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Effect of phosphogypsum and poultry manure on aggregate-associated alkaline characteristics in bauxite residue

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Abstract

Bauxite residue is a highly alkaline solid waste with poor physical structure which ultimately limits plant growth. Ecological reconstruction is an effective strategy to improve its environmental management, although soil formation process still require further investigation. Here, an incubation experiment was used to investigate the effects of phosphogypsum and poultry manure, on aggregate size distribution and aggregate-associated exchangeable bases of bauxite residue. Phosphogypsum and poultry manure additions significantly increased the proportion of 2-1 mm residue aggregates and enhanced mean weight diameter (MWD) of residues in the 0-20 cm and 20-40 cm layers, although little effect was evident in the 40-60 cm layer. Phosphogypsum addition reduced pH and EC values to approximately 8.5 and 200 mS/cm in different size aggregates at 0-20 cm. Exchangeable Ca^{2+} concentration was improved, especially in 0.25-0.05 mm and <0.05 mm aggregates, following amendment additions. The relative contents of katoite and cancrinite in >0.25 mm aggregate fractions were relatively higher, which was consistent with changes in pH. Phosphogypsum and poultry manure changed the microstructure and surrounding pores of residue aggregates, whilst the concentration of Ca on microaggregate surfaces was higher than that on macroaggregates. These findings reveal that application of phosphogypsum and poultry manure directly alter the distribution of exchangeable bases and alkaline indicators within residue aggregates, resulting in aggregate size distribution and microstructure variations.

Highlights

1. Effect of phosphogypsum and poultry manure on aggregate-associated alkaline characteristics in bauxite residue were investigated.
2. Amendment additions increased the proportion of 2-1 mm residue aggregates and enhanced aggregate stability.
3. pH, EC, ESP, and exchangeable bases varied significantly within residue aggregates.
4. Amendment additions changed the micro-structure and surface elemental distribution of residue aggregates.

Keywords

Bauxite residue; amendments addition; aggregate stability; aggregate-associated alkaline characteristics; soil formation

1 Introduction

Bauxite residue is the industrial by-product generated from the extraction of alumina from bauxite ore via the Bayer process, which results in high alkalinity and salinity (Di Carlo et al. 2019). The global inventory reached 4.4 billion tons in 2018, with an annual increase of 200 million tons due to the rapid development of alumina industry in recent years (Xue et al. 2019). In the absence of effective reprocessing options, bauxite residue is disposed in bauxite residue disposal areas (BRDAs), which can occupy a lot of land and create potential water and air pollution problems (Santini and Peng 2017; Li et al. 2019). Revegetation is a promising strategy for comprehensive environmental control of BRDAs, but major limitations to plant growth exist in residues including high pH, salinity and poor physical structure (Di Carlo et al. 2019). Fine residue particles consolidate to form a solid mass, which results in a low water-holding and fertilizer-conserving capacity (Zhu et al. 2017b). A variety of approaches including gypsum and organic waste additions have been trialed in pot or field experiments to improve physical and/or chemical properties prior to plant establishment (Li et al. 2018b; Rezaei Rashti et al. 2019b). Nevertheless, very few papers have reported field cases on long-term plant growth. Microbial community pH tolerance is also significantly correlated to plant establishment (Rath et al. 2019). Given the limitations of this material as a growth medium, establishing a sustainable ecosystem requires a detailed understanding of soil formation processes, especially for regulation of aggregate structure and its stability (Li et al. 2018).

Aggregates, the basic composition unit of soil, are formed by a combination of clay particles with organic residue and inorganic materials. Aggregation is the assembly process of different size mixtures of soil particles and microaggregates into a larger architecture (Wang et al. 2019). Soil aggregation directly influences water infiltration, nutrient accumulation and transport, gas transmission, and microbial metabolism (Chandrasekhar et al. 2019). Maintaining improved aggregate stability is essential for minimizing erosion and improving plant growth. Chemical parameters including pH, cation concentrations, cation exchange capacity and clay mineralogy are the major factors that determine flocculation processes in aggregates or clay particles (Bronick and Lal 2005b). Controlling soil pH is important in soils with dispersive clays due to the dispersion effects of negative surface charge on microaggregates. The use of soil amendments containing Ca^{2+} and Mg^{2+}, such as lime and gypsum, have significant effects on soil aggregation due to bridging with clay particles and organic matter (Huang et al. 2019b). Conversely, sodium has a highly dispersive action, directly resulting in disaggregation (Zhu et al. 2015).

Bauxite residue has high pH values (10.5-12.8), electrical conductivity (EC) (1.4-28.4 mS/cm) and exchangeable sodium percentages (ESP) (, 32-91%), which result in poor aggregate stability (Jones and Haynes 2011). In previous studies, we have identified that gypsum (or phosphogypsum) and organic wastes (e.g. vermicompost) may change the physico-chemical properties and improve aggregate stability of bauxite residue (Xue et al. 2019; Zhu et al. 2017c). However, the effects on the distribution pattern of aggregate-associated salt ions were rarely reported. The hypothesis of this study was that aggregate stability would be improved along with the alteration of typical cations in bauxite residue following phosphogypsum and poultry manure addition. Thus, the objectives of the present study were 1), to investigate changes in residue aggregates and their stability in soil columns, 2), to understand alterations in the distribution of exchangeable bases within aggregate fractions, and 3), to reveal variations in mineralogical composition and micro-morphology of residue aggregates.

Materials and methods

1.1 Materials

Bauxite residue was sampled from an alumina refinery (36°45'15"N, 108°3'35"E) in the Shandong province, China. Phosphogypsum was obtained from a manufacturing enterprise in the Guizhou Province, and poultry manure was purchased from a farm in the Hunan Province. All materials were air-dried, and passed through a 2 mm sieve prior to soil column experiments.

Table 1 Basic properties of materials for the experiment

	pH	EC (µS/cm)	CEC (cmol/kg)	Exchangeable bases (mg/kg)			
				Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}
Bauxite Residue	10.43	197.3	339.49	1327.60	178.71	3.74	2175.86
Phosphogypsum	2.75	165.2	13.59	10.79	397.24	35.624	67.86
Poultry manure	7.15	157.5	60.31	277.12	40.97	0.72	406.18

1.2 Experiment design

Soil columns (100 cm high, 14 cm external diameter and 12 cm inner diameter) were used to simulate the current situation at the disposal area. A 150 µm nylon mesh was placed at the bottom of each column and a quartz sand layer (15 cm high) was added above the nylon mesh to reduce overflow of residue samples. Residue samples were then filled into the columns until the height reached 60 cm. Treatments were as follows: 1) control (CK), 2), 2% (w/w) phosphogypsum (PG), and 3), 2% (w/w) phosphogypsum and 4% (w/w) poultry manure (PM). For treated residues, the amendments were completely mixed with bauxite residue and then the mixtures were filled within the surface layer (0-20 cm). Each column was wetted to 70% water holding capacity and then incubated for 8 weeks. At the end of the incubation period, residue samples from three depths (0-20 cm, 20-40 cm, 40-60 cm) were collected, oven dried at 65℃ for 48 h, and passed through a 2 mm sieve prior to physico-chemical analyses.

1.3 Aggregate separation

Residue samples were separated into 4 classes (<0.05 mm, 0.05-0.25 mm, 0.25-1 mm, and 1-2 mm) by dry sieving (Yin et al. 2016). Aggregates obtained from each sieve were collected and weighed. Mean weight diameter (MWD), a typical indicator to evaluate aggregate stability, was calculated as follows:

$$MWD=\sum_{i=1}^{n} X_{\mathrm{i}} \times W_{i} \tag{1}$$

Where: X_i is the mean diameter of each size fraction (mm), W_i is the proportion of the samples in the corresponding size fraction, and n is the number of size fractions.

1.4 Physico-chemical properties

pH and EC for each size were determined by water extraction (ratio of solid:water 1:5) using a pH/conductivity meter. The contents of exchangeable cations (K^+, Ca^{2+}, Na^+, Mg^{2+}) were extracted with 1mol/L ammonium acetate (pH=7), and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Exchangeable sodium percentage (ESP) was determined as the percentage of exchangeable Na^+ in the four exchangeable bases, whilst sodium adsorption ratio (SAR) was calculated as the relative concentration of Na^+ compared to Ca^{2+} and Mg^{2+} in the saturation paste extracts.

Mineral composition of residue aggregates for each size were analyzed by XRD (X-ray powder diffraction). The specimens were oven-dried, ground and passed through a 300-mesh sieve prior to XRD analysis conducted on a Bruker D8 discover 2500 (Rigaku Corporation, Japan). X-ray diffraction patterns were obtained from 10° to 80° at a step size of 0.04°2θ with a scan rate of 1°2θ min^{-1}. The PANalytical analysis package was applied to quantify the main phases in residue aggregates.

1.5 BSEM-EDS analysis

Reside macroaggregates (2-1 mm) and microaggregates (0.25-0.05 mm) from the three treatments were coated with gold and analyzed using a scanning electron microscope, equipped with energy dispersive X-ray spectroscopy (Quanta-200) (FEI, Portland, Oregon, USA).

1.6 Statistical analysis

All analyses were performed in triplicate. The experimental data were statistically analyzed using IBM SPSS 22.0 software. Significant differences of the relative parameters were determined by one-way ANOVA at $p<0.05$ with the Duncan test. All figures were plotted using Origin Pro 9.0.

2 Results and discussions

2.1 Aggregate size distribution of bauxite residue

Aggregate size distribution of bauxite residue from dry sieving are presented in Fig. 1. The main fraction, 1-0.25 mm aggregates in the untreated residue at 0-20 cm, accounted for between 39% and 45% of the total weight. Aggregate fractions in untreated bauxite residue decreased in the following order: 1-0.25 mm>0.25-0.05 mm>2-1 mm>0-0.05 mm. With an increase in residue depth, the fraction of 1-0.25 mm residue aggregates decreased significantly, whilst the proportion of 0.25-0.05 mm and <0.05 mm residue aggregates increased from 40.56% to 44.79% and 4.18% to 6.31%, respectively.

Phosphogypsum and poultry manure additions significantly changed aggregate size distribution. The main fraction in treated residues (PG and PM) at 0-20 cm was 1-0.25 mm, which accounted for approximately 40% (Fig. 1b). The proportion of treated residue aggregate fractions decreased in the following order: 1-0.25 mm>0.25-0.05 mm>2-1 mm>0-0.05 mm, which was in accordance with the arrayed rule in untreated residue. Furthermore, the 2-1 mm aggregates in PG and PM accumulated from 11.28% to 21.37% and 25.98%, respectively (Fig. 1a). Compared with phosphogypsum addition (PG), the combined additions had significant effects on the proportions of 2-1 mm aggregates, whilst little effect was observed for <0.05 mm aggregates (Fig. 1). This indicated that poultry manure may effectively stimulate formation of 2-1 mm macro-aggregates in bauxite residue. The extra poultry manure addition did not reduce the proportion of <0.05 mm aggregates, as the <0.05 mm fraction in PG and PM were almost the same (Fig. 1d). This suggests that phosphogypsum may have more effect on formation of <0.05 mm microaggregates.

With an increase in residue depth, the proportion of 2-1 and 1-0.25 mm aggregates decreased, whilst the proportion of 0.25-0.05 and <0.05 mm aggregates increased in treated residues (Fig. 1). In this experiment, phosphogypsum and/or poultry manure were added to the residues at 0-20 cm. During periodic water leaching in the soil column, several soluble ions may have migrated to the 20-40 cm and 40-60 cm layers, which may affect the process of particle aggregation. Results for the proportions of four different aggregate fractions in the treated residues (PG and PM) at 40-60 cm changed slightly, which indicated that phosphogypsum and poultry manure had little effect on aggregate formation in the deeper layers.

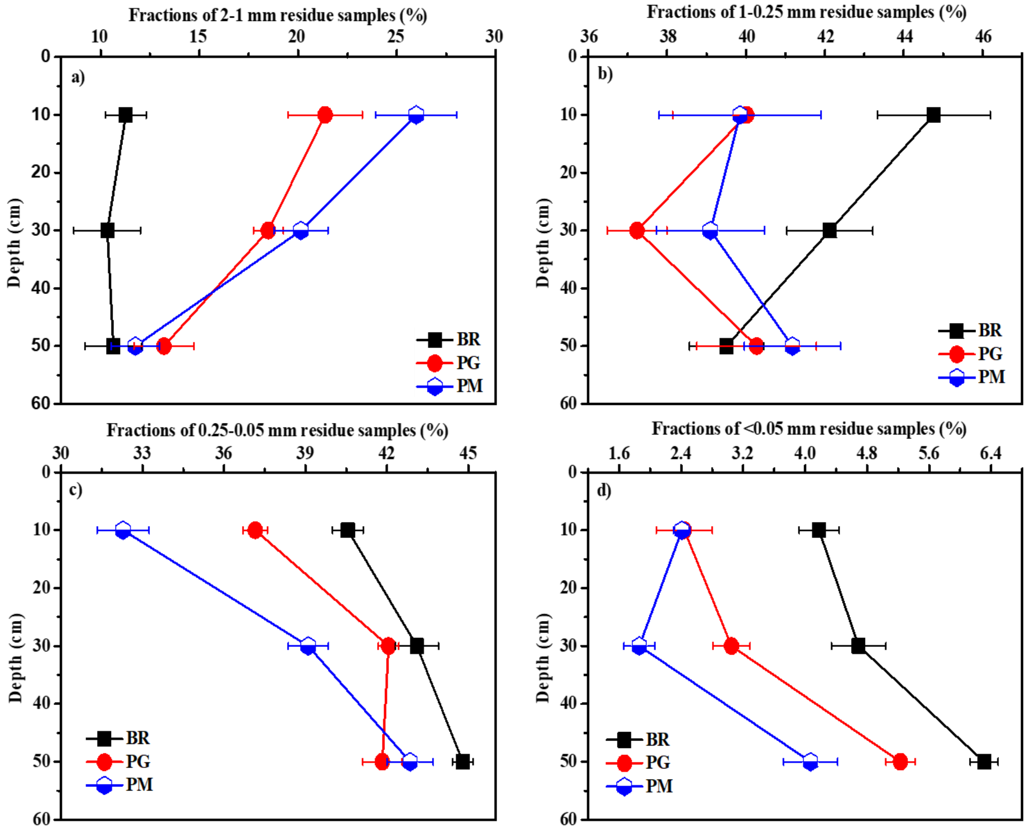


Fig. 1 Aggregate size distribution of bauxite residue from the dry sieving method. Error bars indicate standard errors (n=3)

MWD values for the residues following treatment are presented in Fig. 2. For untreated residue (BR), the MWD values at different depths varied slightly. With an increase in depth, MWD values for treated residues (PG and PM) decreased significantly from 0.62 to 0.51 mm and 0.69 to 0.50 mm, respectively. Furthermore, MWD values of PM were larger than those of PG at the same depth. This revealed that poultry manure had a significant effect on residue aggregate formation.

Bauxite residue was fine grained with a mean particle size diameter of approximately 10 µm, resulting in a high water holding capacity and low infiltration rate (Qi et al. 2018). The fine particles may be bound together to form a large solid mass having few pores, being detrimental to plant root elongation. The improved aggregate structure had positive effects on gas, water and nutrient transport, whilst increasing soil erosion resistance (Wang et al. 2015). Phosphogypsum and poultry manure additions improved the 2-1 mm aggregate fractions. As a result, MWD values of treated residues (PG and PM) increased. Phosphogypsum addition may provide an excessive amount of Ca^{2+}, which may improve the formation of macro-aggregates through cationic bridging with clay-size particles and organic materials. Xue et al. (Xue et al. 2018) found that 2% phosphogypsum improved MWD values of bauxite residue from 0.2 to 0.25 mm following fast wetting. Courtney and Kirwan (Courtney and Kirwan 2012) demonstrated that phosphogypsum was an effective ameliorant to improve the physical properties of bauxite residue. Strong positive linear relationships were observed between MWD and exchangeable Ca^{2+} contents in 2-1 mm, 1-0.25 mm, 0.25-0.05 mm, and <0.05 mm residue aggregates (r=0.738, 0.927, 0.747 and 0.791 respectively, P<0.05). Furthermore, organic carbon was the major binding material and increased organic carbon is usually related to increased aggregation (Zhong et al. 2019). Wang et al. (Wang et al. 2018) discovered that a positive correlation between aggregate stability and aggregate-associated organic carbon content improved vegetation rehabilitation and reduced soil erosion on the Loess Plateau. PM had a greater content of >0.25 mm aggregates and a larger MWD value than PG, which indicated that the combination of amendments was more beneficial to aggregate stability than phosphogypsum alone. Zhu et al. (Zhu et al. 2017) observed that vermicompost significantly increased the fraction of >0.25 mm microaggregates, and phosphogypsum stimulated the flocculation of silt- and clay-size particles. This would imply that the input of organic carbon may enhance the formation of residue marcoaggregates, whilst increasing the MWD value.

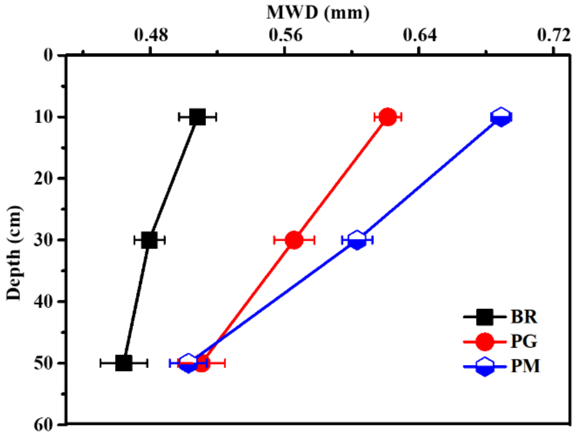


Fig. 2 MWD of bauxite residue from the dry sieving method. Error bars indicate standard errors (n=3)

2.2 Bauxite residue pH and EC

The influence of treatments on residue aggregate size classe pH are presented in Fig. 2. For untreated residues (BR), pH varied from 9.5 to 10.5. Untreated bauxite residue pH at 0-20 cm decreased in the following order: 0.25-0.05 mm>0-0.05 mm>1-0.25 mm>2-1 mm. pH of untreated residues at the surface was lower and steadily increased to a depth of 60 cm. pH of the treated residues were notably lower. Following phosphogypsum addition, the residues had pH values of 8.3-8.7 at 0-20 cm, and increased steadily to 8.4-9.5 at 40-60 cm. Generally, pH of PM at different depths was lower than that of PG. This indicated that although poultry manure did not provide acidic compounds, the combined addition may ameliorate aggregate structure and pore distribution to benefit the migration of alkaline substances across the aggregate size fractions.

EC values for the different treatments are shown in Fig. 3. Generally, with an increase in depth, EC decreased significantly. For untreated residues (BR), EC values ranged from 335 to 546 mS/cm between 0-20 cm. Among them, 1-0.25 mm residue aggregates had the lowest EC value (335 mS/cm). Phosphogypsum addition decreased EC values to about 200 mS/cm. Compared to PG, EC values in PM at a depth of 0-20 cm did not change significantly. Furthermore, at depth, aggregates in PM had lower EC values than those in PG, which indicated that phosphogypsum and poultry manure additions may affect the variation of EC values more significantly than phosphogypsum alone.

The pH of bauxite residue ranged from 9.2 to 12.8 with an average value of 11.3 ± 1.0 (Santini and Banning 2016). The major alkaline anions in the residue liquor were OH^-, CO_3^{2-}, HCO_3^-, $Al(OH)_4^-$. Xue et al. (Xue et al. 2019) investigated salt ion distribution at a disposal area and discovered that CO_3^{2-}, HCO_3^-, Cl^- and SO_4^{2-} were the major soluble anions in bauxite residue. Variation in these alkaline anions directly determined changes in pH. Adding phosphogypsum to the residue liquor decreased the concentrations of alkaline anions, whilst alkaline phases may partly dissolve to sustain the pH by supplying excess quantities of alkaline anions. The EC of bauxite residue ranged over 1.4-28.4 mS/cm with an average value of 7.4 ± 6.0 mS/cm, which required reduction prior to revegetation. Phosphogypsum and poultry manure additions changed residue aggregate size distribution, which should have improved the physical properties of the bauxite residue. Following amendment additions, the 2-0.25 mm aggregate fraction increased, which indicated that the size of pores between residue particles had increased. Therefore, the water leaching process may promote the migration of alkaline anions in the residue liquor revealing a decrease in the EC.

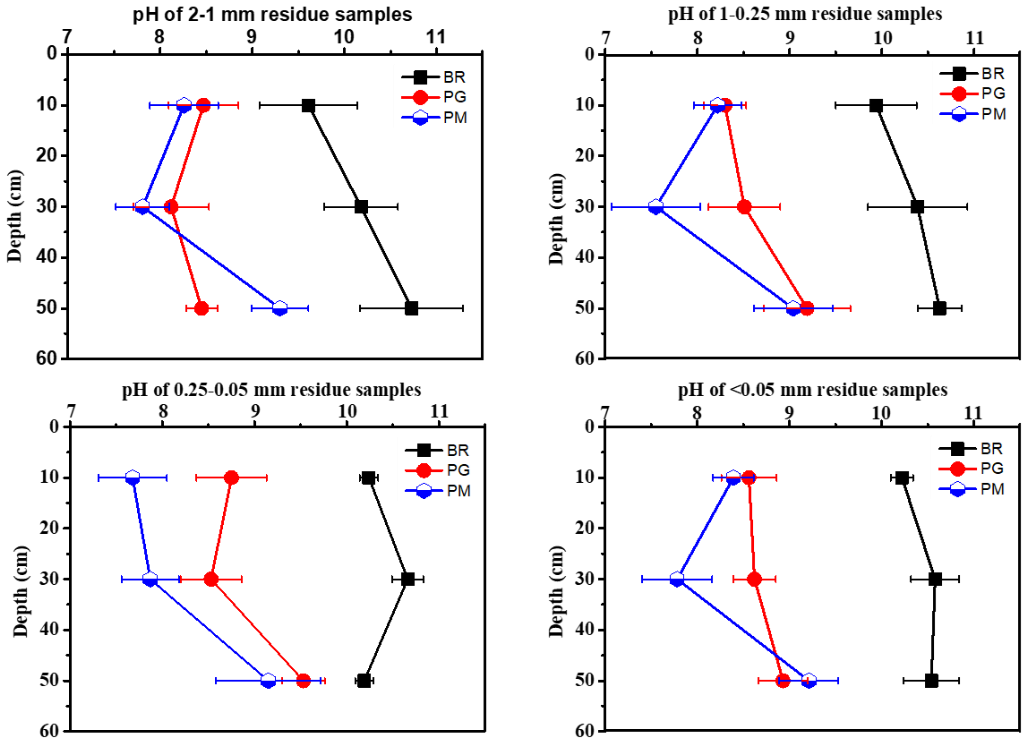


Fig. 3 pH values of residue aggregates with different sizes at different depth within the soil column experiment. Error bars indicate standard errors (n=3)

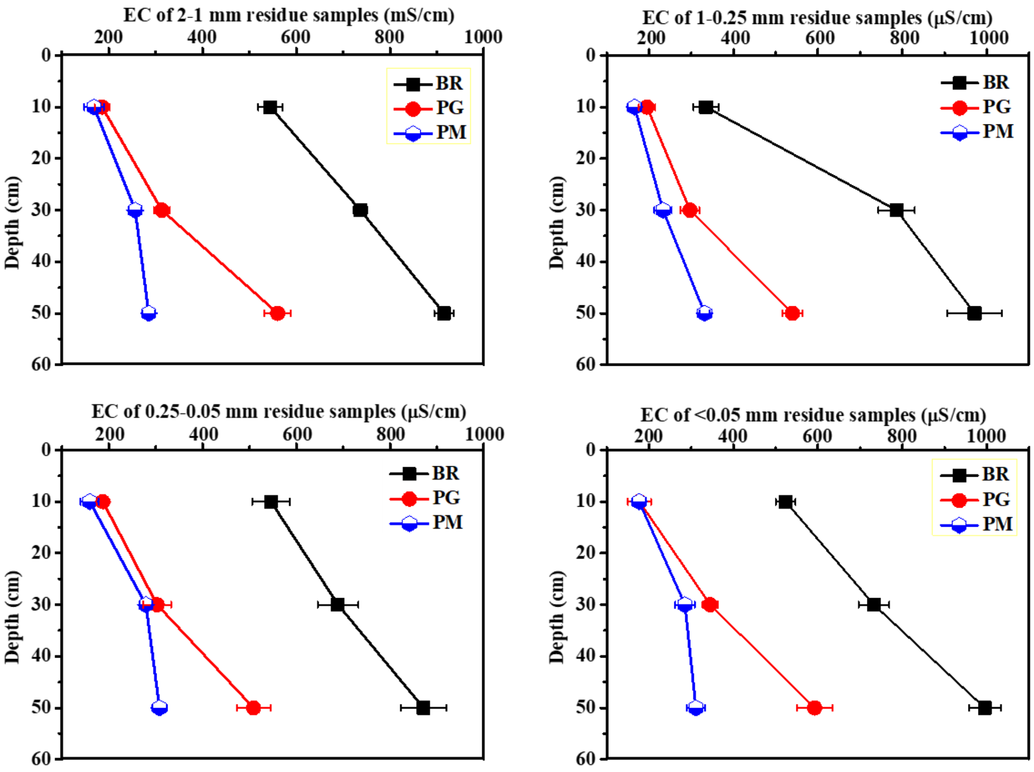


Fig. 4 EC values of residue aggregates with different sizes at different depths within the soil column experiment. Error bars indicate standard errors (n=3)

2.3 Exchangeable bases of bauxite residue

Results for ESP and SAR of bauxite residue with different size aggregates are presented in Fig. 5. ESP and SAR of untreated bauxite residue with different sizes varied from 30.1% to 44.3%, and 20.6% to 35.2%, respectively. Both alkaline indicators decreased in the following order: 2-1 mm>0-0.05 mm>1-0.25 mm>0.25-0.05 mm. Following phosphogypsum and poultry manure additions, ESP and SAR of bauxite residue decreased significantly. Furthermore, ESP and SAR of PG and PM were nearly the same, which indicated that the effects of poultry manure on ESP and SAR were not obvious. Correlation analysis showed that MWD of residue was negatively correlated with ESP and SAR in the different sized aggregates, which indicated that high values of ESP and SAR may result in particle dispersion. Amézketa (1999) stated that high ESP and SAR values produced clay dispersion and swelling and consequently degradation of stable aggregates.

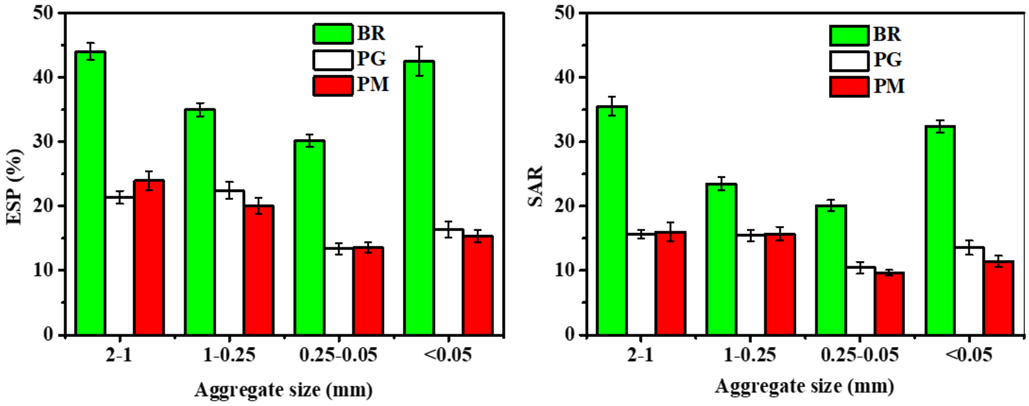


Fig. 5 ESP and SAR of residue aggregates with different sizes. Error bars indicate standard errors (n=3)

Concentrations of the four exchangeable bases decreased as follows: Ca^{2+}>Na^{+}>K^{+}>Mg^{2+}. Following phosphogypsum addition, exchangeable Ca^{2+} increased in residue aggregates. This showed that exchangeable Ca^{2+} in small size aggregates was greater than in larger sized aggregates. Phosphogypsum provided a large amount of exchangeable Ca^{2+} in residue liquor, which may consolidate the fine particles and form large-sized aggregates. A previous study revealed that phosphogypsum could stimulate the formation of silt- and clay-size residue microaggregates (Zhu et al., 2017). Significant changes also occurred in PG and PM for exchangeable Na^{+}, with slight variations for exchangeable Mg^{2+} and K^{+}. The increase in exchangeable Ca^{2+} displaced excess Na^{+} and decreased exchangeable Na^{+} in residue liquor. Variation in exchangeable Na^{+} had a significant effect on aggregate size distribution and aggregate stability of the residues. Negative linear relationships were found between MWD and exchangeable Na^{+} in 2-1mm, 1-0.25 mm, 0.25-0.05 mm and <0.05 mm residue aggregates (r=-0.945, -0.740, -0.958 and -0.970 respectively, $P<0.05$). Furthermore, the accumulation of organic carbon may provide a large amount of adsorption sites to adsorb exchangeable Na^{+}, which resulted in a slightly decrease in exchangeable Na^{+} in PM with different size aggregates generally. Jones et al. (2011) observed that the addition of organic amendments had a greater absorption capacity for sodium in residue solutions.

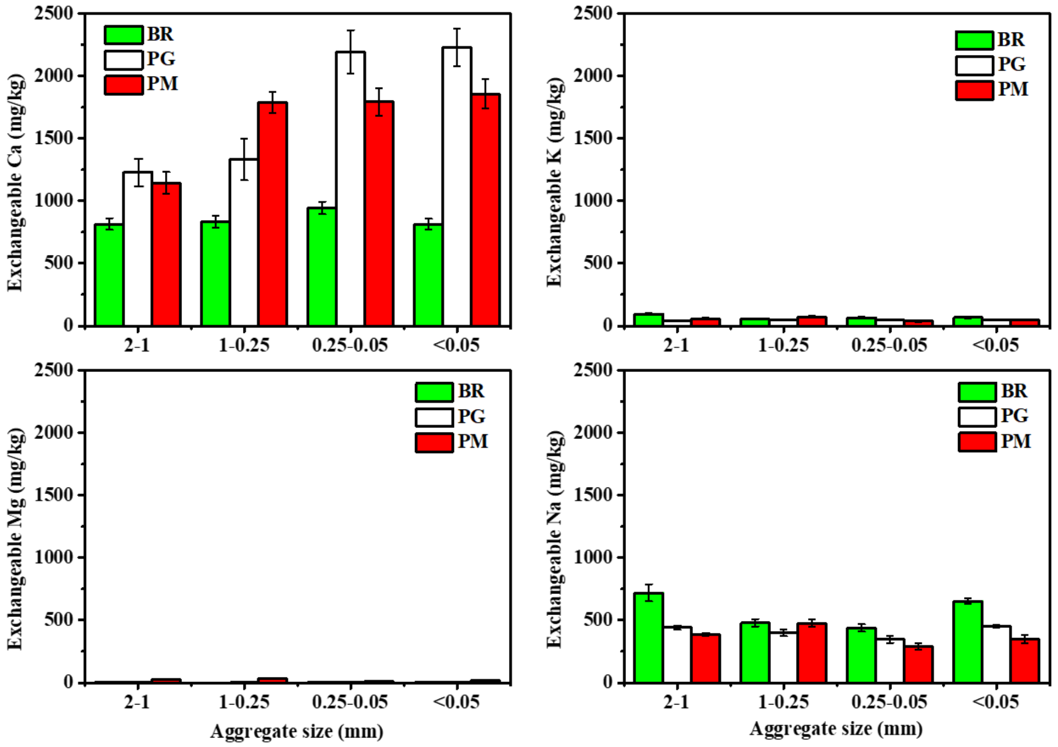


Fig. 6 Concentrations of aggregates associated with exchangeable bases. Error bars indicate standard errors (n=3)

2.4 Mineralogical composition of bauxite residue

Phosphogypsum and poultry manure additions changed the chemical properties (pH, EC, and exchangeable bases) of residue aggregates. XRD analysis of BR, PG and PM are revealed in Figure 7. The major alkaline minerals in untreated bauxite residue (BR) included TCA (tricalcium aluminate, $Ca_3Al_2(OH)_{12}$), katoite ($Ca_3Al_2(SiO_4)(OH)_8$), calcite ($CaCO_3$) and cancrinite ($Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2$) (Fig. 7). The quantified XRD results (Fig. 8) indicated that untreated residues (BR) contained 35-45% alkaline compositions, which mainly depended on bauxite source, NaOH digestion and CaO addition (Kong et al. 2016). Relative contents of katoite, calcite and cancrinite were also higher than TCA. The relative contents of katoite and cancrinite in 1-0.25 mm aggregate fractions were also relatively higher. Katoite, calcite and cancrinite may dissolve in water slowly and release alkaline ions to sustain the high alkalinity. The dissolution reactions of these alkaline minerals are summarized as follows (Eqs. 1-3):

$$Ca_3Al_2(SiO_4)(OH)_8 + 4H_2O \rightarrow 3Ca^{2+} + 2Al(OH)_3 + 6OH^- + H_2SiO_4 \tag{1}$$

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \tag{2}$$

$$Na_8Al_6Si_6O_{24}(CO_3)(H_2O)_2 + 22H_2O \rightarrow 8Na^+ + 6Al(OH)_3 + 6H_4SiO_4 + 6OH^- + CO_3^{2-} \tag{3}$$

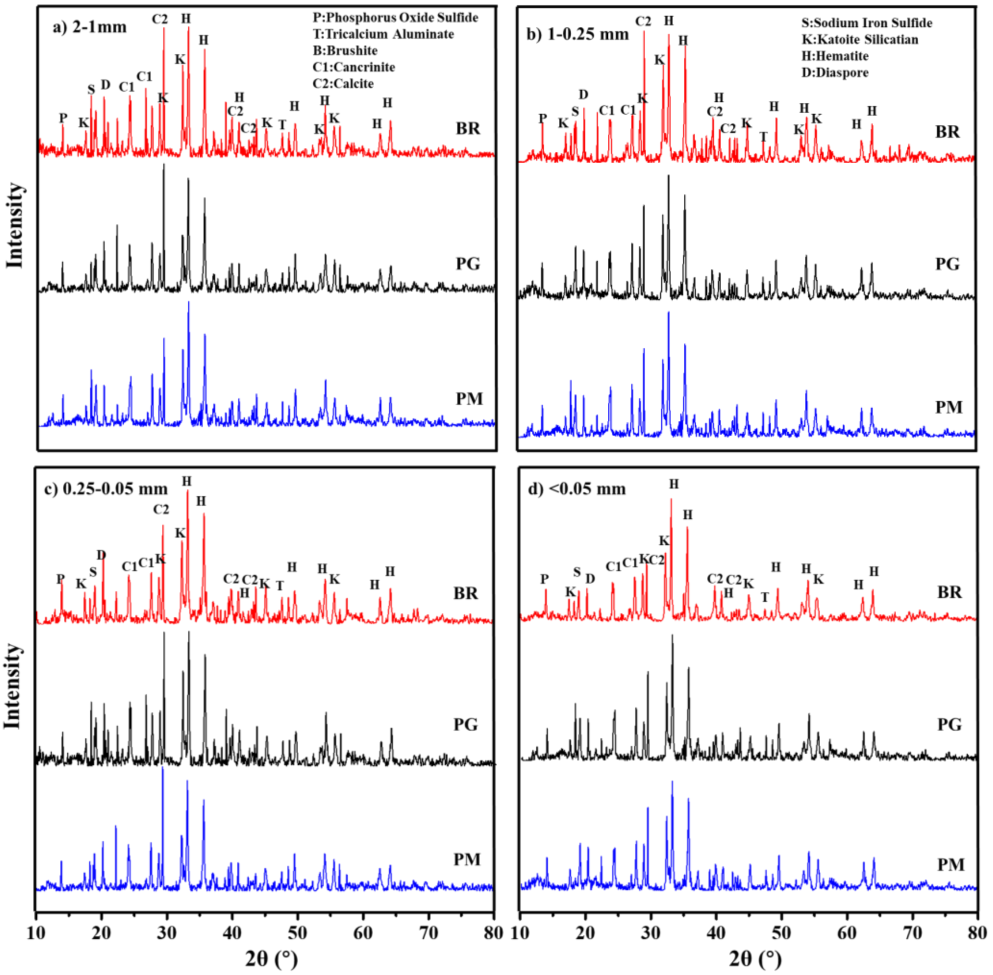


Fig. 7 XRD patterns of residue aggregates with different sizes following phosphogypsum and poultry manure additions.

Quantification of cancrinite and katoite indicated that they were dissolved into solution and leached out during the incubation period following amendment additions. Phosphogypsum had a significant effect on the dissolution of cancrinite and katoite. The effect of combined amendments on variation in the contents of cancrinite and katoite was not obvious. Furthermore, phosphogypsum and/or poultry manure were more beneficial to the dissolution of cancrinite and katoite in the smaller sized aggregates (Fig. 8). Phosphogypsum may also provide excess H^+ (Eq. 4). The smaller sized aggregates had larger specific surface areas, and the mineral phases neutralized with more H^+ in solution.

$$CaSO_4 + 2H_2O \rightarrow Ca(OH)_2 + H^+ + HSO_4^- \qquad (4)$$

Semiquantitative mineralogical analyses of calcite showed that the relative contents of calcite ranged from 7% to 8% in the treated residues with different aggregate sizes (PG and PM). The correlationships between calcite content and aggregate sizes was not significant, which indicated that precipitation and dissolution reactions directly affected variations in calcite content. Santini and Fey (2013) observed that precipitation and dissolution processes were responsible for variations in calcite content rather than particle size sorting according to the results from the weathered disposal areas.

TCA in treated residues (PG and PM) varied from 4% to 6% (Fig. 8d). Application of phosphogypsum reduced pH, as the existance of excess Ca^{2+} ensured TCA formation in the treated residues (Eq. 5-6). Courtney and Kirwan (2012) observed that phosphogypsum was effetive at reducing pH by supplying excess soluble salts. Furthermore, under certain environmental conditions, TCA may be transformed to calcite. Khaitan et al. (2010) discovered that calcite in residue was formed due to dissolution of TCA following natural weathering processes (Eq. 7-8). Concentrations of OH^- and Ca^{2+} in residue soulutions may be responsible for variations in calcite and TCA contents.

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \qquad (5)$$

$$3Ca^{2+} + 4OH^- + 2Al(OH)_4^- \rightarrow Ca_3Al_2(OH)_{12} \qquad (6)$$

$$Ca_3Al_2(OH)_{12} \rightleftharpoons 3Ca(OH)_2 + 2Al(OH)_3 \qquad (7)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (8)$$

XRD patterns and semiquantitative mineralogical analyses revealed variations of in the major mineral phases following phosphogypsum and poultry manure treatments. In this study, pH of the treated residues ranged from 7.5-9.0. In this range, the related mineral phases may partly dissolve. Bauxite residue neutralized H^+ due to the alkaline mineral phases, being determined by their acid neutralization capacity. Klauber et al. (2011) observed that the inflection points on acid neutralization capacity curves indicated major alkaline mineral phases dissolution. Wong and Ho, (1991) found that cancrinite began to dissolve at pH 6.3 and finally disappeared at pH 5.4. Furthermore, the effects of the combined addition (PM) on variations of cancrinite, katoite, calcite and TCA were not obvious compared to phosphogypsum (PG). Indeed, the input of poultry manure changed aggregate size distribution, which may affect ion migration during water leaching. However, the undissolved alkaline minerals may continue to release OH^- to supply the reduced ions which may result in higher pH values in bauxite residue.

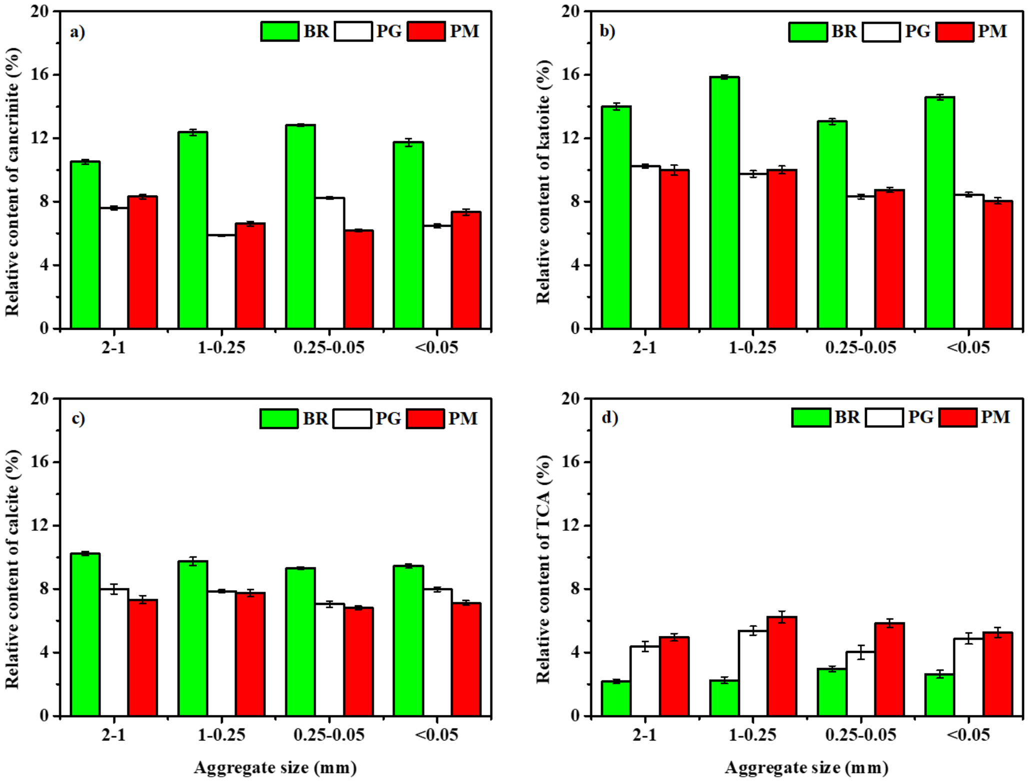
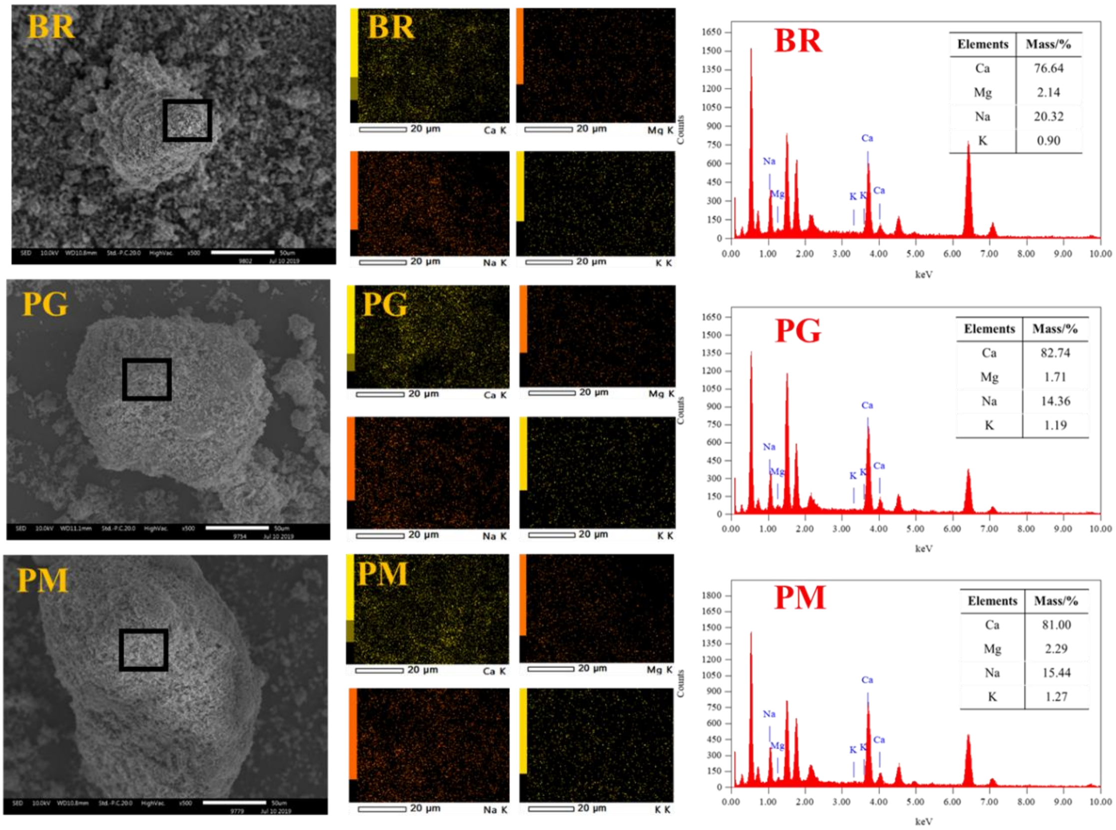


Fig. 8 Mineral composition of residue aggregates with different sizes following phosphogypsum and poultry manure addition.

2.5 Micro-morphology of bauxite residue

Phosphogypsum and poultry manure changed the salt distribution in residue aggregates. Here, BSEM-EDS was used to understand surface morphology, which was one of the critical factors influencing aggregate formation. Macro-aggregates (2-1 mm) and micro-aggregates (0.25-0.05 mm) were selected to illustrate the effects of amendments on micromorphology and distribution characteristics of the major elements (Fig. 9-10).

From the BSE images, 40-60 μm particles were the major fraction in BR macro-aggregates (Fig. 9). With addition of phosphogypsum and/or poultry manure, aggregate sizes increased and their surfaces became smoother. Furthermore, SEM imaging revealed that amendment additions decreased fine particles surrounding the aggregates and increased porosity. The more intensive and brighter the yellow dots in mapping images, the higher the contents of the corresponding elements on aggregate surfaces. Mapping images revealed that following amendment additions, Ca on the surface of residue aggregates increased, with an associated decrease in Na (Fig. 9). According to EDS analysis, the relative mass fractions of Ca, Mg, K and Na on the surfaces accounted for 76.64%. 2.14%, 20.32%, and 0.90%, respectively (Fig. 9). Addition of phosphogypsum significantly enhanced Ca whilst reducing Na. Phosphogypsum may provide exchangeable Ca^{2+} and replace exchangeable Na^+ on colloidal surfaces.



BR

Elements	Mass/%
Ca	76.64
Mg	2.14
Na	20.32
K	0.90

PG

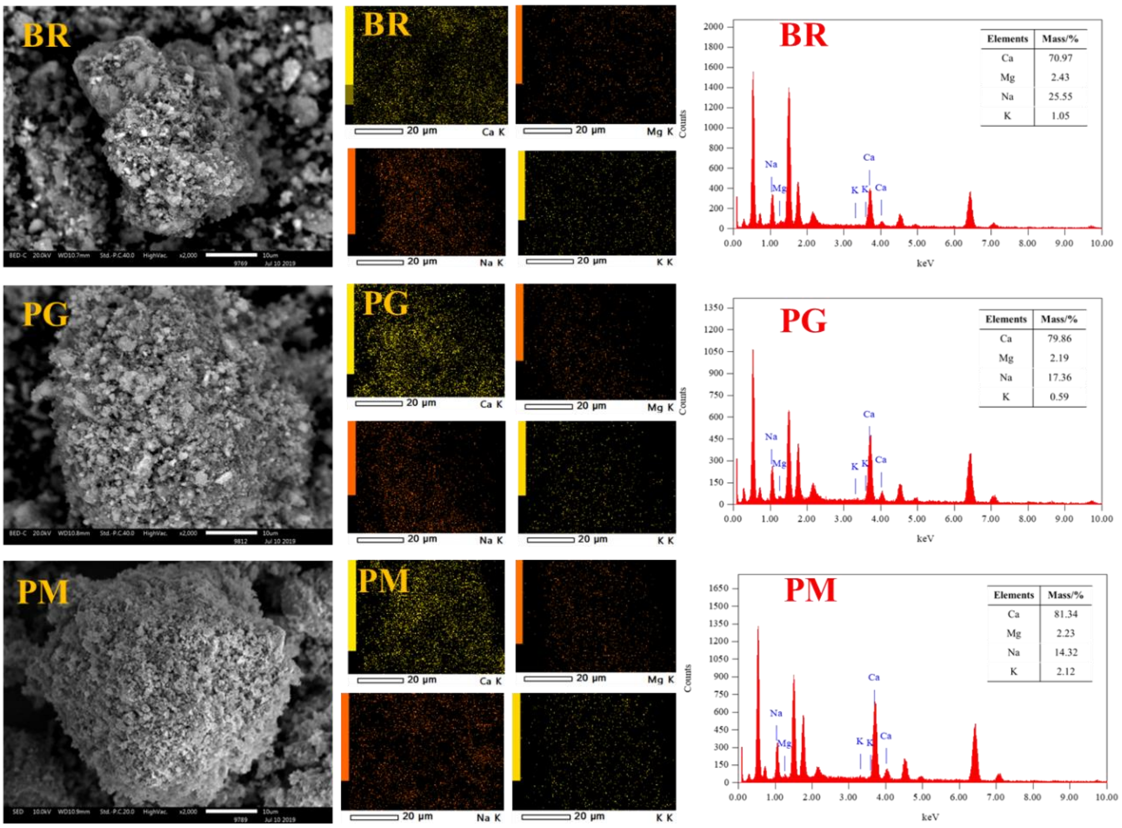
Elements	Mass/%
Ca	82.74
Mg	1.71
Na	14.36
K	1.19

PM

Elements	Mass/%
Ca	81.00
Mg	2.29
Na	15.44
K	1.27

Fig. 9 Backscattered scanning electron microscope (BSEM) showing micro-morphology of 2-1 mm residue aggregates. The data of mass/% in EDS shows the mass percent for an element for four elements.

From the BSE images in Fig. 10, the fine particles were bond together to form large size aggregates and the pores between particles accumulated significantly. Phosphogypsum addition decreased the relative mass of Na on the 0.25-0.05 mm aggregate surface from 25.55% to 17.36%. Compared to 2-1 mm aggregates, the yellow dots were more intense following amendment additions, which indicated that Ca had a more positive effect on the formation of silt-size particles. Hierarchical theory of aggregation revealed that microaggregates (<0.25 mm) were formed from organic molecules attached to clay particles and polyvalent cations to form compound particles (Cl-P-OM), which may be joined with other particles (Cl-P-OM) to form macroaggregates (>0.25 mm) (Bronick and Lal 2005). Huang et al. (2019) observed that organic fertilization may enhance the availability of Ca for C binding possibly by forming organo-Ca complexes and improve soil aggregation. In this study, the combined addition of phosphogypsum and poultry manure changed the salt distribution on residue aggreagtes and stimulated the formation of macroaggregates.



BR

Elements	Mass/%
Ca	70.97
Mg	2.43
Na	25.55
K	1.05

PG

Elements	Mass/%
Ca	79.86
Mg	2.19
Na	17.36
K	0.59

PM

Elements	Mass/%
Ca	81.34
Mg	2.23
Na	14.32
K	2.12

Fig. 10 Backscattered scanning electron microscope (BSEM) showing micro-morphology of 0.25-0.05 mm residue aggregates. The data of mass/% in EDS shows the mass percent of an element for four elements.

2.6 Environmental management for bauxite residue disposal

Ecological reconstruction at the disposal areas would be an effective measure to reduced potential alkaline dust and groundwater pollution and thereby improve the environmental safety of bauxite residue at the disposal areas. The typical physical and chemical properties of bauxite residue limits plant growth. The results in this study have revealed that phosphogypsum and poultry manure may well change salt distribution of residue aggregates and accelerate the process of aggregate formation. The combination of amendments should be effective ameliorants, allowing plant establishment at these sites.

Nevertheless, global clean-up of ~5 billion tons of bauxite residue, using phosphogypsum and poultry manure may not be practical considering cost implications. In China, there are many disposal areas requiring rehabilitation. Different types of industrial and agricultural solid wastes and their combinations should be screened in an attempt to improve alkaline conditions, aggregate structure and fertility characteristics prior to vegetation establishment. The combination of phosphogypsum with other organic wastes (e.g. vermicompost, poultry manure, rice straw) have demonstrated their effects on alkalinity reduction and aggregate formation. However, there are limited gypsum storage areas surrounding bauxite residue disposal areas in many provinces, meaning that manpower and cost may be a problem. Several acid organic materials including furfural residue and stillage could be taken into consideration for future research. Furthermore, numerous natural-artificial polymers have been tested in saline-alkali soils which have low-cost and a high ability for particle aggregation.

3 Conclusions

This work investigated the effects of phosphogypsum and poultry manure on aggregate size distribution and aggregate-associated exchangeable bases of bauxite residue using an incubation experiment. Following amendment additions, the proportion of 2-1 mm residue aggregates increased in the 0-20 and 20-40 cm layers, which resulted in an increase in mean weight diameter. Phosphogypsum decreased pH and EC to approximately 8.5 and 200 mS/cm in aggregates between 0-20 cm. Treated residue ESP and SAR also decreased significantly. Following amendment additions, exchangeable Ca^{2+}, especially in the 0.25-0.05 mm and <0.05 mm aggregates, increased. The relative contents of katoite and cancrinite in >0.25 mm aggregate fractions were relatively higher. Amendments reduced fine particles and improved the porosity surrounding both 2-1 mm and 0.25-0.05 mm aggregates. On aggregate surfaces in treated residues, Ca increased, whilst Na decreased. The present study suggests that application of phosphogypsum and poultry manure directly altered the distribution of exchangeable bases and alkaline indicators within residue aggregates. Future research should evaluate the effects of water regulation on salt removal and aggregate formation.

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