capacity. Considering the potential risks (e.g. the release of potentially toxic elements and the decreased storage space) in the application of FGD gypsum, the dosage of FGD gypsum should be investigated [22]. Generally, the solid phase reaction is accompanied at high temperature and pressure. Mechanical activation could reduce the thermal stability of the reactants and promote the reaction between the solid phases at a low temperature through changing the morphology and crystal structure of the materials, and the activation of the Fe-, Al-, and Si-contained compounds [23,24].

WU et al [10] proposed the application of mechanical ball milling to bauxite residue; however, its effect on the dealkalization of bauxite residue remains unknown. In this study, the alkaline conversion and dealkalization of bauxite residue through integration of FGD gypsum and mechanical ball milling were investigated. The objective of this study was to: (1) investigate the effect of mechanical ball milling time and FGD gypsum dosage on the change of free alkali and chemically alkaline solids in bauxite residue; (2) explore the effect of different treatments on the dissolution rate of basic ions; (3) analyze the acid neutralization capacity of bauxite residue under different treatment conditions; (4) investigate the long-term stability of bauxite residue under different treatment conditions; (5) analyze the changes in mineral composition and surface morphology of bauxite residue after treatments.

2 Experimental

2.1 Materials

The fresh bauxite residue was collected from a disposal area in Zhengzhou City, China. The samples were air-dried and then passed through a 2 mm sieve. The pH of residue leachate was 10.73 ± 0.01 . The main mineral phases were hematite, quartz, sodalite, and cancrinite.

2.2 Experimental design

Bauxite residue was treated with FGD gypsum at two different contents (5% and 10%, mass fraction), and/or ball ground for three different time (0, 15, and 30 min). Bauxite residue treated by FGD gypsum was named as GBR. Wet grinding was carried out using a ball mill (QM-QX, Nanjing University Instrument Factory). Six treatments were set up as follows: (1) 5 g of FGD gypsum and 100 g of bauxite residue were mixed and stirred in a flask with 200 mL of deionized water for 2 d (GBR 5%); (2) 10 g of FGD gypsum and 100 g of bauxite residue were mixed and stirred in a flask with 200 mL of deionized water for 2 d (GBR 10%); (3) 5 g of FGD gypsum, 100 g of bauxite residue, and 200 mL of deionized water were added in a ball mill tank and ground for 15 min at a speed of 400 r/min (GBR 5%-15 min); (4) 10 g of FGD gypsum, 100 g of bauxite residue, and 200 mL of deionized water were added in a ball mill tank and ground for 15 min at a speed of 400 r/min (GBR 10%-15 min); (5) 5 g of FGD gypsum, 100 g of bauxite residue, and 200 mL of deionized water were added in a ball mill tank and ground for 30 min at a speed of 400 r/min (GBR 5%-30 min); (6) 10 g of FGD gypsum, 100 g of bauxite residue, and 200 mL of deionized water were added in a ball mill tank and ground for 30 min at a speed of 400 r/min (GBR 10%-30 min). According to the method described by KINNARINEN et al [25], the mass ratio of the ball: water: bauxite residue was set to be 8:2:1. The revolution speed and ball grinding time were 400 r/min, and 15, and 30 min, respectively.

2.3 Alkaline indicators analysis

Electrical conductivity (EC) and pH were measured at a solid–liquid ratio of 1:5 (bauxite residue: deionized water) by electrical conductivity meter and pH meter, respectively [26]. The

expansion coefficient was measured as follows: 6 g of the treated bauxite residue was added in a 100 mL centrifuge tube which contained 50 mL of ultrapure water. The mixture was shaken at 25 °C and a speed of 180 r/min for 15 min, and then stood for 10 d. The final volume was measured. Soluble/exchangeable cations (Na^+ and Ca^{2+}) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after extraction using deionized water/ammonium acetate (pH=7) [27].

A titration procedure was used to evaluate the acid neutralization capacity of the treated residues. 5 g of the treated residue was put into centrifuge tubes, in which 0.1 mol/L of dilute hydrochloric acid solution with varying volumes of 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, and 3.2 mL was respectively added. The deionized water was added to maintain the mixture volume at 50 mL. Then, the solution was oscillated at 25 °C and a speed of 120 r/min for 1 min and let stand. The pH of the supernatant was measured on the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 12th, and 18th day, respectively.

The volume, pH, and EC of the leachate in each group were measured after filtration. The concentrations of Na^+ , Ca^{2+} , and Al^{3+} in the leachate were determined by inductively coupled plasma spectrometer (ICP-AES, Optima 5300DV, PerkinElmer). The solids after separation were collected and oven-dried at 75 °C for 24 h.

2.4 Chemical composition and microstructure analysis

The main chemical composition of the solids was determined using X-ray fluorescence (XRF, PANalytical Axios, Panak). The mineral composition of the solids was identified by X-ray diffraction (XRD, Rigaku TTR-III, Philips Co., Ltd.) with a LynxEye detector. The relative contents of crystalline and amorphous phases in the treated sample were fitted and calculated using Jade v.7 software. The microstructure of the treated samples was characterized using scanning electron microscopy (SEM, HITACHI SU3500). Back-scattered electron (BSE) imaging and electron dispersive X-ray spectroscopy (EDS) were carried out to determine the element distribution on the surface of the solids [28].

2.5 Statistical analysis

All data were analyzed with Excel 2016 and

SPSS 19.0. All figures were constructed with Origin 2021.

3 Results and discussion

3.1 Effect of mechanical ball milling on solution chemistry

The changes in pH and EC of bauxite residue leachates obtained after solid–liquid separation through different treatments were presented in Fig. 1. FGD gypsum could neutralize the basic ions of bauxite residue through the release of H^+ . Moreover, Ca^{2+} released from FGD gypsum could precipitate the alkaline ions in the bauxite residue leachate [19]. As a result, the pH of the leachate decreased significantly. Notably, there were no significant differences between GBR 5% and GBR 10%, indicating that the excessive gypsum addition limited the effect on alkalinity removal from bauxite residue. Notably, the dealkalinization

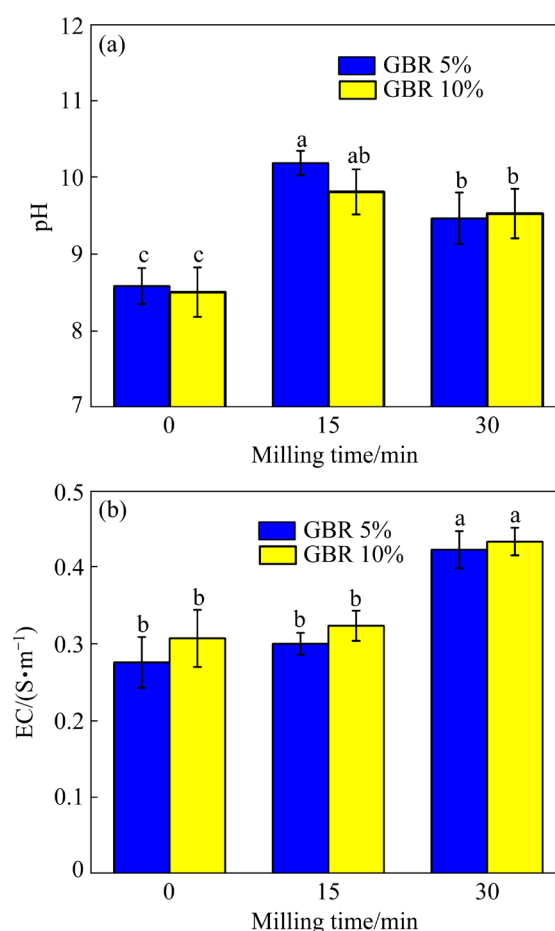


Fig. 1 Effect of mechanical ball milling on pH (a) and EC (b) of bauxite residue leachate (Different letters indicate significant differences between different treatments (significance $p < 0.05$))

efficiency did not increase with the increase in the amount of FGD gypsum. FGD gypsum usually reacted with the free alkali in bauxite residue leachate and decreased the pH quickly. However, due to the low solubility of alkaline minerals in bauxite residue, the precipitation reaction rate was relatively slow, resulting in a stable state of the alkalinity in bauxite residue leachate. Therefore, it was difficult to further reduce the alkalinity of bauxite residue by excessive addition of FGD gypsum. Furthermore, the EC value of bauxite residue leachate increased with the increase of FGD gypsum. Ca^{2+} released from FGD gypsum could replace the Na^+ on or within the residue particles by ion exchange, which increased the EC value [18].

Ball milling significantly increased the pH of the leachate (Fig. 1). With the prolongation of ball milling time, the pH of the leachate first increased and then decreased. This indicated that milling time affected the dissolution of alkaline minerals in the bauxite residue and the pH of leachate. The long ball milling time increased the dissolution of FGD gypsum, leading to a high concentration of Ca^{2+} in the solution. The released Ca^{2+} precipitated with the excessive OH^- , $\text{Al}(\text{OH})_4^-$ and CO_3^{2-} into $\text{Ca}(\text{OH})_2$, $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ and CaCO_3 , respectively, thereby decreasing the pH [18]. Meanwhile, soluble salt produced from the dissolution of FGD gypsum significantly increased the EC of the leachate.

To investigate the effects of FGD gypsum and ball milling time on the release of cations from the bauxite residue, the concentration changes of Na^+ , Ca^{2+} and Al^{3+} in the leachate were analyzed (Fig. 2). When the additive proportion of FGD gypsum was more than 5%, the increase of soluble cations in the leachate was limited, which was consistent with the changes of EC values. With the increase of ball milling time from 0 to 30 min, the concentration of Na^+ in the leachate with 5% FGD gypsum increased from 407.3 to 961.8 mg/L. However, it just increased from 418.9 to 927 mg/L when the proportion of FGD gypsum reached to 10%. Meanwhile, no significant change in the concentration of Ca^{2+} was observed. In addition, the concentration of $\text{Al}(\text{OH})_4^-$ increased first and then decreased with the increase of milling time.

Previous studies [29,30] showed that the concentration of $\text{Al}(\text{OH})_4^-$ in the leachate of bauxite residue remained stable with the decrease in pH,

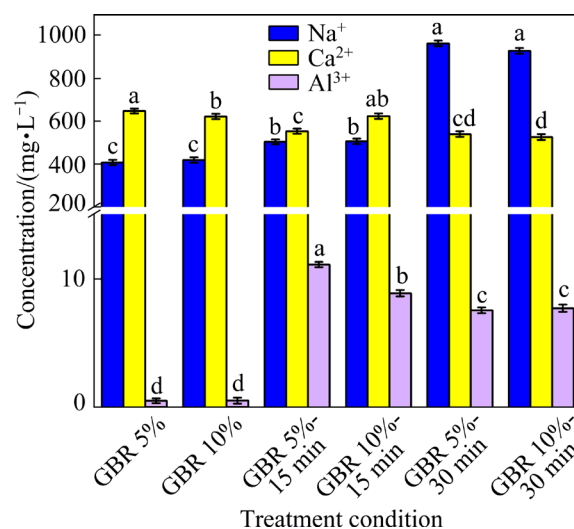
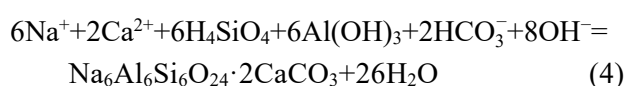
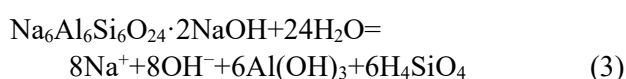


Fig. 2 Concentrations of Na^+ , Ca^{2+} and Al^{3+} in solution of bauxite residue treated with mechanical ball milling and FGD gypsum (Different letters indicate significant differences between different treatments ($p < 0.05$))

which was probably consistent with the results in this study. The excessive addition of FGD gypsum resulted in the saturation of Ca^{2+} in the leachate. Furthermore, FGD gypsum could continuously provide Ca^{2+} , which preferentially precipitated with alkaline ions such as OH^- , CO_3^{2-} , and $\text{Al}(\text{OH})_4^-$ released from bauxite residue (Reactions (1) and (2)). Meanwhile, Ca^{2+} could convert the soluble alkaline components in bauxite residue including NaOH , Na_2CO_3 , and $\text{NaAl}(\text{OH})_4$ into insoluble $\text{Ca}(\text{OH})_2$, CaCO_3 , and $\text{Ca}_3\text{Al}_2\text{O}_6$, respectively [18]. Subsequently, the excessive Ca^{2+} may replace Na^+ through ion exchange. For example, sodalite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2\text{NaX}$, where X is OH^- or CO_3^{2-}) could be converted into cancrinite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2\text{CaCO}_3$) due to the difference in solubility of these two minerals (Reactions (3) and (4)). Therefore, the alkalinity of bauxite residue could be stabilized [19]. Mechanical ball milling significantly accelerated the replacement rate between Na^+ and Ca^{2+} , thus achieving a great alkaline stability effect.



3.2 Effect of mechanical ball milling on solid chemistry

3.2.1 pH and EC

Mechanical ball milling increased the pH of the treated bauxite residue solution (as shown in Fig. 3(a)). Mechanical ball milling significantly

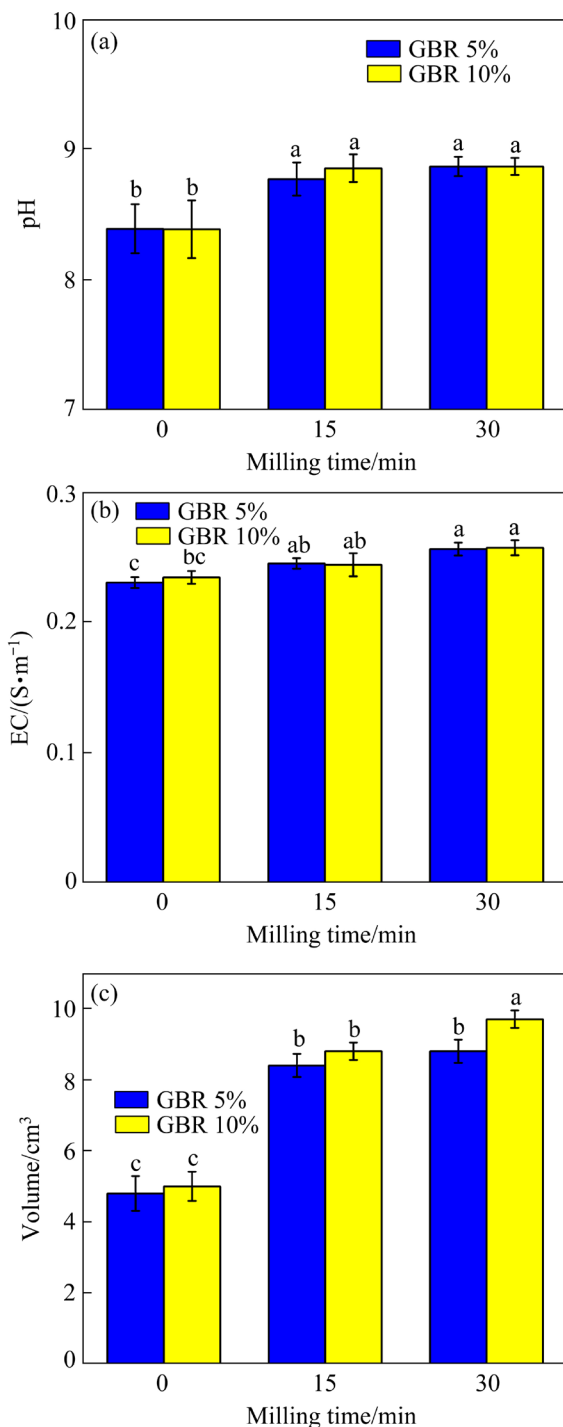


Fig. 3 Effect of mechanical ball milling and FGD gypsum treatment on physicochemical properties of bauxite residue: (a) pH; (b) EC; (c) Volume (Different letters indicate significant differences between different treatments ($p < 0.05$))

promoted the release of soluble alkaline components intermingled between the residue particles, thus leading to an increase in the pH of the bauxite residue solution. The changes in EC of the solid were similar to those of the solution. With the prolongation of the ball milling time from 0 to 30 min, the EC of the bauxite residue system significantly increased from 0.231 to 0.256 S/m (Fig. 3(b)). FGD gypsum addition increased the concentration of soluble salt ions through the release of Ca^{2+} and SO_4^{2-} . Furthermore, the presence of FGD gypsum changed the physical properties (like permeability) of bauxite residue, which improved the release of sodium, aluminum, and other soluble salts [31]. Meanwhile, the release process could also be improved by mechanical ball milling.

After adding the same volume of deionized water and standing for 10 d, the volume of bauxite residue obviously changed after different treatments. The initial volume of the bauxite residue was about 5 cm³. After mechanical ball milling, the volume of bauxite residue expanded (Fig. 3(c)). With increasing ball milling time from 15 to 30 min, the expansion coefficient of bauxite residue increased from 25.00% to 102.08%. The structure of the particles was fractured during the process of mechanical ball milling. As a result, mechanical ball milling reduced the size of the particles, decreased the apparent density, and increased the specific surface area. The mechanochemical effect greatly improved the chemical and physical properties of bauxite residue [10]. During the process of mechanical ball milling, the particle size of bauxite residue continuously decreased. New activation sites may continue to form on the residue surface. Meanwhile, cracks may form inside the bauxite residue, which results in a uniform dispersion of the residue slurry [32]. AROGUNDADE et al [33] observed that mechanical ball milling increased the porosity between bauxite residue particles, thus improving bulk density. Accordingly, the minerals in bauxite residue could be sufficiently contacted with the FGD gypsum, which contributed to the initial chemical reactions. During the dealkalization through mechanical ball milling, the physical and chemical properties of bauxite residue were improved.

3.2.2 Alkaline cations

The free alkali and exchangeable sodium are

mainly responsible for the alkalinity in bauxite residue [16]. The free alkali substances directly determined the alkalinity of bauxite residue [34]. The amount of the exchangeable sodium was positively correlated with the degree of alkalinity of bauxite residue, which was considered as an important indicator for the alkalinity. The concentrations of the soluble and exchangeable Na^+ and Ca^{2+} in the treated residues are presented in Fig. 4. There was no significant difference in the concentrations of dissolved Ca^{2+} with the increase of FGD gypsum, which indicated that 5% of FGD gypsum could provide sufficient Ca^{2+} during the dealkalization process. With the increase of ball milling time, the concentrations of soluble and exchangeable Na^+ increased. It showed that mechanical ball milling promoted the release of alkaline substances, and accumulated the adsorption sites on the surface of the residue particles, thereby allowing an excessive amount of Na^+ to participate in the ion exchange reaction [10]. The soluble Na^+ concentrations of GBR 5%, GBR 5%-15 min, and GBR 5%-30 min were 6.76, 8.26, and 10.82 mg/L, respectively. It could be concluded that mechanical ball milling significantly promoted the replacement of Ca^{2+} for Na^+ between bauxite residue and FGD gypsum, which could further reduce the content of Na^+ in bauxite residue, stabilize the alkaline minerals, thus achieving deep dealkalization [10].

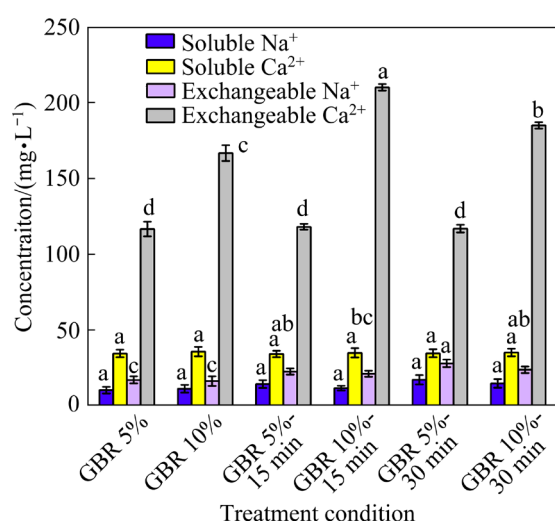


Fig. 4 Concentrations of soluble and exchangeable Na^+ and Ca^{2+} in bauxite residue treated with mechanical ball milling and FGD gypsum (Different letters indicate significant differences between different treatments ($p < 0.05$))

3.2.3 Minerals chemistry

With the increase of mechanical ball milling time, the XRD peak intensity of bauxite residue gradually weakened (Fig. 5). The crystal minerals in bauxite residue probably transformed into the amorphous substances during the process of mechanical ball milling, which resulted in slight damage and lattice defects in these minerals [35]. There were four major mineral phases in bauxite residue including hematite, calcite, cancrinite and boehmite after FGD gypsum treatment. These four mineral phases may undergo cyclic process of dissolution and precipitation during the leaching. Thus, the major alkaline minerals provided strong acid buffering for bauxite residue [19]. The low solubility of FGD gypsum contributed to its stable in bauxite residue. Compared with the residues treated with 5% of FGD gypsum, the increased addition of FGD gypsum had little effect on the changes of alkaline minerals, which indicated that 5% of FGD gypsum was sufficient to regulate alkalinity of bauxite residue. The XRD semi-quantitative results indicated that the alkaline mineral (e.g. cancrinite) component of the bauxite residue decreased after mechanical ball milling. However, the content of calcite increased after mechanical ball milling (Table 1). It may be because mechanical ball milling promoted the replacement of Ca^{2+} for Na^+ in the bauxite residue

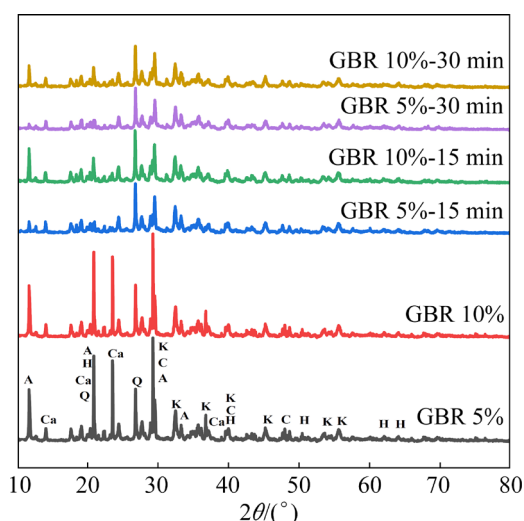


Fig. 5 XRD patterns showing effects of mechanical ball milling and FGD gypsum on mineral compositions of bauxite residue: H–Hematite (Fe_2O_3); C–Calcite (CaCO_3); Q–Quartz (SiO_2); Ca–Cancrinite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$); K–Boehmite ($\text{AlO}(\text{OH})$); A–Gypsum (CaSO_4)

and stimulated the dissolution of alkaline minerals, which resulted in an increase in the pH of the bauxite residue solution after mechanical ball milling. Mechanical ball milling could destroy the crystal structure of minerals into the dissociated or amorphous state, which was consistent with the results of SEM analysis [10].

The XRF analysis of bauxite residue after six groups of the treatments was presented in Table 2. The results showed that, the contents of SiO₂ and Fe₂O₃ in bauxite residue decreased after the addition of FGD gypsum, but slightly increased with the extension of milling time. The Si- and Fe-contained minerals wrapped in other insoluble minerals after mechanical ball milling were unable to dissolve further. Instead, the content of CaO gradually decreased with the extension of ball milling time, which might be due to further dissolution of FGD gypsum. Generally, the content of Na₂O was used to evaluate the dealkalization efficiency of bauxite residue. The content of Na₂O in bauxite residue significantly decreased after mechanical ball milling. After ball milling for 30 min, the content of Na₂O in GBR 5% and GBR 10% decreased from 6.37% to 4.41% and 4.40%, respectively. This indicated that mechanical

ball milling decreased Na⁺ in the bauxite residue and enhanced the dealkalization effects, which was consistent with the results obtained from the solution chemistry of the leachate. Therefore, the appropriate FGD gypsum amount and ball milling time could improve the dealkalization efficiency.

3.3 Acid neutralization capacity

The acid neutralization capacity could directly reflect the response of alkaline ions to H⁺ and the changes in the alkalinity, which was closely related to the dissolution behavior of alkaline minerals in bauxite residue [36]. The changes in the pH of the residue solution after different treatments with addition of different volumes of HCl (0.1 mol/L) were observed within 18 d (Fig. 6). The pH of the treated bauxite residue solution firstly increased, then decreased, and finally increased. Within a 5 d reaction period, H⁺ was easier to replace Ca²⁺ than Na⁺. After the titration process, the pH was less than 9.0. Generally, calcite, a typical alkaline mineral, could be dissolved under certain acid conditions. FGD gypsum could continuously provide Ca²⁺ to form CaCO₃ (Reactions (5) and (6)). The exogenous acids accelerated the dissolution of TCA (tricalcium aluminate) to promote the

Table 1 Mineral compositions of bauxite residue after different treatments

Mineral phase		Content/wt.%					
Name	Formula	GBR 5%	GBR 10%	GBR 5%- 15 min	GBR 10%- 15 min	GBR 5%- 30 min	GBR 10%- 30 min
Hematite	Fe ₂ O ₃	13.2	14.1	13.5	14.3	14.7	15.0
Calcite	CaCO ₃	5.9	5.5	6.9	7.5	6.5	7.2
Quart	SiO ₂	15.3	14.7	15.1	14.5	15.1	14.4
Cancrinite	Na ₈ Al ₆ Si ₆ O ₂₄ · CaCO ₃ ·2H ₂ O	15.3	14.7	13.5	13.7	10.9	11.0
Boehmite	AlO(OH)	3.5	2.9	3.1	2.8	3.0	2.7
Amorphous mineral		46.8	48.1	47.9	47.2	49.8	49.7

Table 2 Chemical compositions of bauxite residue sample in terms of equivalent oxides (wt.%)

Treatment condition	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂
GBR 5%	6.37	24.14	23.33	22.71	9.74	6.45
GBR 10%	6.37	25.16	22.83	21.79	9.06	6.06
GBR 5%-15 min	4.58	23.07	23.62	25.34	10.50	6.01
GBR 10%-15 min	4.50	23.97	22.07	24.75	10.34	5.59
GBR 5%-30 min	4.41	23.43	22.93	25.48	10.64	6.17
GBR 10%-30 min	4.40	23.95	21.81	24.84	10.24	5.58

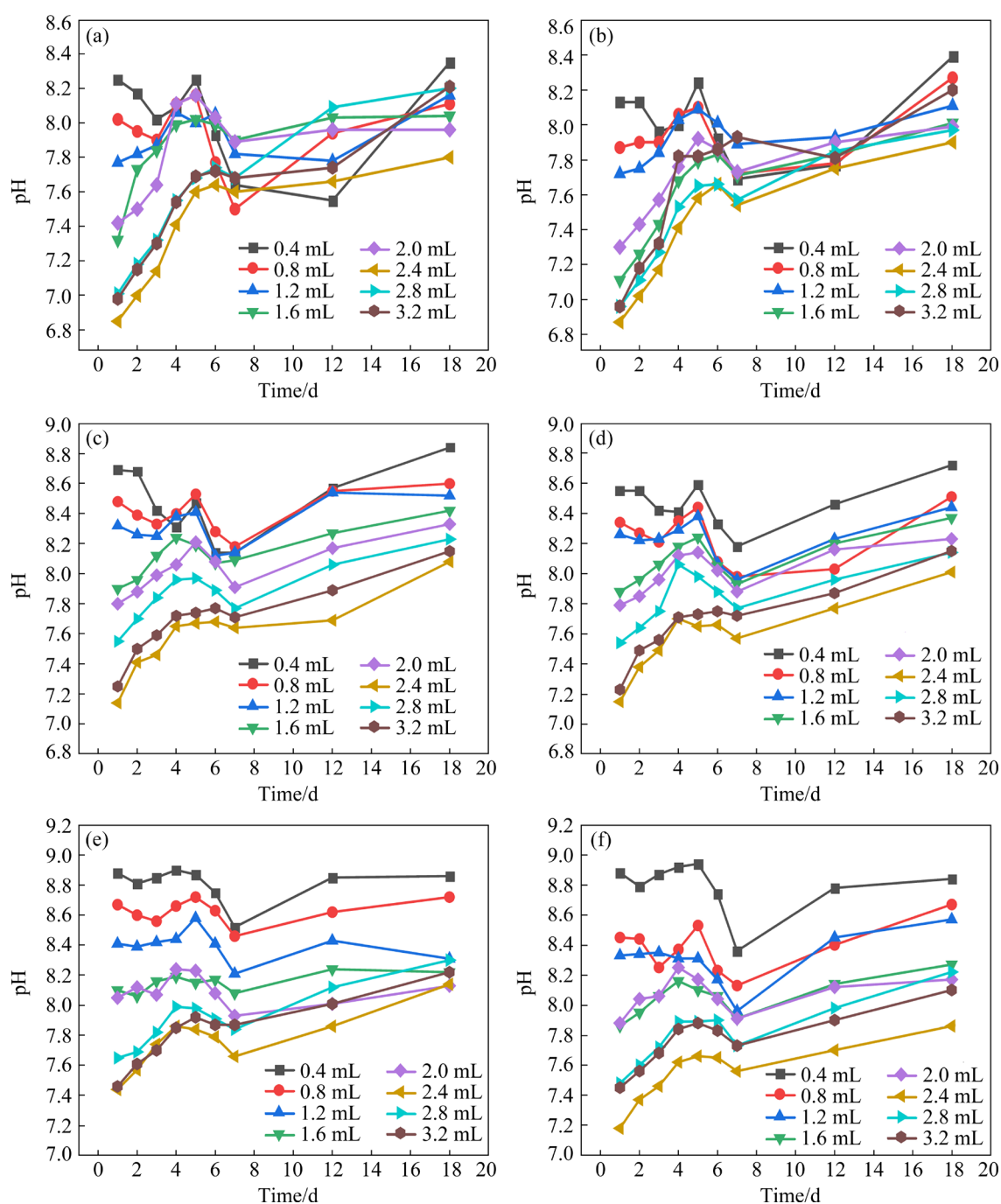


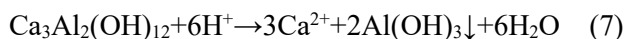
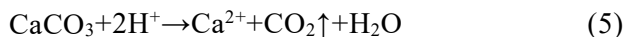
Fig. 6 Effect of mechanical ball milling on acid neutralization capacity of bauxite residue at different volumes of 0.1 mol/L HCl: (a) GBR 5%; (b) GBR 10%; (c) GBR 5%-15 min; (d) GBR 10%-15 min; (e) GBR 5%-30 min; (f) GBR 10%-30 min

transformation of alkaline materials in bauxite residue (Reaction (7)). These alkaline minerals, including cancrinite, hydrogarnet, calcite, and TCA, acted as alkaline reservoirs, and buffered the system at pH less than 9.0 [19]. Previous studies [19,34] showed that the pH of bauxite residue would be further reduced when the acid buffering capacity was consumed. Meanwhile, mechanical ball milling

enhanced the stability of the alkalinity in bauxite residue. Therefore, mechanical ball milling could improve the dealkalization efficiency and stimulate the alkaline components reaching a stable state quickly in bauxite residue [10].

Overall, due to the replacement of Ca^{2+} for Na^{+} , a certain amount of bonded alkaline solids was dissolved, which resulted in the increase of the pH

in a short time [37]. With the increase of reaction time, the intermediate reactions gradually reached equilibrium. The unreacted alkaline minerals such as cancrinite and calcite in the bauxite residue may keep a stable pH. Therefore, the integration of mechanical ball milling and FGD gypsum could achieve an efficient dealkalization.



3.4 Changes in surface morphology and element distribution

Backscattered electron (BSE) imaging and electron dispersive X-ray spectroscopy (EDS) were applied to observing the morphology and element distribution of bauxite residue after different

treatments (Fig. 7). Residue particles gradually became fine with the increase of ball milling time. The bauxite residue without ball milling, mainly composed of irregular polygonal amorphous materials, was compact. The diameter of bauxite residue was less than 5 μm . The surface of the samples became rough after ball milling for 15 min. After ball milling for 30 min, the diameter of bauxite residue particles was 2 μm , and the particle size distribution was uniform. Mechanical ball milling broke the residue particles, which might improve the chemical reactivity of bauxite residue [10]. With the increase in milling time, the distribution of major metal elements on the surface of bauxite residue was increasingly dispersed and uniform. Mechanical ball milling could destroy the crystalline structure of the Fe-, Al- and Si-contained minerals into dissociated states or

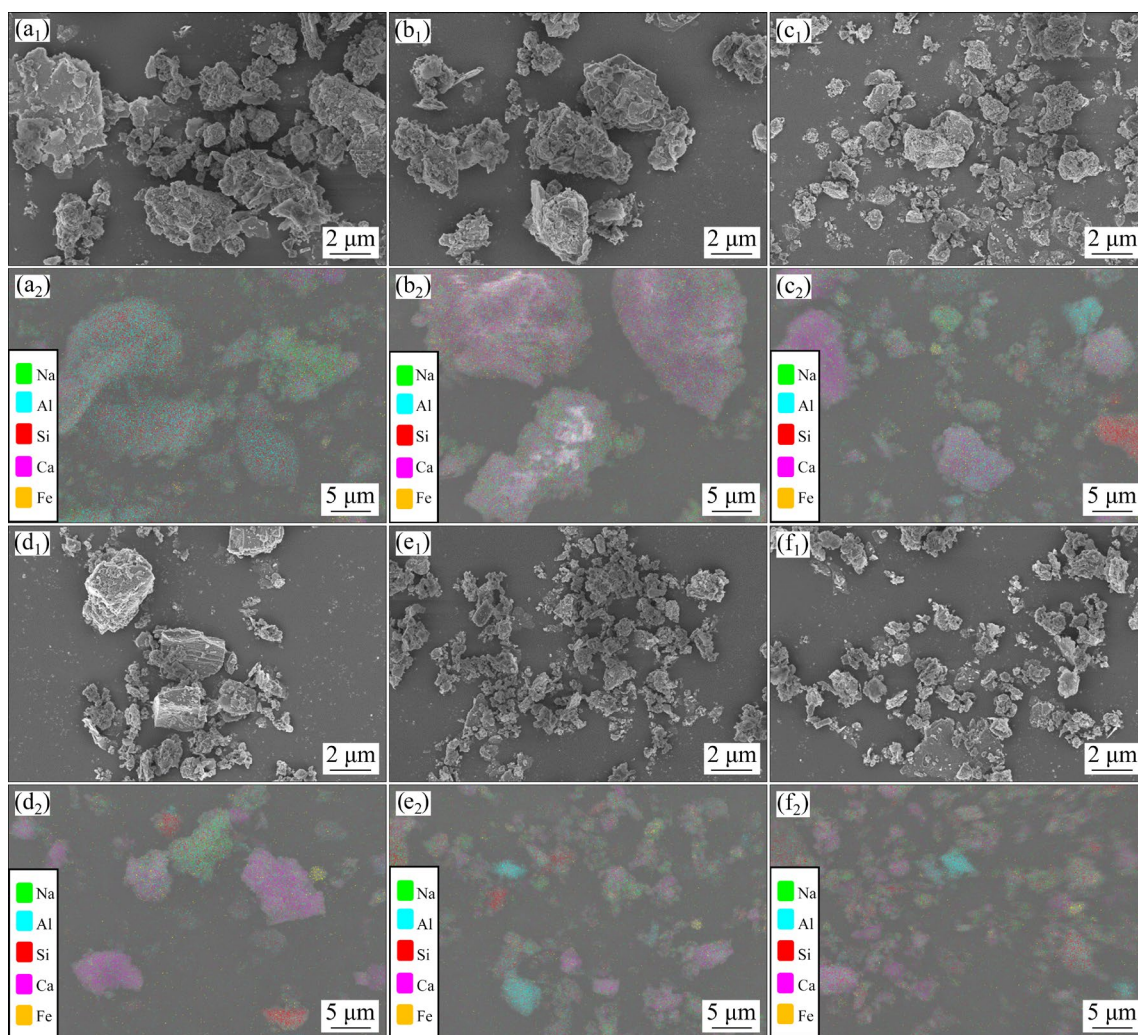


Fig. 7 Morphology (a_1 – f_1) and element distribution (a_2 – f_2) of bauxite residue with different treatments obtained by SEM–EDS: (a_1 , a_2) GBR 5%; (b_1 , b_2) GBR 10%; (c_1 , c_2) GBR 5%–15 min; (d_1 , d_2) GBR 10%–15 min; (e_1 , e_2) GBR 5%–30 min; (f_1 , f_2) GBR 10%–30 min

amorphous forms [38]. With the increase of FGD gypsum, the distribution of Na, Al, Si, Ca, and Fe had limited changes, which indicated that 5% of FGD gypsum was sufficient for the dealkalization of bauxite residue. It is worth noting that the relative content of Na increased with the increase of mechanical milling time, indicating that mechanical ball milling activated the active components in the minerals and exposed Na⁺ from the interior of Na-containing minerals, which might improve the ion exchange efficiency [34]. Therefore, mechanical ball milling reinforced the dealkalization of bauxite residue by FGD gypsum.

4 Conclusions

(1) FGD gypsum could remove the free alkali by precipitation and balance the chemically-bonded alkali by ion exchange. The addition of 5% FGD gypsum was appropriate for the dealkalization of bauxite residue.

(2) Mechanical ball milling of 30 min increased the expansion coefficient of bauxite residue, and changed the physical structure and element distribution of residue particles, thus promoting the ions exchange efficiency of Ca and Na in bauxite residue.

(3) The integration of FGD gypsum (5%) and mechanical ball milling (30 min) increased the Na⁺ concentration from 407.3 to 961.8 mg/L in the residue leachate, and significantly decreased the Na₂O content in the residue solid, showing an effective strategy for alkaline regulation of bauxite residue.

CRedit authorship contribution statement

Feng ZHU: Conceptualization, Investigation, Writing – Original draft; **Xu-yao GUO:** Writing – Review & editing, Data curation, Formal analysis; **Jun JIANG:** Writing – Review & editing, Funding acquisition; **Kai-bin CHEN:** Investigation; **Xuan-zhi ZHU:** Investigation; **Dan-dan DENG:** Investigation; **Yu-jun WU:** Writing – Review & editing, Visualization, Investigation; **Yu-wei HUANG:** Investigation; **Sheng-guo XUE:** Writing – Review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this paper.

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References

- [1] JIANG Yi-fan, QIN Xin-feng, ZHU Feng, ZHANG Yi-fan, ZHANG Xian-chao, HARTLEY W, XUE Sheng-guo. Halving gypsum dose by *Penicillium oxalicum* on alkaline neutralization and microbial community reconstruction in bauxite residue [J]. Chemical Engineering Journal, 2023, 451: 139008.
- [2] XUE Sheng-guo, WU Yu-jun, LI Yi-wei, KONG Xiang-feng, ZHU Feng, HARTLEY W, LI Xiao-fei, YE Yu-zhen. Industrial wastes applications for alkalinity regulation in bauxite residue: A comprehensive review [J]. Journal of Central South University, 2019, 26: 268–288.
- [3] ZHU Feng, CHENG Qing-yu, XUE Sheng-guo, LI Chu-xuan, HARTLEY W, WU Chuan, TIAN Tao. Influence of natural regeneration on fractal features of residue microaggregates in bauxite residue disposal areas [J]. Land Degradation & Development, 2018, 29: 138–149.
- [4] KE Wen-shun, ZHANG Xian-chao, ZHU Feng, WU Hao, ZHANG Yi-fan, SHI Yan, HARTLEY W, XUE Sheng-guo. Appropriate human intervention stimulates the development of microbial communities and soil formation at a long-term weathered bauxite residue disposal area [J]. Journal of Hazardous Materials, 2021, 405: 124689.
- [5] ZHU Feng, HOU Jing-tao, XUE Sheng-guo, WU Chuan, WANG Qiong-li, HARTLEY W. Vermicompost and gypsum amendments improve aggregate formation in bauxite residue [J]. Land Degradation & Development, 2017, 28: 2109–2120.
- [6] GUO Ying, ZHU Feng, WU Chuan, TIAN Tao, RICHARD J. H, XUE Sheng-guo. Dynamic change and diagnosis of physical, chemical and biological properties in bauxite residue disposal areas [J]. Journal of Central South University, 2019, 26: 410–421.
- [7] HUANG Nan, TANG Lu, ZHU Feng, WU Chuan, HARTLEY W, ZHOU Jing-ju, XUE Sheng-guo. Salt ions accumulation and distribution characteristics of pioneer plant species at a bauxite residue disposal area, China [J]. Journal of Central South University, 2019, 26: 323–330.
- [8] WU Yu-jun, LI Meng, ZHU Feng, HARTLEY W, LIAO

- Jia-xin, AN Wen-hui, XUE Sheng-guo, JIANG Jun. Variation on leaching behavior of caustic compounds in bauxite residue during dealkalization process [J]. *Journal of Environmental Sciences*, 2020, 92: 141–150.
- [9] KONG Xiang-feng, LI Meng, XUE Sheng-guo, HARTLEY W, CHEN Cheng-rong, WU Chuan, LI Xiao-fei, LI Yi-wei. Acid transformation of bauxite residue: Conversion of its alkaline characteristics [J]. *Journal of Hazardous Materials*, 2017, 324: 382–390.
- [10] WU Yu-jun, JIANG Yi-fan, JIANG Jun, CHEN Li, QIN Xin-feng, HARTLEY W, XUE Sheng-guo. Conversion of alkaline characteristics of bauxite residue by mechanical activated pretreatment: Implications for its dealkalization [J]. *Journal of Environmental Management*, 2022, 305: 114446.
- [11] LIU Yong, LIN Chu-xia, WU Yong-gui. Characterization of red mud derived from a combined Bayer process and bauxite calcination method [J]. *Journal of Hazardous Materials*, 2007, 146: 255–261.
- [12] LI Yi-wei, LI Qi-hou, SUN Wei, PENG Zhi-hong, MILLAR G J, XUE Sheng-guo, JIANG Jun. Migration of alkaline constituents and restoration evaluation in bauxite residue disposal areas [J]. *Bulletin of Environmental Contamination and Toxicology*, 2022, 109: 20–29.
- [13] COURTNEY R, HARRIS J A, PAWLETT M. Microbial community composition in a rehabilitated bauxite residue disposal area: A case study for improving microbial community composition [J]. *Restoration Ecology*, 2014, 22: 798–805.
- [14] SANTINI T C, KERR J L, WARREN L A. Microbially-driven strategies for bioremediation of bauxite residue [J]. *Journal of Hazardous Materials*, 2015, 293: 131–157.
- [15] CHEN Li, CHENG Qing-yu, ZHANG Xian-chao, ZHU Ming-xing, HARTLEY W, ZHU Feng. Novel plant growth-promoting bacteria isolated from bauxite residue: The application for revegetation [J]. *Bulletin of Environmental Contamination and Toxicology*, 2022, 109: 3–12.
- [16] LYU F, HU Y H, WANG L, SUN W. Dealkalization processes of bauxite residue: A comprehensive review [J]. *Journal of Hazardous Materials*, 2021, 403: 123671.
- [17] POWER G, GRAEFE M, KLAUBER C. Bauxite residue issues: I. Current management, disposal and storage practices [J]. *Hydrometallurgy*, 2011, 108: 33–45.
- [18] TIAN Tao, ZHANG Chao-lan, ZHU Feng, YUAN Shan-xin, GUO Ying, XUE Sheng-guo. Effect of phosphogypsum on saline-alkalinity and aggregate stability of bauxite residue [J]. *Transactions of Nonferrous Metals society of China*, 2021, 31: 1484–1495.
- [19] XUE Sheng-guo, LI Meng, JIANG Jun, MILLAR G J, LI Chu-xuan, KONG Xiang-feng. Phosphogypsum stabilization of bauxite residue: Conversion of its alkaline characteristics [J]. *Journal of Environmental Sciences*, 2019, 77: 1–10.
- [20] BURKE I T, PEACOCK C L, LOCKWOOD C L, STEWART D I, MORTIMER R J G, WARD M B, RENFORTH P, GRUIZ K, MAYES W M. Behavior of aluminum, arsenic, and vanadium during the neutralization of red mud leachate by HCl, gypsum, or seawater [J]. *Environmental Science & Technology*, 2013, 47: 6527–6535.
- [21] LI Ya-ying, HAYNES R J, CHANDRAWANA I, ZHOU Ya-feng. Properties of seawater neutralized bauxite residues and changes in chemical, physical and microbial properties induced by additions of gypsum and Chock organic matter [J]. *Journal of Environmental Management*, 2018, 223: 489–494.
- [22] FU Yan-rong, HE Kun, ZHOU Chun-liang, MAO Yu-mei. Improvement of saline-alkaline soil via flue gas desulfurization gypsum and safety analysis of the associated heavy metals [J]. *Journal of Physics: Conference Series*, 2021, 1838: 012051.
- [23] ZOLTÁN J A. Aspects of mechanochemical activation in terms of comminution theory [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1998, 141: 449–462.
- [24] ZHOU Yuan, WANG Yun-yan, LIANG Yan-jie, ZHOU Yi-wei, LIU Zhen-xing, PENG Cong, KE Yong, MIN Xiao-bo. Microstructure and magnetic properties of FeAs with coarse-grain and nanocrystalline structure [J]. *Transactions of Nonferrous Metals Society of China*, 2022, 32: 972–979.
- [25] KINNARINEN T, HOLLIDAY L, HAKKINEN A. Dissolution of sodium, aluminum and caustic compounds from bauxite residues [J]. *Minerals Engineering*, 2015, 79: 143–151.
- [26] GUO Ying, QIN Xin-feng, GUO Xu-yao, JIANG Yi-fan, TIAN Tao, ZHU Feng, XUE Sheng-guo. Dynamic variations of soil-formation indicators in bauxite residue driven by the integration of waste solids and microorganisms [J]. *Bulletin of Environmental Contamination and Toxicology*, 2022, 109: 202–208.
- [27] ZHU Feng, XUE Sheng-guo, HARTLEY W, HUANG Ling, WU Chuan, LI Xiao-fei. Novel predictors of soil genesis following natural weathering processes of bauxite residues [J]. *Environmental Science and Pollution Research*, 2016, 23: 2856–2863.
- [28] LI Xiao-bin, ZHOU Zhao-yu, WANG Yi-lin, ZHOU Qiu-sheng, QI Tian-gui, LIU Gui-hua, PENG Zhi-hong. Enrichment and separation of iron minerals in gibbsitic bauxite residue based on reductive Bayer digestion [J]. *Transactions of Nonferrous Metals Society of China*, 2020, 30: 1980–1990.
- [29] HUA T, HAYNES R J, ZHOU Y F, BOULLEMANT A, CHANDRAWANA I. Potential for use of industrial waste materials as filter media for removal of Al, Mo, As, V and Ga from alkaline drainage in constructed wetlands—Adsorption studies [J]. *Water Research*, 2015, 71: 32–41.
- [30] BURKE I T, MAYES W M, PEACOCK C L, BROWN A P, JARVIS A P, GRUIZ K. Speciation of Arsenic, Chromium, and Vanadium in red mud samples from the Ajka Spill Site, Hungary [J]. *Environmental Science & Technology*, 2012, 46: 3085–3092.
- [31] BANNING N C, PHILLIPS I R, JONES D L, MURPHY D V. Development of microbial diversity and functional potential in bauxite residue sand under rehabilitation [J]. *Restoration Ecology*, 2011, 19: 78–87.
- [32] WU Yu-jun, LI Xiao-fei, JIANG Jun, HARTLEY W, ZHU Feng, XUE Sheng-guo. Integrating column leaching experiments and geochemical modelling to predict the long-term alkaline stability during erosion process for

- gypsum amended bauxite residue [J]. Journal of Environmental Management, 2021, 289: 112479.
- [33] AROGUNDADE A I, MEGAT-YUSOFF P S M B, AHMAD F, BHAT A H. Ball milled bauxite residue as a reinforcing filler in phosphate-based tumescent system [J]. Metallurgical and Materials Engineering, 2017, 23: 353–362.
- [34] YANG Wan-zhang, MA Wen-hui, LI Peng-fei, LIU Zhan-wei, YAN Heng-wei. Alkali recovery of bauxite residue by calcification [J]. Minerals, 2022, 12: 636.
- [35] GENG Jun-jun, ZHOU Min, ZHANG Ting, WANG Wei-xing, WANG Teng, ZHOU Xian, WANG Xiao-shu, HOU Hao-bo. Preparation of blended geopolymer from red mud and coal gangue with mechanical co-grinding preactivation [J]. Materials and Structures, 2017, 50: 109.
- [36] KONG Xiang-feng, GUO Ying, XUE Sheng-guo, HARTLEY W, WU Chuan, YE Yu-zhen, CHENG Qing-yu. Natural evolution of alkaline characteristics in bauxite residue [J]. Journal of Cleaner Production, 2017, 143: 224–230.
- [37] LI Yi-wei, LUO Xing-hua, LI Chu-xuan, MILLAR G J, JIANG Jun, XUE Sheng-guo. Variation of alkaline characteristics in bauxite residue under phosphogypsum amendment [J]. Journal of Central South University, 2019, 26: 361–372.
- [38] XU Jian-lin, REN Shi-bo, KANG Cheng-hu, CUI Fan-dong, LI Cheng-si, FAN Ji-liang. Study on the ball milling modification of attapulgite [J]. Materials Research Express, 2020, 7: 115006.

机械球磨与烟气脱硫石膏联用对赤泥脱碱的影响

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摘 要: 结合溶液化学、矿物学和微观形貌分析, 研究机械球磨和烟气脱硫石膏联用对赤泥碱性调控的影响。结果表明, 经机械球磨 30 min 后用烟气脱硫石膏处理的赤泥中 Na_2O 含量降低了 30% (质量分数) 以上; 机械球磨改变了赤泥矿物表面元素分布和晶型结构, 促进了赤泥碱性矿物的溶解, 从而提高了脱碱后赤泥的酸中和能力。5% (质量分数) 烟气脱硫石膏和 30 min 球磨时间可实现赤泥脱碱。

关键词: 赤泥; 碱性调控; 烟气脱硫石膏; 机械活化; 赤泥土壤化

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