

# Evaluating aggregate stability, surface properties and disintegration behavior of bauxite residue induced by Ca/Na

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**Harper Adams  
University**

1 **Evaluating aggregate stability, surface properties and disintegration**  
2 **behavior of bauxite residue induced by Ca/Na**

3

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10 **ABSTRACT**

11 Bauxite residue contains large concentrations of exchangeable Na<sup>+</sup>, which fragments aggregate  
12 structure and limits plant growth. Understanding the potential mechanisms of Ca/Na on the formation  
13 process of residue aggregates will benefit the screening of appropriate amendments for ecological  
14 reconstruction on bauxite residue disposal areas. A method for evaluating aggregate behavior and  
15 stability by integration of Le Bissonnais' and laser diffraction measurements, was determined on bauxite  
16 residues following Ca/Na additions. With increasing Ca<sup>2+</sup> addition, mean weight diameter (MWD)  
17 increased, indicating improved resistance to dispersion. Ca<sup>2+</sup> had a positive effect on flocculation of silt-  
18 size microaggregates, whilst disintegration was induced following Na<sup>+</sup> addition. Repeated laser  
19 diffraction analysis of residue samples circulating in 50 mmol L<sup>-1</sup> electrolyte solution (Ca<sup>2+</sup>/Na<sup>+</sup>)  
20 provided a detailed view of the changes in particle size distribution as aggregates fragmented. The  
21 visualized 3D surface map revealed that Na<sup>+</sup> promotes the disintegration of residue aggregates into finer  
22 dispersed particles, whilst Ca<sup>2+</sup> protects the microaggregates from fragmenting into smaller particles.  
23 Variation in electrochemical properties of aggregate surfaces affected the micro-morphology  
24 significantly. The findings provide a new approach to specify pedogenic aggregate behavior of bauxite  
25 residue, whilst revealing the effects of Ca<sup>2+</sup>/Na<sup>+</sup> on aggregate stability, surface electrochemical properties  
26 and its micromorphology. This new approach will be beneficial to the assessment of soil formation and  
27 ecological reconstruction on bauxite residue disposal areas.

28 **HIGHLIGHTS**

- 29 1. Aggregate behavior and stability of bauxite residue induced by Ca/Na are evaluated.  
30 2. Integration of Le Bissonnais' and laser diffraction methods may effectively reveal aggregate  
31 fragmentation.  
32 3. Ca/Na addition transformed surface electrochemical properties and micro-morphology of residue  
33 aggregates.  
34 4. Ca<sup>2+</sup> stimulated aggregate formation, whilst Na<sup>+</sup> resulted in particles dispersion.

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1 **Keywords**

2 Bauxite residue, aggregate stability, laser diffraction, surface electrochemistry, soil formation

3

## 4 1. Introduction

5 Bauxite residue, a highly alkaline solid waste, is produced by alumina extraction from bauxite ore  
6 by the Bayer process (Santini et al., 2015; Kong et al., 2017). Globally, the inventory of bauxite residue  
7 has reached 4.6 Gt, and increased at a rate of 200 Mt per annum (Xue et al., 2019). Disposing and storing  
8 these large volumes of residue still remains an increasing environmental risk (Burke et al., 2013).  
9 Ecological reconstruction is a promising way forward for the remediation of bauxite residue on a large  
10 scale, reducing environmental risks (Xue et al., 2016). Nevertheless, bauxite residue has high salinity  
11 (electrical conductivity $\approx 7.4$  mS cm $^{-1}$ ) and alkalinity (pH $\approx 11.3$ , exchangeable sodium percentage $\approx 69$  %),  
12 and a fine particle composition (Grafe et al., 2012); these properties result in poor aggregate structure  
13 and water holding capacity, which limit plant survival (You et al., 2019).

14 During the last few decades, a number of studies have focused on the removal of alkalinity and  
15 salinity in the residues prior to field rehabilitation. However, it has been increasingly recognized that for  
16 successful cover establishment on mine residues, the processes of soil development is critical. Soil  
17 aggregates are the basic unit of soil structure and aggregate stability affects the exchange of water,  
18 nutrients, gases and heat in soil, as well as the growth and metabolism of animals and microorganisms  
19 (Papadopoulos et al., 2009; Tang et al., 2011; Yang et al., 2019). Various methods including wet sieving  
20 and Le Bissonnais' (LB's) method have been proposed to characterize aggregate formation due to the  
21 complexity of mechanisms on particle aggregation or disintegration (Barthès and Roose, 2002;  
22 Almajmaie et al., 2016). Amongst them, Le Bissonnais' method (LB) can simulate different wetting  
23 conditions and energies to identify different disaggregation mechanisms. These stability tests do not  
24 exhibit the rate of aggregate slaking and the disintegration behavior of the intermediate stages, which  
25 may be critical to understanding the response of aggregates to rainfall or other destructive processes.  
26 Field et al. (2006) used a combined method of ultrasonication and sieving to destroy soil aggregates and  
27 found that aggregate disintegration may be modeled as a first-order reaction to represent aggregate  
28 behavior. Kasmerchak et al. (2018) applied repetitive laser diffraction measurements on soil samples to  
29 characterize aggregate stability and assess the effects of organic carbon and other chemical properties on  
30 soil aggregate behavior. The circulation time of 180 minutes was appropriate to monitor aggregate  
31 decomposition following laser diffraction measurement (Mason et al., 2011).

32 Dispersion or flocculation of aggregates was related to pH, electrolyte and exchangeable base  
33 concentrations (Shainberg and Singer, 2011). Curtin et al. (1995) found that Na addition caused clay  
34 expansion and disintegration of unstable aggregates. Le Bissonnais et al. (Le bissonnais, 1996a) observed  
35 that the cation hydration radius and valence states were important factors which affected aggregate  
36 stability; multivalent cations had a strong flocculation effect, whilst monovalent cations had a strong  
37 dispersion effect. Furthermore, the interaction force between soil particles was the intrinsic driving force  
38 for agglomerate fragmentation (Li et al., 2013). Compared to the various external forces in the erosion  
39 theory, the internal forces, including electrostatic repulsion between soil particles, were more able to  
40 determine soil disaggregation (Hu et al., 2015). According to the DLVO theory of colloidal particle  
41 interaction, electrostatic repulsion was controlled by the electric field around the particle, and electric  
42 field intensity was determined by the ion interface reaction characteristics (Santos and Yan, 2011). Salt  
43 ions in bauxite residue pore water are dominated by Na $^{+}$ , K $^{+}$ , Ca $^{2+}$ , Mg $^{2+}$ , Al(OH) $_{4}^{-}$ , SO $_{4}^{2-}$ , CO $_{3}^{2-}$ , and

44 OH<sup>-</sup> (Xu et al., 2018). The high concentrations of soluble ions and exchangeable bases may significantly  
45 affect aggregate formation and its stability.

46 Calcium-contained solid wastes have been applied to ameliorate physical and chemical properties  
47 of bauxite residue to support plant growth. However, understanding the potential mechanisms of  
48 Ca<sup>2+</sup>/Na<sup>+</sup> on aggregate behavior and its stability for bauxite residue remain scarce. The hypothesis for  
49 this study was that following Ca<sup>2+</sup> or Na<sup>+</sup> addition, surface properties and disintegration behavior varied,  
50 which changed aggregate size distribution and micro-morphology of residue aggregates. The objectives  
51 of this research were to 1) investigate aggregate size distribution and its stability using LB's method  
52 following Ca<sup>2+</sup> or Na<sup>+</sup> addition; 2) analyze the effect of Ca<sup>2+</sup> or Na<sup>+</sup> on variations of surface  
53 electrochemical properties of residue aggregates; 3) to quantify the disintegration rate of residue  
54 aggregates using Laser diffraction analysis.

## 55 2. Materials and methods

### 56 2.1 Materials

57 Fresh bauxite residue was collected to a depth of 20 cm from a bauxite residue disposal area in  
58 Central China. The climate is warm temperate continental monsoon, with an average daily temperature  
59 of 12.2-14.8 °C and mean annual precipitation of 600-700 mm. Samples were subsequently stored in  
60 polyethylene bags, returned to the laboratory, air-dried at room temperature for 2 weeks and then passed  
61 through a 2 mm sieve prior to analysis.

### 62 2.2 Aggregate disintegration

63 Different concentrations of NaCl and CaCl<sub>2</sub> solutions (0, 5, 10, 20, 50, 80, 100, and 200 mmol/L)  
64 were selected to determine aggregate disintegration using the modified Le Bissonnais' (LB) method (Le  
65 Bissonnais, 1996). This method included three disruptive tests: fast wetting (FW), slow wetting (SW)  
66 and wet stirring (WS). For the FW test, 6 g of 1-2mm residue aggregates were quickly immersed in NaCl  
67 or CaCl<sub>2</sub> solutions for 10 min. For SW, 6 g of 1-2mm residue aggregates were placed on filter paper upon  
68 a sponge soaked in ethanol for 30 min. For WS, 6 g of 1-2mm residue aggregates were gently immersed  
69 in ethanol for 10 min prior to immersion in NaCl or CaCl<sub>2</sub> solutions and subsequently shaken in ethanol.  
70 The aggregates were then collected by sieving (1mm, 0.25mm and 0.05mm) and the fractions in each  
71 sieve collected, dried at 40 °C for 24 h and weighed. Mean weight diameter (MWD) and percentage  
72 aggregate destruction (PAD) of the residue samples were calculated using the following equations:

$$73 \quad \text{MWD} = \sum_{i=1}^n \bar{X}_i \times W_i \quad (1)$$

$$74 \quad \text{PDA}_{x/w} = \frac{W_w - W_x}{W_w} \times 100\% \quad (2)$$

75 Where  $\bar{X}_i$  was the mean diameter over the adjacent sieves (mm),  $W_i$  was the percentage of residue  
76 aggregates in the size range and  $n$  was the number of sample sieves.  $W_w$  was the percentage of  $>X$  mm  
77 residue aggregates after wet sieving using deionized water, and  $W_x$  was the percentage of  $>X$  mm residue  
78 aggregates after wet sieving using the electrolyte solution.

79 **2.3 Surface electrochemical properties of residue aggregates**

80 Bauxite residue, which was treated by different concentrations of NaCl or CaCl<sub>2</sub> solutions, was  
 81 separated through a 0.05 mm sieve and the <0.05 mm fractions were dried at 40 °C for 24 h. The  
 82 fractions were then added to a HCl solution (0.1 mol/L) (v:w=5:1), oscillated for 5 hours, centrifuged at  
 83 a speed of 4000 rpm for 5 min, washed several times using deionized water to remove excess Cl<sup>-</sup> in the  
 84 suspension and separated to obtain the residues. 5 g of the residue was added into a 50 ml centrifuge tube  
 85 and mixed with 10 mL Ca(OH)<sub>2</sub> and NaOH solution (0.015 mol/L). The mixtures were oscillated for 24  
 86 hours and subsequently adjusted to pH 7 using HCl. The concentrations of Ca<sup>2+</sup> and Na<sup>+</sup> in the  
 87 supernatant were then determined using ICP-MS (Hu et al., 2015).

88 The surface potential (φ(V)), surface electric field intensity (E), and specific surface area (S) of  
 89 residue aggregates were calculated by the following equations (Li et al., 2011):

90 
$$\phi = \frac{2RT}{(2\beta_{Ca} - \beta_{Na})F} \ln \frac{a_{Ca}^0 N_{Na}}{a_{Na}^0 N_{Ca}} \quad (3)$$

91 
$$E = \frac{4\pi}{\epsilon} \sigma \quad (4)$$

92 
$$S = \frac{N_{Na} k}{ma_{Na}^0} e^{\frac{F\phi\beta_{Na}}{2RT}} = \frac{N_{Ca} k}{ma_{Ca}^0} e^{\frac{F\phi\beta_{Ca}}{2RT}} \quad (5)$$

93 
$$K = \sqrt{\frac{8\pi F^2 \left( \frac{1}{2} \sum a_i^0 Z_i^2 \right)}{\epsilon RT}} \quad (6)$$

94 
$$a_i^0 = \gamma_i c_i^0 \quad (7)$$

95 
$$\log \gamma_i = 0.512 Z_i^2 \left( \frac{I^{1/2}}{I + I^{1/2}} - 0.3I \right) \quad (8)$$

96 
$$\beta_{Ca} = 0.0213 \ln(I^{0.5}) + 1.2331 \quad (9)$$

97 
$$\beta_{Na} = 0.0213 \ln(I^{0.5}) + 0.7669 \quad (10)$$

98 
$$m = 0.5259 \ln(c_{Na}^0 / c_{Ca}^0) + 1.992 \quad (11)$$

99 Where R(J/K mol) is a universal gas constant, T(K) the system temperature, F(C/mol) the Faraday  
 100 constant, k (1/dm) the Debye-Huckel constant, and ε the dielectric constant of water. I (mol/L) was the  
 101 ionic strength, a<sub>Na</sub><sup>0</sup> and a<sub>Ca</sub><sup>0</sup> (mol/L) respectively for the activity of Na<sup>+</sup> and Ca<sup>2+</sup> in the solution at  
 102 equilibrium, N<sub>Na</sub> and N<sub>Ca</sub>(mol) are the adsorption capacities of Na<sup>+</sup> and Ca<sup>2+</sup> in the residue, respectively.  
 103 c<sub>Na</sub><sup>0</sup> and c<sub>Ca</sub><sup>0</sup> (mol/L) were concentration of Na<sup>+</sup> and Ca<sup>2+</sup> in the solution at equilibrium. β<sub>Na</sub> and β<sub>Ca</sub> were  
 104 correction coefficients for correcting the effective charge amount of Na<sup>+</sup> and Ca<sup>2+</sup>, respectively.

105 **2.4 Analysis of aggregate behavior**

106 In order to investigate the effect of Ca or Na on residue aggregation, residue samples which were  
 107 treated by 50 mmol/L NaCl and CaCl<sub>2</sub> solutions were selected to determine aggregate behavior using a  
 108 laser particle analyzer (Malvern Mastersizer 2000). The analytical method is described by Mason et al.  
 109 (2011) and Kasmerchar et al. (2018) as follows: selected aggregate samples were added continuously

110 into a beaker containing 500ml of deionized water or 50 mmol/L CaCl<sub>2</sub>/NaCl solutions until the solution  
111 obscuration reached 5%-10%. Then the particle size distributions (PSD) of residue aggregates can be  
112 measured through a laser diffraction analysis cell. The PSD was measured every two minutes for the first  
113 20 minutes and every ten minutes for the last 160 minutes. During the 180-minute measurement period,  
114 the solution was constantly stirred at a constant speed of 2000 rpm and pumped to the laser diffraction  
115 analysis cell. According to the methodology of Mason et al. (Mason et al., 2011), variations of >250 μm  
116 and <20 μm fractions were determined and fitted using the following equations:

117 
$$\% > 250\mu\text{m} = A_1 \times \exp(-K_1 T) + C1 \quad (12)$$

118 
$$\% < 20\mu\text{m} = A_2 * [1 - \exp(-K_2 T)] + C2 \quad (13)$$

119 where K<sub>1</sub> and K<sub>2</sub> are rate constants, T is circulation time, A<sub>1</sub> and A<sub>2</sub> are rate coefficients, C<sub>1</sub> is the  
120 final percentage of >250 μm fractions, and C<sub>2</sub> represents the initial percentage of <20 μm fractions in the  
121 residue aggregates. The parameters A<sub>1</sub>, A<sub>2</sub>, k<sub>1</sub>, k<sub>2</sub>, C<sub>1</sub> and C<sub>2</sub> were determined using the obtained PSD  
122 data to fit Eqs. (15-16) and minimize the quadratic sum of residuals from models (Field and Minasny,  
123 1999).

## 124 2.5 Morphological analysis

125 SEM-EDS of <0.05 mm residue aggregates from the three different treatments (DI, and 50 mmol/L  
126 NaCl/CaCl<sub>2</sub>) were scanned using a scanning electron microscope (ESEM, Quanta-200). The samples  
127 were sprayed with Au prior to scanning using a GSED field emission gun.

## 128 2.6 Statistical methods

129 All data were analyzed in Excel 2010, IBM® SPSS® Statistics version.21, OriginLab® Origin® r.  
130 9.0. and MATLAB R2017b. All figures and lines representing first-order models were constructed by  
131 Origin 9.0. The three-dimensional surface map of the particle size distribution of bauxite residue  
132 aggregates after different ion treatments was draw by MATLAB R2017b.

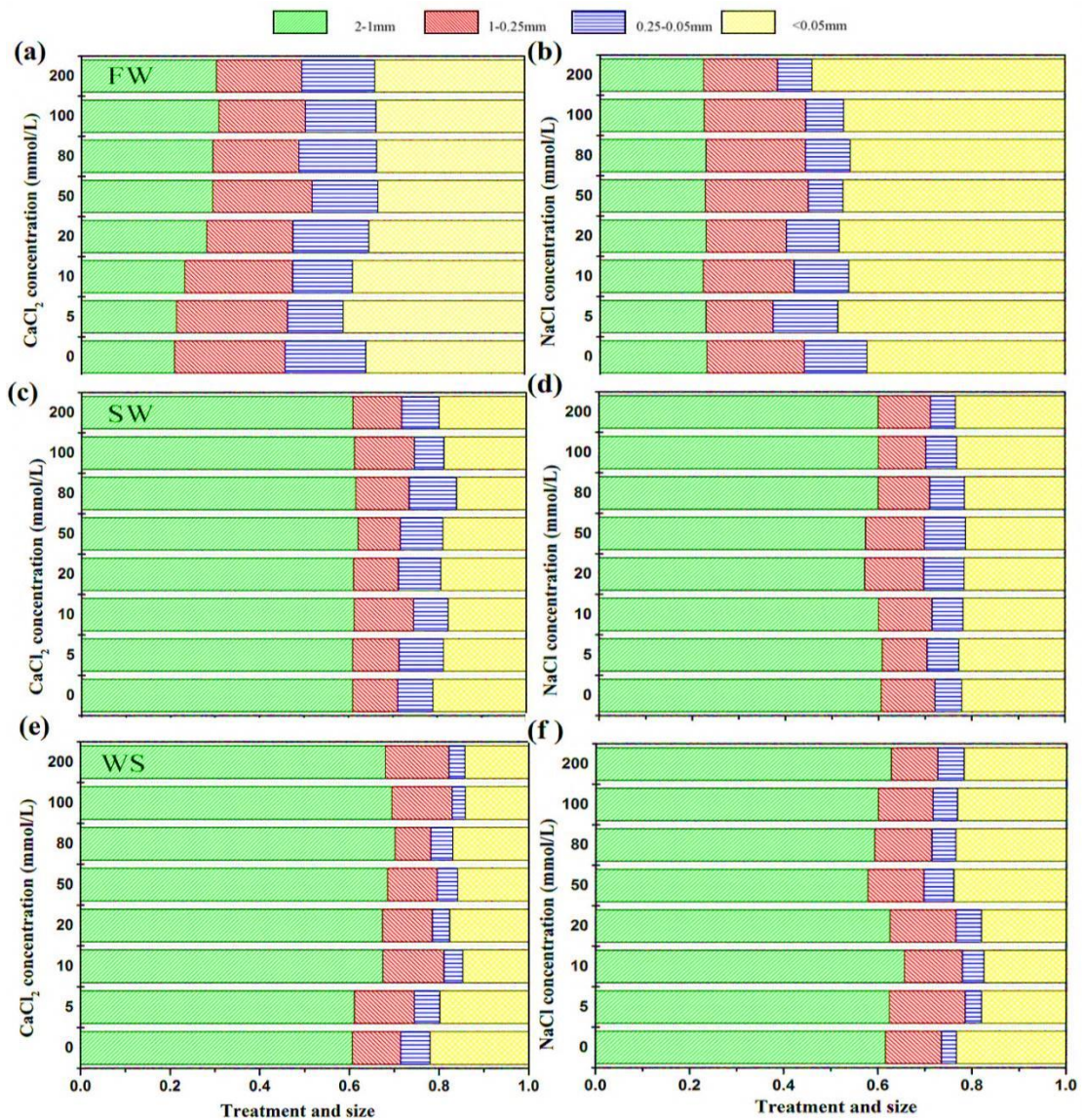
## 133 3. Results and discussion

### 134 3.1 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on aggregate size distribution

135 Aggregate size distribution of bauxite residue following different treatments is presented in Fig. 1.  
136 For the FW test (simulating the slaking process), <0.05 mm aggregates were the major fraction. With  
137 CaCl<sub>2</sub> treatment, the proportion of 2-0.25 mm aggregates ranged from 45.92% to 52.02%, which were  
138 higher than in untreated residues. With increasing Na<sup>+</sup> concentration, the proportion of <0.05 mm  
139 microaggregates increased from 42.5% to 54.4%. For the SW test (simulating differential clay swelling  
140 processes) and the WS test (simulating the mechanism of breakdown processes), 2-1 mm aggregates  
141 were the major fractions. With CaCl<sub>2</sub> treatment, the proportions of 2-1 mm aggregates increased from  
142 60.9% to 62.2% and 69.8% for the SW and WS test, respectively.

143 Ca<sup>2+</sup> and Na<sup>+</sup> are the critical cations in bauxite residue (Xue et al., 2019), and their concentrations  
144 can significantly affect aggregation processes. Aggregate size distribution from the modified LB method  
145 revealed that Ca may increase the proportion of water-stable aggregates (>0.25 mm), whilst Na<sup>+</sup> resulted

146 in disaggregation of larger sized aggregates.



147

148 Fig. 1 Effect of  $\text{Ca}^{2+}/\text{Na}^{+}$  on aggregate fraction distribution of the treated residues from the modified Le Bissonnais' method: a &  
 149 b) FW test; c & d) SW test; e & f) WS test.

150 MWD is a characteristic indicator used to evaluate aggregate stability and a large MWD indicates  
 151 improved aggregate stability (Mbagwu and Auerswald, 1999; You et al., 2018; Cui et al., 2019). Variation  
 152 in MWD following NaCl and  $\text{CaCl}_2$  additions are presented in Fig. 2. For the three different tests,  $\text{CaCl}_2$   
 153 addition increased MWD due to the accumulation of larger sized fractions. With increasing NaCl  
 154 concentration, MWD decreased, although this did fluctuate. When the electrolyte concentration was 50  
 155 mmol/L, MWD of  $\text{CaCl}_2$  treated samples reached a relatively high value, whilst a relatively low value  
 156 occurred for NaCl treatments.

157 Electrolyte concentration, and cation valence state, significantly affected the formation of stable  
 158 aggregates, especially for flocculation and dispersion of clay-size particles (Olis, 1989). Multivalent  
 159 cations, including  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , all formed ion bridges, compressing the thickness of the electric  
 160 double layer, and promoting particle flocculation (Jiang et al., 2012). In this study, addition of  $\text{CaCl}_2$



161 accumulated the proportion of macroaggregates ( $>0.25$  mm), improved aggregate stability and enhanced  
 162 erosion resistance of residues. The residue contained a large amount of  $\text{Na}^+$ , which resulted in particle  
 163 dispersion and poor physical condition. Results demonstrated that NaCl increased the proportion of  $<0.05$   
 164 mm microaggregates whilst reducing the stability of residue aggregates. **Monovalent cations disperse**  
 165 **aggregates whilst multivalent cations promote flocculation.** Le Bissonnais ( Le Bissonnais, Y., 2016.)  
 166 **considered that multivalent cations may effectively promote flocculation of aggregates, whilst**  
 167 **monovalent cations have a strong dispersive effect.** An excess of  $\text{Na}^+$  may weaken covalent interaction  
 168 between organic molecules and clay-sized particles, which may lead to aggregate dispersion. Zhu et al.,  
 169 (2017) observed that  $\text{Na}^+$  was negatively correlated with aggregate stability in bauxite residue following  
 170 amendment addition, which was consistent with the results of this study.

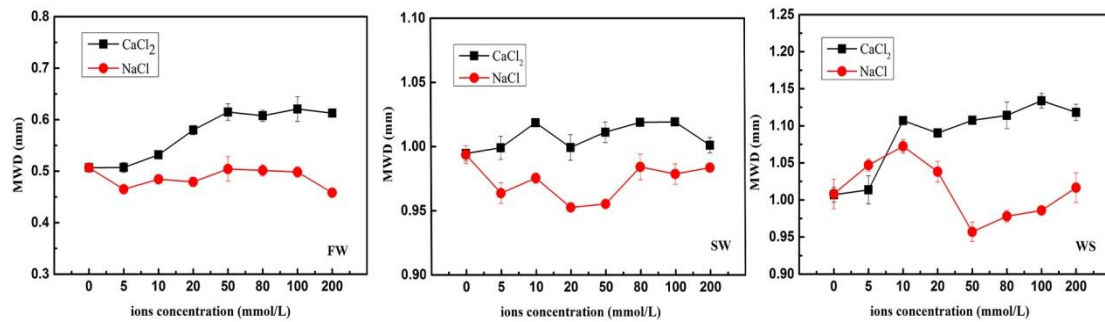
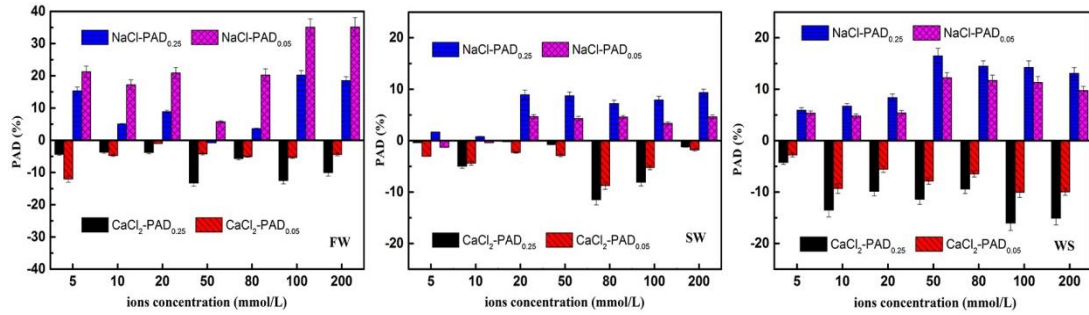


Fig.2 Effect of  $\text{Ca}^{2+}/\text{Na}^+$  on aggregate stability of bauxite residue. a) FW test; b) SW test; c) WS test.

173 The percentage of aggregate destruction ( $\text{PAD}_x$ ), which is the fraction of  $>x$  mm aggregates after  
 174 wet sieving, may be used to evaluate variation in water-stable aggregates (GUBER et al., 2005). A  
 175 positive value for  $\text{PAD}_x$  indicates dispersion, whilst a negative value indicates aggregation. The larger  
 176 the absolute value of  $\text{PAD}_x$ , the stronger the corresponding effects. Variation in  $\text{PAD}_x$  in the treated  
 177 residues is presented in Fig. 3. For FW treatments, the absolute values of  $\text{PAD}_{0.25}$  were 3.71%, 3.80%,  
 178 13.2%, 5.68%, 12.52%, and 10.02% when the concentration of  $\text{CaCl}_2$  solution was 10, 20, 50, 80, 100,  
 179 and 200 mmol/L, respectively. This indicated that  $\text{CaCl}_2$  had a significant protective effect on  $>0.25$  mm  
 180 residue aggregates. Compared to  $\text{PAD}_{0.25}$ , the absolute value of  $\text{PAD}_{0.05}$  was smaller, which indicated that  
 181  $\text{CaCl}_2$  had a stronger aggregation effect on  $>0.25$  mm aggregates. The values of  $\text{PAD}_{0.25}$  and  $\text{PAD}_{0.05}$  for  
 182 NaCl treated residues were positive, and significantly higher than those following  $\text{CaCl}_2$  treatment. This  
 183 demonstrates that NaCl had an clear dispersive effect on residue aggregates. For FW, SW or WS  
 184 treatments, the absolute values of  $\text{PAD}_{0.25}$  and  $\text{PAD}_{0.05}$  balance with the concentrations of NaCl or  $\text{CaCl}_2$   
 185 ranging from 50 mmol/L to 80 mmol/L, but then decrease gradually. Zhu et al., (2016) observed that with  
 186 the removal of salinity, clay-sized aggregates increased and microaggregate stability decreased in bauxite  
 187 residues. Soluble salts may exist as a solid state and bind fine particles to improve aggregation (Bronick  
 188 and Lal, 2005). Amézqueta (1999), stated that low electrolyte concentrations and high SAR (Sodium  
 189 Adsorption Ratio) values produced clay dispersion and swelling. With the increase in soluble ions,  
 190 electrolyte concentrations of the residue solutions increased, which may have resulted in particle  
 191 aggregation. Furthermore,  $\text{Na}^+$  addition increased the SAR values which may have led to a loss in  
 192 aggregate structure. Therefore, following NaCl or  $\text{CaCl}_2$  additions, the values of  $\text{PAD}_{0.25}$  and  $\text{PAD}_{0.05}$   
 193 varied in volatility.



194

195

Fig. 3 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on the percentage of aggregate destruction of bauxite residues. a) FW test; b) SW test; c) WS test.

196

### 3.2 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on aggregate surface properties

197

Variations in pH of bauxite residue microaggregates (<0.05 mm) following the different electrolyte treatments are presented in Table 1. pH declined gradually with less than 20 mmol/L Ca<sup>2+</sup>, but decreased sharply to approximately 8 when Ca<sup>2+</sup> exceeded 50 mmol/L. Ca<sup>2+</sup> may bind to alkaline anions (e.g. CO<sub>3</sub><sup>2-</sup>) in the residues to form insoluble calcium-containing minerals to decrease the pH of the solution. With addition of Na<sup>+</sup>, pH did not change. pH varied the composition of cations in solution, which may affect electrochemical properties (e.g. charge density, surface potential, surface charge) of the surface of residue aggregates. Calcium reduced the OH<sup>-</sup> concentration and the negative surface charge on residue particles, which may reduce particle repulsion and improve aggregation.

202

203

204

205

Table. 1 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on pH of bauxite residue

pH	Electrolyte concentration (mmol/L)							
	0	5	10	20	50	80	100	200
Na <sup>+</sup>	11.18±0.21	10.89±0.13	10.94±0.12	10.69±0.22	10.60±0.30	10.66±0.20	10.64±0.19	10.67±0.22
Ca <sup>2+</sup>	11.13±0.31	10.82±0.15	10.65±0.40	10.16±0.21	8.21±0.32	7.64±0.13	7.72±0.34	7.79±0.10

206

The composition of ions significantly varied soil surface properties including electric field intensity, surface potential, and specific surface area of aggregates. Effects of Ca<sup>2+</sup>/Na<sup>+</sup> on surface properties of <0.05 mm residue aggregates are presented in Fig. 4. With an increase in electrolyte concentration, both electric field intensity and surface potential decreased. Parsons et al., (2011) observed that the increased electrolyte concentration had a strong compression effect, reducing the electric double layer of colloidal particles, which may improve the counter ions to shield the surface charge and decrease the surface potential of microaggregates. Ca<sup>2+</sup> is a divalent ion, which may produce a stronger compression effect on the electric double layer than that of Na<sup>+</sup> (Pashley, 1981). Therefore, the surface potential of microaggregates following Ca<sup>2+</sup> addition was smaller. With an increase in Ca<sup>2+</sup> concentration, the specific surface area of microaggregates decreased from 6.12 m<sup>2</sup>/g to 0.68 m<sup>2</sup>/g. Furthermore, the specific surface area increased to 13.3 m<sup>2</sup>/g following Na<sup>+</sup> addition. This was because flocculation or dispersion of particles determined the changes of specific surface area. Ca<sup>2+</sup> promoted the stability of microaggregates, whilst Na<sup>+</sup> resulted in particle dispersion

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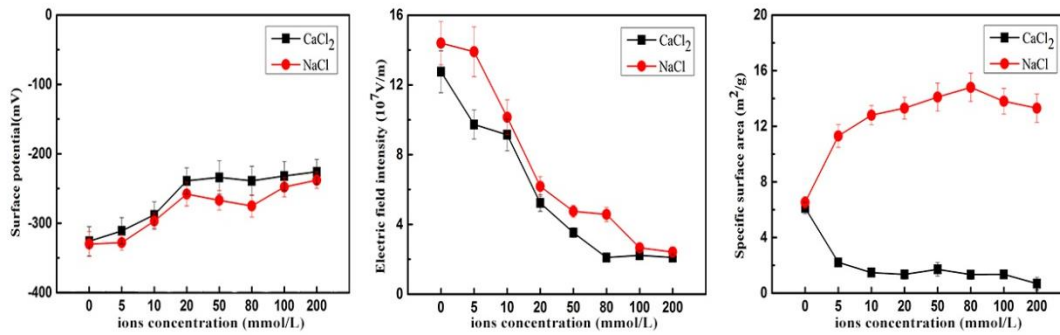


Fig.4 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on surface properties of <0.05 mm residue aggregates.

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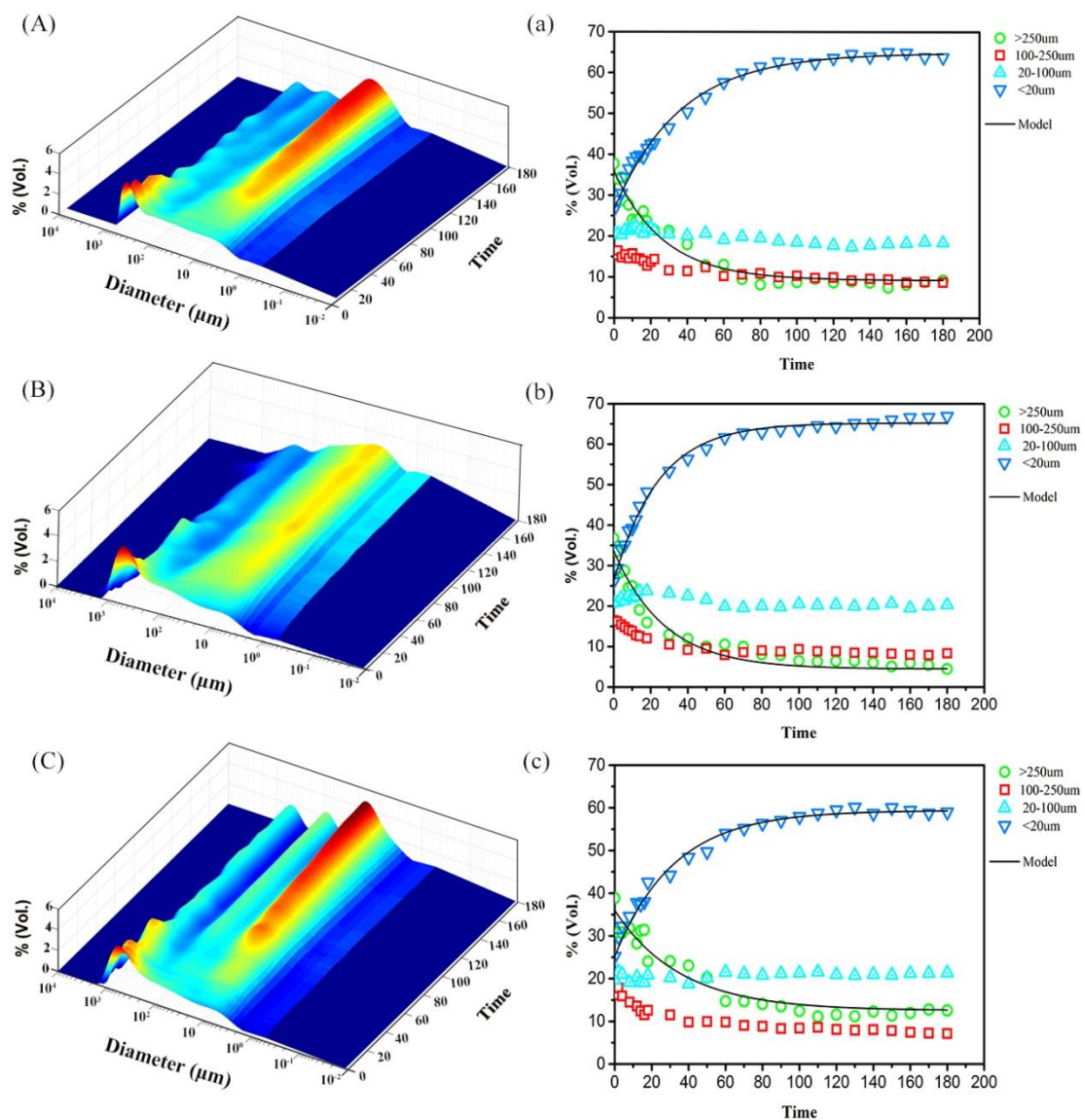
### 221 3.3 Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on pedogenic aggregate behavior

222 Aggregate behavior results are depicted as either continuous surfaces plots which portray changes  
 223 in the overall size distribution over time (Fig. 5A-C), or in the proportion of individual size fractions (Fig.  
 224 5a-c). This represents a detailed view of aggregate disintegration and hydrodynamic behavior in  
 225 deionized water and other solution electrolytes. For the different treatments, the fastest disintegration  
 226 rate in the first 20 minutes decreased as follows: Na>DI>Ca (Fig. 5A-C). PSD of the three samples varied  
 227 in the first 60 minutes and then approached a stable state. Variation in PSD in the salt solutions was  
 228 different, which indicated that residue aggregates exhibited diverse disintegration and hydrodynamic  
 229 behaviors under the effects of different ions.

230 For NaCl treated residues, the initial PSD peak disintegrated following a 30-minute circulation, but  
 231 then stabilized and persisted during the remaining circulation time (Fig. 5A). During circulation, a peak  
 232 of 20-50 μm appeared, revealing that fractions >250 μm disintegrated into 20-50 μm smaller particles.  
 233 For the control samples, the initial flat peak of PSD occurred in the range of 2-250 μm after a 20-min  
 234 circulation period (Fig. 5B). This indicated that large size aggregates may disintegrate into  
 235 microaggregates in the presence of Na<sup>+</sup>. For CaCl<sub>2</sub> treated residues, the initial peak of PSD collapsed at  
 236 a circulation time of 40 minutes, and the peak height remained at approximately 1.5% at the end of the  
 237 circulation period (Fig. 5C).

238 Tisdall and Oades, (1982) proposed a hierarchical model according to the soil aggregate formation  
 239 process; principally, primary particles (<20 μm) and the cements bond together to form microaggregates  
 240 (20-250 μm), and thereby form larger aggregates (>250μm). Variations between the size fractions (>250  
 241 μm, 100-250 μm, 20-100 μm and <20 μm) over time and the aggregate disintegration model by the first-  
 242 order rate equation are presented in Fig. 2a-c. In most cases, the first-order rate equation can fit the trend  
 243 of PSD, which provided details of aggregation behavior that could not be clearly expressed in the three-  
 244 dimensional surface map. The first-order rate equation parameters for different partial particles in  
 245 different treatments are presented in Table 2. After circulation for 180-minutes, variations in C<sub>1</sub> and C<sub>2</sub>  
 246 values revealed that Ca<sup>2+</sup> addition increased the water-stable aggregate content, whilst Na<sup>+</sup> promoted  
 247 dispersion of residue aggregates. The >250 μm aggregate fraction mainly included macro-aggregates,  
 248 medium to coarse sand grains, and larger coarse mineral fragments. This fraction dispersed rapidly, with  
 249 at least half of the decline occurring in the first 20 minutes and almost all of it within approximately 60  
 250 minutes (Fig. 5a-c). The 100-250 μm aggregate fraction included medium sand grains and large size  
 251 micro-aggregates. Following the first 10 minutes of circulation, the 100-250 μm aggregate fraction fell

252 sharply, but then slowly declined. This reflected that the 100-250  $\mu\text{m}$  aggregates were rapidly  
 253 disaggregated into  $<100 \mu\text{m}$  aggregates, followed by slow disintegration of the latter into primary mineral  
 254 particles and smaller microaggregates. The short-term fluctuation of  $>250 \mu\text{m}$  and 100-250  $\mu\text{m}$   
 255 aggregates was probably due to a relatively small number of sand-sized particles, and aggregates or  
 256 coarse organic fractions that could not be acquired homogeneously by the particle size analyzer pump,  
 257 thereby producing substantial fluctuations. Furthermore, the 20-100  $\mu\text{m}$  aggregates varied monotonically,  
 258 representing a slightly decrease in microaggregates with small particle size with long-term circulation.  
 259 This indicates that  $>100 \mu\text{m}$  fractions disaggregate into finer particles under the action of hydraulic power.  
 260 In contrast, trends for  $<20 \mu\text{m}$  aggregates increased rapidly with almost all within 60 minutes, clearly  
 261 reflecting disintegration of microaggregates. The  $<20 \mu\text{m}$  fractions included clay-size particles, humic  
 262 materials and other cements. The results demonstrated that residue aggregates with a large size mainly  
 263 disaggregated into  $<20 \mu\text{m}$  fractions according to the trends of these fractions with circulation time.



264

265 Fig.5 Surfaces representing change in particle size distribution with time, for bauxite residue after  $\text{Ca}^{2+}/\text{Na}^+$  treatment. Height of  
 266 surface represents volumetric percentage in each particle diameter class, as it changes over time from 0 to 180 min of circulation.

267 Variations for multiple size fractions over the course of the experiment, lines represent first-order models fit to decrease of >250  
 268  $\mu\text{m}$  or increase of <20  $\mu\text{m}$  fraction. A & a) control, B & b),  $\text{Na}^+$  and C & c)  $\text{Ca}^{2+}$ .

269 The results showed that the method described by Mason et al., (2011) and Kasmerchak et al. (2018)  
 270 could evaluate aggregate behavior of bauxite residue following  $\text{Ca}^{2+}$  or  $\text{Na}^+$  treatments. Three-  
 271 Dimensional surfaces and variations of specific particles intuitively reflect aggregate behavior during  
 272 180 minutes of circulation. Zeng et al., (2011) investigated the effects of monovalent and divalent salt-  
 273 based ions on soil aggregation, and observed that the >0.25 mm macroaggregates contained higher  
 274 contents of salt ions, especially for multivalent metal ions than those in microaggregates. The increase in  
 275 monovalent ions and the leaching of divalent ions may lead to the dispersion of aggregates and the  
 276 deterioration of soil quality. All treatments revealed that the majority of >0.25 mm aggregates  
 277 disintegrated and the small sized aggregates persisted after circulation. The presence of water molecules  
 278 swelling the mineral crystal lattice, may have stimulated clay dispersion (Pashley and Israelachvili, 1984).  
 279 Furthermore, residue aggregates disintegrated more rapidly in the presence of  $\text{Na}^+$ , whilst  $\text{Ca}^{2+}$  in solution  
 280 could form ion bridges in the electric double layer and reduce the expansion of water molecules.

281 Table 2. Parameters used to model aggregate breakdown as a first-order process

treatment	$A_1$	$K_1$	$C_1$	$R_1^2$	$A_2$	$K_2$	$C_2$	$R_2^2$	a	b	c
control	26.6140	0.0371	9.2105	0.9669	38.2703	0.0278	26.5515	0.9922	25.6455	37.2222	0.6890
$\text{Na}^+$	29.2771	0.0365	4.4581	0.9630	39.2036	0.0418	26.0496	0.9938	28.2280	37.6005	0.7507
$\text{Ca}^{2+}$	23.4984	0.0280	12.5148	0.9406	34.1733	0.0313	25.2214	0.9842	22.8493	33.1199	0.6899

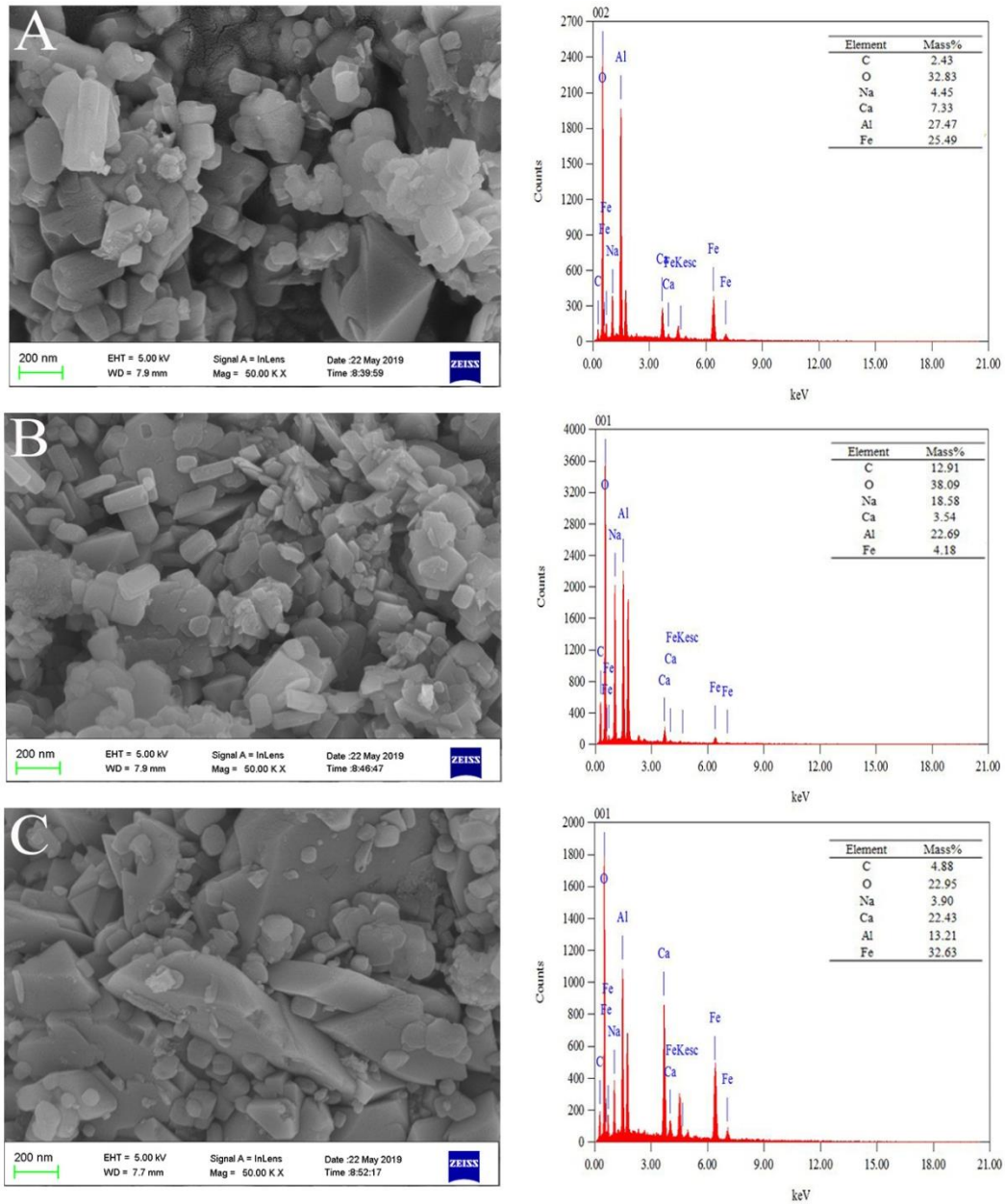
282 \*  $a=A_1 \cdot \exp(-k_1)$   $b=A_2 \cdot \exp(-k_2)$   $c=a/b$

### 283 3.4 Effect of $\text{Ca}^{2+}/\text{Na}^+$ on aggregate micro-morphology

284 The presence of Ca or Na changed the surface properties, affected aggregate behavior, and varied  
 285 aggregate size distribution of bauxite residue. SEM-EDS analysis was used to determine changes in  
 286 micro-morphology and elemental distribution of <0.05 mm residue aggregates. SEM images of the three  
 287 treatments ( $\text{Na}^+$ , DI, and  $\text{Ca}^{2+}$ ) are presented in Fig. 6. Scanning electron microscope imaging of control  
 288 samples revealed that 0.2-1  $\mu\text{m}$  particles were the major fraction present. Control residue  
 289 microaggregates had sheet- or prismatic-like structures and there were relatively few fine fragments.  
 290 With addition of NaCl, microaggregates sizes became smaller and the fine fragments increased. The  
 291 major fractions of Ca-treated microaggregates were 0.5-1  $\mu\text{m}$  particles and their structure was converted  
 292 from a sheet-like to prismatic-like form. The variation in residue micro-morphology directly reflected  
 293 the input of  $\text{Ca}^{2+}$ , by revealing that it could improve aggregate structure and enhance aggregate stability  
 294 of residues. Similarly, using a combination methods including SEM-EDS and synchrotron-based X-  
 295 ray micro-computed tomography, gypsum has been shown to improve particle size of residue aggregates,  
 296 enhancing the number of large pore spaces (Xue et al., 2019). Multivalent ions such as  $\text{Ca}^{2+}$  may bind  
 297 clay particles and organic matter to enhance particle agglomeration, or  $\text{Ca}^{2+}$  may exist as carbonate  
 298 precipitates to form carbonate coatings and bind mineral particles together to inhibit clay dispersion  
 299 (Jiang et al., 2012). Kong et al., (2017) investigated acid transformation of bauxite residue, they found  
 300 that gypsum addition promoted the leaching of sodium ions and accelerated the 0.2-1  $\mu\text{m}$  particle fraction  
 301 in 2-5  $\mu\text{m}$  aggregates due to calcium's positive effect.

302 According to EDS analysis, Na, Ca, Al and Fe on the surfaces of residue aggregates were the major

303 chemical elements. The mass fractions of Na, Ca, Al and Fe on the surfaces accounted for 4.45%, 7.33%,  
 304 27.47%, and 25.49%, respectively. Addition of  $\text{CaCl}_2$  significantly accumulated Ca whilst reducing Na.  
 305 This indicated that  $\text{Ca}^{2+}$  could replace exchangeable  $\text{Na}^+$  on the surface of the particles and the extra  $\text{Na}^+$   
 306 would be leached out in solution.  $\text{Ca}^{2+}$  on the aggregate surface may then improve aggregate structure  
 307 and micro- morphology of the residues.



308  
 309 Fig.6 Morphological structure and energy-dispersive x-ray analysis spectrums of <0.05 mm residue aggregates. A, Control; B,  
 310  $\text{Na}^+$  (50 mmol/L); C,  $\text{Ca}^{2+}$  (50 mmol/L)

#### 311 4. Conclusion

312 Aggregate behavior and stability of bauxite residue as affected by  $\text{Ca}^{2+}/\text{Na}^+$  additions were evaluated  
 313 in this study. With increasing  $\text{Ca}^{2+}$  content, mean weight diameter (MWD) increased due to the

314 flocculation of silt-sized microaggregates. Water-stable aggregates >0.25 mm disintegrated significantly  
315 following Na<sup>+</sup> addition. Surface potential and electric field intensity of residue microaggregates gradually  
316 decreased with increasing electrolyte concentration. Furthermore, surface potential and electric field  
317 intensity in the Ca<sup>2+</sup> system was lower than that in the Na<sup>+</sup> system, which may contribute to aggregate  
318 flocculation. Laser diffraction analysis allowed for continuous monitoring of aggregate disintegration  
319 during 180 minutes of circulation in solutions. Aggregate size, structure and elemental distribution  
320 changed significantly following Ca<sup>2+</sup>/Na<sup>+</sup> treatments. These findings provide a new approach to  
321 determine the pedogenic behavior of aggregates, whilst revealing the effects of major salt ions on  
322 aggregate stability and micromorphology. Future research should focus on application of this technique  
323 in order to reveal pedogenic aggregate behavior at bauxite residue disposal areas following ameliorant  
324 and microorganism applications.

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