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

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ABSTRACT

Bauxite residue contains large concentrations of exchangeable Na⁺, which fragments aggregate structure and limits plant growth. Understanding the potential mechanisms of Ca/Na on the formation process of residue aggregates will benefit the screening of appropriate amendments for ecological reconstruction on bauxite residue disposal areas. A method for evaluating aggregate behavior and stability by integration of Le Bissonnais' and laser diffraction measurements, was determined on bauxite residues following Ca/Na additions. With increasing Ca²⁺ addition, mean weight diameter (MWD) increased, indicating improved resistance to dispersion. Ca²⁺ had a positive effect on flocculation of silt-size microaggregates, whilst disintegration was induced following Na⁺ addition. Repeated laser diffraction analysis of residue samples circulating in 50 mmol L⁻¹ electrolyte solution (Ca²⁺/Na⁺) provided a detailed view of the changes in particle size distribution as aggregates fragmented. The visualized 3D surface map revealed that Na⁺ promotes the disintegration of residue aggregates into finer dispersed particles, whilst Ca²⁺ protects the microaggregates from fragmenting into smaller particles. Variation in electrochemical properties of aggregate surfaces affected the micro-morphology significantly. The findings provide a new approach to specify pedogenic aggregate behavior of bauxite residue, whilst revealing the effects of Ca²⁺/Na⁺ on aggregate stability, surface electrochemical properties and its micromorphology. This new approach will be beneficial to the assessment of soil formation and ecological reconstruction on bauxite residue disposal areas.

HIGHLIGHTS

1. Aggregate behavior and stability of bauxite residue induced by Ca/Na are evaluated.
2. Integration of Le Bissonnais' and laser diffraction methods may effectively reveal aggregate fragmentation.
3. Ca/Na addition transformed surface electrochemical properties and micro-morphology of residue aggregates.
4. Ca²⁺ stimulated aggregate formation, whilst Na⁺ 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⁺, Ca²⁺, Mg²⁺, Al(OH)₄⁻, SO₄²⁻, CO₃²⁻, and

44 OH⁻ (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 Ca²⁺/Na⁺ on aggregate behavior and its stability for bauxite residue remain scarce. The hypothesis for
49 this study was that following Ca²⁺ or Na⁺ 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 Ca²⁺ or Na⁺ addition; 2) analyze the effect of Ca²⁺ or Na⁺ 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 CaCl₂ 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 CaCl₂ 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 CaCl₂ 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 CaCl₂ 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⁻ 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)₂ 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 Ca²⁺ and Na⁺ 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
$$S = \frac{N_{Na} k}{m a_{Na}^0} e^{\frac{F\phi\beta_{Na}}{2RT}} = \frac{N_{Ca} k}{m a_{Ca}^0} e^{\frac{F\phi\beta_{Ca}}{2RT}} \quad (5)$$

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_{Na}⁰ and a_{Ca}⁰ (mol/L) respectively for the activity of Na⁺ and Ca²⁺ in the solution at
 102 equilibrium, N_{Na} and N_{Ca}(mol) are the adsorption capacities of Na⁺ and Ca²⁺ in the residue, respectively.
 103 c_{Na}⁰ and c_{Ca}⁰ (mol/L) were concentration of Na⁺ and Ca²⁺ in the solution at equilibrium. β_{Na} and β_{Ca} were
 104 correction coefficients for correcting the effective charge amount of Na⁺ and Ca²⁺, 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 CaCl₂ 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 CaCl₂/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
$$\% > 250 \mu\text{m} = A_1 \times \exp(-K_1 T) + C_1 \quad (12)$$

118
$$\% < 20 \mu\text{m} = A_2 * [1 - \exp(-K_2 T)] + C_2 \quad (13)$$

119 where K₁ and K₂ are rate constants, T is circulation time, A₁ and A₂ are rate coefficients, C₁ is the
120 final percentage of >250 μm fractions, and C₂ represents the initial percentage of <20 μm fractions in the
121 residue aggregates. The parameters A₁, A₂, k₁, k₂, C₁ and C₂ 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/CaCl₂) 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.

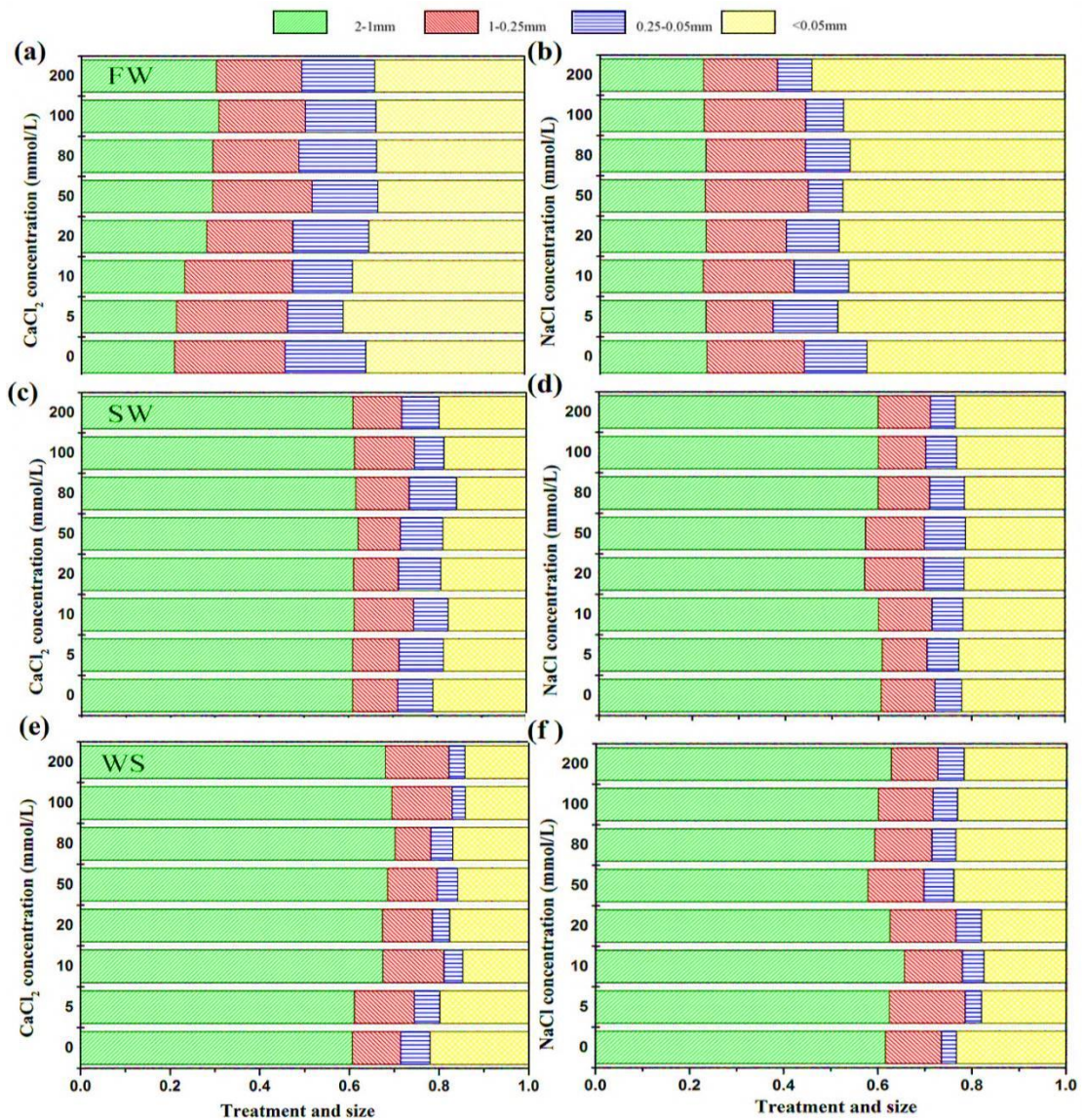
133 3. Results and discussion

134 3.1 Effect of Ca²⁺/Na⁺ 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 CaCl₂ 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⁺ 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 CaCl₂ 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 Ca²⁺ and Na⁺ 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⁺ resulted

146 in disaggregation of larger sized aggregates.



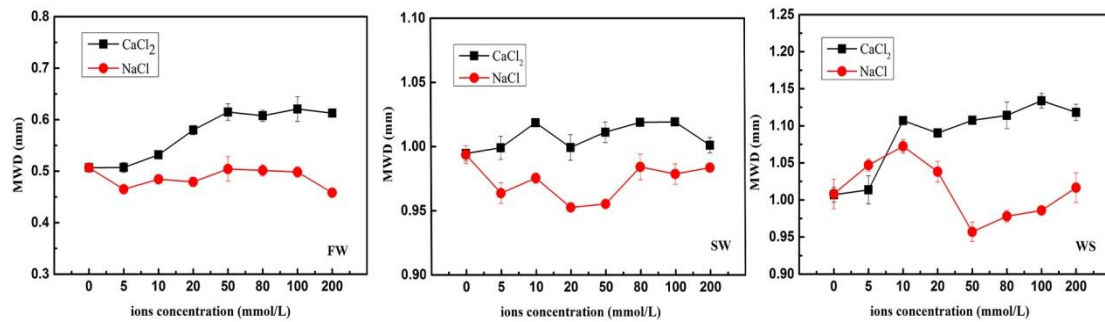
147

148 Fig. 1 Effect of Ca²⁺/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 CaCl₂ additions are presented in Fig. 2. For the three different tests, CaCl₂
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 CaCl₂ treated samples reached a relatively high value, whilst a relatively low value
156 occurred for NaCl treatments.

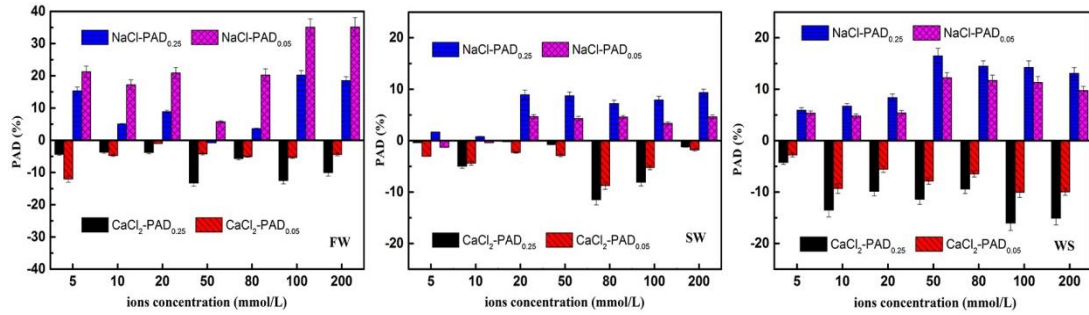
157 Electrolyte concentration, and cation valence state, significantly affected the formation of stable
158 aggregates, especially for flocculation and dispersion of clay-size particles (Olis, 1989). Multivalent
159 cations, including Ca²⁺, Fe³⁺ and Al³⁺, all formed ion bridges, compressing the thickness of the electric
160 double layer, and promoting particle flocculation (Jiang et al., 2012). In this study, addition of CaCl₂

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 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 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 Na^+ was negatively correlated with aggregate stability in bauxite residue following
 170 amendment addition, which was consistent with the results of this study.



171
 172 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 (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 PAD_x indicates dispersion, whilst a negative value indicates aggregation. The larger
 176 the absolute value of PAD_x, the stronger the corresponding effects. Variation in PAD_x in the treated
 177 residues is presented in Fig. 3. For FW treatments, the absolute values of PAD_{0.25} were 3.71%, 3.80%,
 178 13.2%, 5.68%, 12.52%, and 10.02% when the concentration of CaCl_2 solution was 10, 20, 50, 80, 100,
 179 and 200 mmol/L, respectively. This indicated that CaCl_2 had a significant protective effect on >0.25 mm
 180 residue aggregates. Compared to PAD_{0.25}, the absolute value of PAD_{0.05} was smaller, which indicated that
 181 CaCl_2 had a stronger aggregation effect on >0.25 mm aggregates. The values of PAD_{0.25} and PAD_{0.05} for
 182 NaCl treated residues were positive, and significantly higher than those following 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 PAD_{0.25} and PAD_{0.05} balance with the concentrations of NaCl or 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, Na^+ addition increased the SAR values which may have led to a loss in
 192 aggregate structure. Therefore, following NaCl or CaCl_2 additions, the values of PAD_{0.25} and PAD_{0.05}
 193 varied in volatility.



194

195

Fig. 3 Effect of Ca²⁺/Na⁺ on the percentage of aggregate destruction of bauxite residues. a) FW test; b) SW test; c) WS test.

196

3.2 Effect of Ca²⁺/Na⁺ 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 Ca²⁺, but decreased sharply to approximately 8 when Ca²⁺ exceeded 50 mmol/L. Ca²⁺ may bind to alkaline anions (e.g. CO₃²⁻) in the residues to form insoluble calcium-containing minerals to decrease the pH of the solution. With addition of Na⁺, 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⁻ concentration and the negative surface charge on residue particles, which may reduce particle repulsion and improve aggregation.

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Table. 1 Effect of Ca²⁺/Na⁺ on pH of bauxite residue

pH	Electrolyte concentration (mmol/L)							
	0	5	10	20	50	80	100	200
Na ⁺	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 ²⁺	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

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The composition of ions significantly varied soil surface properties including electric field intensity, surface potential, and specific surface area of aggregates. Effects of Ca²⁺/Na⁺ 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. Ca²⁺ is a divalent ion, which may produce a stronger compression effect on the electric double layer than that of Na⁺ (Pashley, 1981). Therefore, the surface potential of microaggregates following Ca²⁺ addition was smaller. With an increase in Ca²⁺ concentration, the specific surface area of microaggregates decreased from 6.12 m²/g to 0.68 m²/g. Furthermore, the specific surface area increased to 13.3 m²/g following Na⁺ addition. This was because flocculation or dispersion of particles determined the changes of specific surface area. Ca²⁺ promoted the stability of microaggregates, whilst Na⁺ resulted in particle dispersion

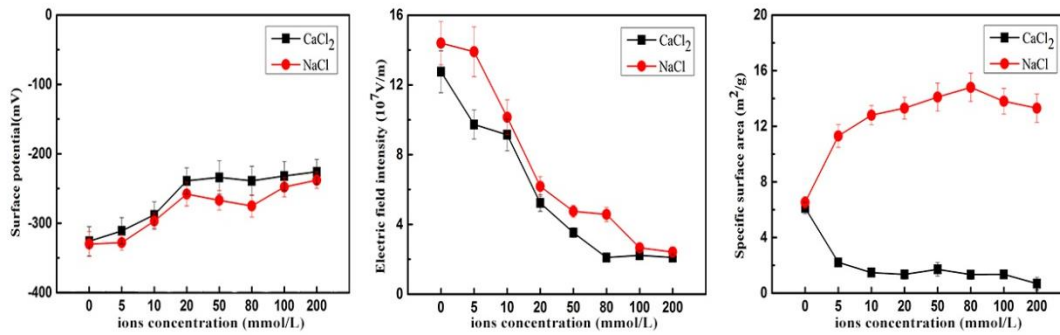


Fig.4 Effect of Ca²⁺/Na⁺ on surface properties of <0.05 mm residue aggregates.

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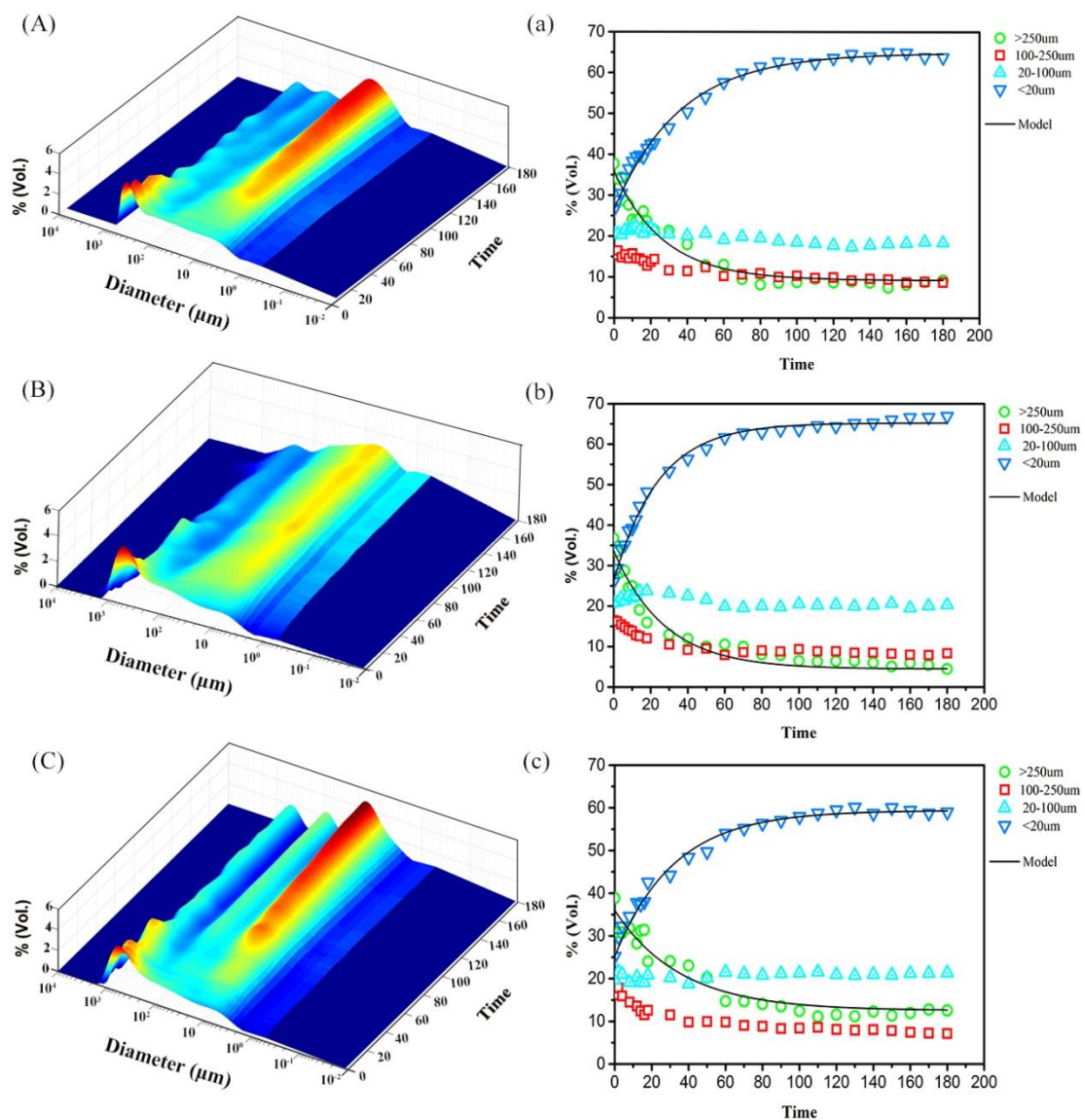
221 3.3 Effect of Ca²⁺/Na⁺ on pedogenic aggregate behavior

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⁺. For CaCl₂ 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 C₁ and C₂
 246 values revealed that Ca²⁺ addition increased the water-stable aggregate content, whilst Na⁺ 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 μm 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 μm
 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 μm 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 μm or increase of <20 μm fraction. A & a) control, B & b), Na^+ and C & c) 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 Ca^{2+} or 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 Na^+ , whilst 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
Na^+	29.2771	0.0365	4.4581	0.9630	39.2036	0.0418	26.0496	0.9938	28.2280	37.6005	0.7507
Ca^{2+}	23.4984	0.0280	12.5148	0.9406	34.1733	0.0313	25.2214	0.9842	22.8493	33.1199	0.6899

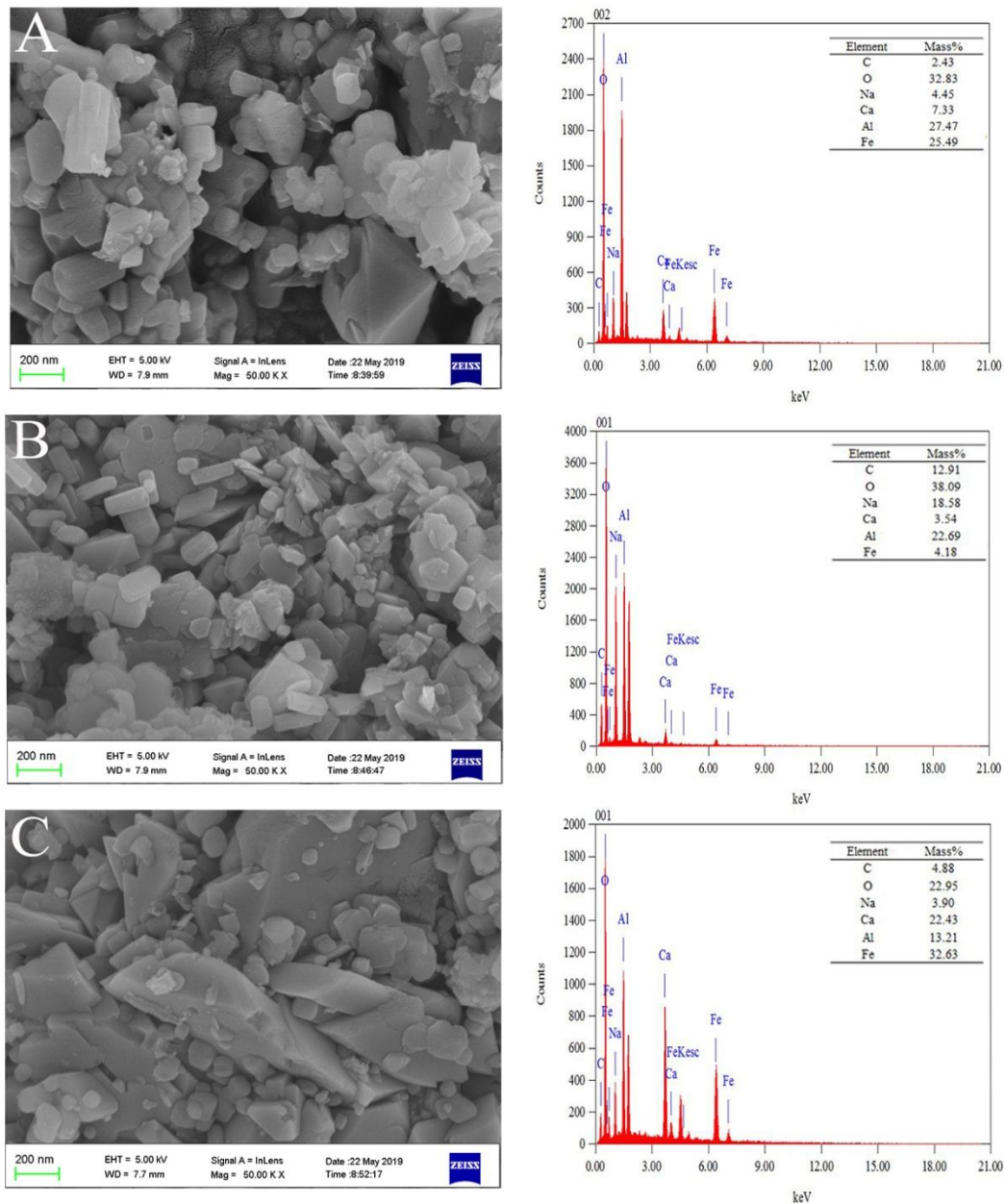
282 * $a = A_1 \cdot \exp(-k_1)$ $b = A_2 \cdot \exp(-k_2)$ $c = a/b$

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 (Na^+ , DI, and Ca^{2+}) are presented in Fig. 6. Scanning electron microscope imaging of control
 288 samples revealed that 0.2-1 μm 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 μm 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 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 Ca^{2+} may bind
 297 clay particles and organic matter to enhance particle agglomeration, or 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 μm particle fraction
 301 in 2-5 μm 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 CaCl_2 significantly accumulated Ca whilst reducing Na.
 305 This indicated that Ca^{2+} could replace exchangeable Na^+ on the surface of the particles and the extra Na^+
 306 would be leached out in solution. 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 spectra of <0.05 mm residue aggregates. A, Control; B,
 310 Na^+ (50 mmol/L); C, 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 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⁺ 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 Ca²⁺ system was lower than that in the Na⁺ 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 Ca²⁺/Na⁺ 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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