

# Evaluation of aggregate microstructures following natural regeneration in bauxite residue as characterized by synchrotron-based X-ray micro-computed tomography

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1                   **Evaluation of aggregate microstructures following natural**  
2                   **regeneration in bauxite residue as characterized by**  
3                   **synchrotron-based X-ray micro-computed tomography**

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9                   **Abstract**

10                  Bauxite residue often has poor physical conditions which impede plant growth. Native plant  
11                  encroachment on a bauxite residue disposal area in Central China reveals that natural regeneration may  
12                  improve its physicochemical properties. Residue samples collected from three different disposal ages  
13                  were assessed to evaluate residue micromorphology and three-dimensional (3D) aggregate  
14                  microstructure under natural regeneration. The residue aggregates in different disposal ages were  
15                  divided in two sections: macro-aggregate (2-1 mm) and micro-aggregate (0.25-0.05 mm). Residue  
16                  aggregate micromorphology was determined by scanning electron microscope and energy dispersive  
17                  X-ray spectroscopy, and the residue aggregate microstructure was determined by synchrotron-based  
18                  X-ray micro-computed tomography (SR- $\mu$ CT) and image analysis techniques. Natural regeneration  
19                  may improve residue aggregate stability and form a stable aggregate structure. Calcium content  
20                  increased whilst sodium content decreased significantly on the surface of residue aggregates. Under  
21                  natural soil-forming processes bauxite residue porosity, specific surface area, average length of paths,  
22                  and average tortuosity of paths all significantly increased. This demonstrated that natural regeneration  
23                  may stimulate the formation of stable aggregate structure in residues. Further understanding should  
24                  focus on particle interaction forces and agglomeration mechanisms with the addition of external  
25                  ameliorations.

26  
27                  **Highlights**

- 28                  1. Physicochemical properties improved over time due to weathering.  
29                  2. Weathering stimulated the formation of stable aggregate structures in residues.  
30                  3. Weathering changed aggregate microstructures, including pore throat and shape parameters.

31                  **Keywords:**

32                  Bauxite residue; soil-forming processes; micro-computed tomography; aggregate microstructure;  
33                  pore-throat network

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## 1 1. Introduction

2 Management and disposal of solid waste discharge from the non-ferrous metal refining process is  
3 a global environmental concern (Wu et al., 2016). Bauxite residue, a highly alkaline by-product, is  
4 generated when alumina is extracted from bauxite ores by the Bayer process (Kaur et al., 2016).  
5 Although many efforts have been made to utilize bauxite residue, few of them are commercially  
6 applied (Liu et al., 2014). Compared to marine disposal or lagooning, large volumes of bauxite residue  
7 are discharged to disposal areas using the dry-stacking method in which the residue slurry is thickened  
8 to a paste with a liquid-solid ratio of approximately 1.0 and then pumped to the stacking areas (Power  
9 et al., 2011). The global inventory of bauxite residue currently stored in such impoundments is  
10 estimated to be more than 3.4 billion tons, with an annual growth rate of approximately 120 million  
11 tons (Xue et al., 2016). Bauxite residue has high alkalinity, salinity and fine-grained particulates which  
12 create a series of environmental and ecological pollution issues (Renforth et al., 2012; Gelencsér et al.,  
13 2011). Safe and effective disposal of this solid waste is one of the critical ecological issues to  
14 sustainable development of the alumina industry. Weathering and subsequent revegetation of the  
15 residue converts it to a soil-like medium which is now regarded as the most promising method to  
16 ecologically manage this waste material (Jones and Haynes, 2011).

17 Significant challenges including elevated pH (10-12), salinity (30-60 dS/m) and exchangeable  
18 sodium percentage (50-90%), combined with low organic carbon and reduced concentrations of  
19 potentially plant-available N, P, K, Ca, Mg, Mn, Cu and Zn, limit sustainable plant cover establishment  
20 at the disposal areas (Jones and Haynes, 2011). Furthermore, poor physical conditions are one of the  
21 major limitations to revegetation as elevated sodium (Na) and its fine structure deteriorate its ability to  
22 sustainably support vegetation (Ruyters et al., 2011). A number of strategies have been used to improve  
23 revegetation including soil capping, field neutralization, and incorporation of amendments, whilst  
24 plants species including *Holcus lanatus*, *Festuca rubra* and *Acacia nilotica* have been selected to grow  
25 on the disposal areas (Xue et al., 2016). Gypsum and organic matter are regarded as appropriate  
26 ameliorants as gypsum is a slightly soluble salt which provides calcium and decreases alkalinity, whilst  
27 organic matter will provide organic carbon, plant nutrients and stimulate microbial activity (Courtney  
28 and Kirwan, 2012; Chauhan and Ganguly, 2011). Although the addition of amendments may ameliorate  
29 the adverse physicochemical properties of bauxite residue, it is now recognized that for successful  
30 ecosystem establishment, soil formation and development are crucial to the rehabilitation process  
31 (Biederman et al., 2008). Several physical indicators, such as bulk density, porosity, aggregate size  
32 distribution and aggregate stability are widely used in order to evaluate the physical quality of mine  
33 residues (Asensio et al., 2013). Courtney et al. (2009) found that the addition of spent mushroom  
34 compost and gypsum affected residue pH, EC and salinity, which positively impacted on residue  
35 microaggregate stability, preventing clay dispersion. Courtney et al. (2013) selected bulk density,  
36 porosity and water stable aggregates to assess soil formation in restored bauxite residue and found that  
37 the combined addition of gypsum and organic fertilizer increased aggregate stability and stimulated soil  
38 formation. Zhu et al. (2016) discovered that natural weathering processes may increase porosity and  
39 promote aggregate stability. However, little attention on aggregate microstructure has been considered  
40 (Gräfe and Klauber, 2011).

41 Soil aggregation and its stability influence carbon stabilization, water infiltration, nutrient  
42 transport, and the ability to resist water retention (Cheng et al., 2015). Aggregate size distribution and  
43 stability, and the size of pore spaces between and inside soil aggregates, indicate soil physical structure

1 (Annabi et al., 2011). A detailed understanding of aggregate microstructure can provide information on  
2 soil aggregation processes. Recently, computed tomography (CT) has been introduced to explore 3D  
3 soil aggregate structure which is more visual and accurate than the 2D digital images of soil thin  
4 sections (Udawatta et al., 2008). Ma et al. (2015) used synchrotron-based X-ray micro-computed  
5 tomography to evaluate soil aggregate microstructure and stability under wetting and drying cycles and  
6 provided insights for improving our understanding of the changes in soil microstructure.

7 Under natural weathering processes, bauxite residue has been converted to a soil-like medium to  
8 support plant growth, whilst aggregate structure and aggregate stability of bauxite residue have been  
9 improved (Zhu et al., 2016). The hypothesis of this research is that natural regeneration may improve  
10 residue aggregation which can lead to significant differences in morphology and microstructure of  
11 residue aggregates. The objectives of this study were to 1) investigate residue aggregate morphology  
12 and the variation of elements on the surface of residue aggregates and 2) quantify the 3D  
13 microstructure of residue aggregates to evaluate the effects of natural regeneration on particle  
14 aggregation in bauxite residues.

## 15 **2. Materials and methods**

### 16 *2.1 Site description and residue sampling*

17 A bauxite residue disposal area in Central China (35° 24' N, 113° 25' E) was selected as the study  
18 site as it has naturally weathered without human disturbance. It is located in a warm temperate  
19 continental monsoon climate characterized by four seasons and having a mean annual daily  
20 temperature of 13°C-15°C. Long-term average annual rainfall ranges from 600 mm to 1200 mm. More  
21 than 75% of precipitation occurs from June to September. Native vegetation has spontaneously  
22 encroached upon several areas of the disposal area.

23 Bauxite residue samples from three different locations related to disposal age were studied. These  
24 included (a) 1-year-old bauxite residue (Z1), (b) 10-year-old bauxite residue (Z2), and (c) 20-year-old  
25 bauxite residue with spontaneous native grass growing on it (Z3). All locations were sampled during  
26 August to September in 2014. The residues of depth 0-20 cm were sampled at three randomly chosen  
27 points at each location (a-c). Undisturbed bulk samples were stored in polyethylene bags, air dried in  
28 the laboratory at room temperature for two weeks and subsequently passed through a 2mm sieve prior  
29 to analysis.

### 30 *2.2 Physical and chemical analysis*

31 Mechanical composition of bauxite residue was determined with a Malvern Mastersizer 2000  
32 (Malvern Instruments Ltd., UK) (Santini and Fey, 2013). The pH and EC (electrical conductivity) of  
33 the residue samples were measured in water (ratio of solid:water 1:5) (Johnston et al., 2010).  
34 Exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  were determined by a method of extraction with 1 M ammonium  
35 acetate (pH = 7) and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES)  
36 (Zhu et al., 2016). Exchangeable sodium percentage (ESP) was calculated by the percentage of  
37 exchangeable sodium content in total exchangeable bases (Ca, Mg, K, Na). Total organic carbon (TOC)  
38 was measured by the dry burning method (Yilmaz, 2014).

### 39 *2.3 Residue aggregate stability analysis*

40 Aggregate stability of the residue was determined by sieving 50 g of <2 mm samples through  
41 sieves of 1, 0.25 and 0.05 mm with a 34 stroke frequency for 3 min in distilled water (Karami et al.,

1 2012). Each aggregate fraction was dried at 75°C prior to weighing. The mean weight diameter (MWD)  
2 of each sample by wet sieving were calculated as  $\sum_{i=1}^n \bar{X}_i \times W_i$ , where  $\bar{X}_i$  was the mean diameter of  
3 size fraction (mm) and  $W_i$  is the proportion of aggregates in that size range.

#### 4 *2.4 Residue morphological analysis*

5 The residue aggregates in three different locations (Z1, Z2, and Z3) had been separated into two  
6 sections: macroaggregates (2-1 mm) and microaggregates (0.25-0.05 mm). Micro-morphological  
7 studies of the residue fractions were carried out using a scanning electron microscope, equipped with  
8 energy dispersive X-ray spectroscopy (ESEM, Quanta-200) (Newson et al., 2006). The specimen was  
9 sputter coated with a layer of gold prior to examination.

#### 10 *2.5 CT scanning and image processing*

11 Residue aggregates were scanned with a synchrotron-based  $\mu$ -CT, beam line BL13W1 (Shanghai  
12 Synchrotron Radiation Facility (SSRF)). Aggregates were fixed in a plastic tube mounted on a rotary  
13 stage which as rotated from 0° to 180° with a same step interval of approximately 0.1°. Samples were  
14 scanned with the SR-  $\mu$  CT at a photon energy of 19.5 keV. Reconstructed image slices from the  
15 radiographs used a filtered back-projection algorithm. A total of 1000 slices with a size of 1200\*1000  
16 pixels for each slice were reconstructed for each aggregate.

17 ImageJ 1.48 was used to create images, visualization, and quantification of the obtained slices.  
18 Image segmentation by ImageJ removed obvious ring artifacts (Zhou et al., 2013). Images were firstly  
19 transformed from Cartesian space into polar space (Polar transformer plugin). To avoid edge effects, a  
20 volume of 300\*300\*300 voxels was extracted from the 3D aggregates (Schmid et al., 2010).

21 In this study, as has been successfully used in evaluating soil microstructure, the indicator kriging  
22 method was used for image segmentation and pore space geometry which were determined with  
23 3DMA-rock software (Zhou et al., 2012). Voxels (300×300×300) were cropped from the central part of  
24 each image. In order to reduce light variation among images, the stacked images were normalized using  
25 ImageJ before segmentation. Residue pores from the solid phase were extracted using the indicator  
26 kriging method (Oh and Lindquist, 1999). 3DMA-rock was used to analyze the pore space geometry  
27 and quantify 3D microstructure of residue aggregates (Lindquist et al., 2000).

#### 28 *2.6 Data analysis*

29 All data was analyzed in Excel 2003 and SPSS 19.0. Paired sample t-test analysis (95%  
30 confidence interval) was carried out to determine the residue samples with different disposal ages.  
31 ImageJ and 3DMA-rock were used to analyze the images and pore microstructure. All of the figures  
32 were constructed by Origin 8.0.

### 33 **3. Results**

#### 34 *3.1 Bauxite residue properties*

35 With increasing disposal age, the proportion of sand significantly increased, whilst the proportions  
36 of silt and clay decreased which may due to the changes in disposal practice (Table 1). Natural  
37 weathering processes decreased the salinity and pH of stored residues. With increasing disposal age,  
38 pH decreased from 10.98 to 9.45 and the value of EC significantly decreased from 3.73 to 0.36 mS/cm.

1 Organic carbon content increased from 5.71 g/kg to 10.81 g/kg. Mean weight diameter (MWD) ranged  
2 from 0.24 mm to 0.52 mm which indicated that under natural vegetation encroachment, not only  
3 chemical properties, but also physical conditions of the residue improved.

### 4 *3.2 Residue micromorphology*

5 Residue aggregate (2-1 mm) SEM images following natural regeneration are shown in Fig. 1. The  
6 newly stacked residue macroaggregates (Z1) had a sheet-like structure with many fine fragments. The  
7 aggregate surface was coarse leading to a comparatively loose structure. Residue aggregates stacked  
8 for 20 years (Z3) had a dense structure and granular particles were distributed uniformly. With  
9 increasing disposal age, aggregate structure appears to improve and become more stable in the bauxite  
10 residue. Calcium and sodium contents varied significantly following natural weathering processes. The  
11 total calcium content increased from 3.34% to 16.74%, whilst the total sodium content decreased from  
12 10.05% to 1.42% (Figure 1) which was consistent with the results of exchangeable calcium and  
13 sodium.

14 According to ESEM images and following natural regeneration processes, the 0.25-0.05 mm size  
15 fraction increased in size, the number of pores between microaggregates decreased, surface particle  
16 distribution became uniform and microaggregate structure varied from loose to dense (Fig. 2). The  
17 change in microaggregate surface Ca and Na contents was similar to macroaggregates. Calcium content  
18 increased from 7.62% to 20.69%, whilst Na content decreased from 9.33% to 1.02%. Furthermore, Ca  
19 content in microaggregate surfaces was greater than in macroaggregate surfaces.

### 20 *3.3 Visualization of soil aggregates*

21 The scanned macro- and microaggregates from the three different locations are shown in Fig. 3.  
22 Pores within the macro- or micro-aggregates were visually classified as inter- or intra-sub-aggregate  
23 pores based on pore positions. In three different residue samples, inter-sub-aggregate pores included  
24 channels and vughs. The residues which were stacked for the longest had larger channels and vughs.  
25 Intra-sub-aggregate pores were dominant in Z3, suggesting a more porous sub-aggregate structure to  
26 support plant growth as compared to Z1 and Z2. An overall perspective of the pore structure in residue  
27 aggregates could be speculated from the 3D images of the pore systems (Fig. 3). The pore system of Z3  
28 was more continuous than in Z1 and Z2. As for microaggregates (Fig. 4), with increasing disposal age,  
29 the diversity of intra-aggregate pores was not so obvious, whilst inter-aggregate pores increased. 3D  
30 structure of the residue microaggregates shows this result visually (Fig. 4).

### 31 *3.4 Porosity and pore-size distribution*

32 General quantitative information about the 3D pore system and pore throat networks within  
33 residue aggregates from different disposal ages is presented in Table 2. Total porosity showed  
34 statistically significant differences between residue macroaggregates and microaggregates under  
35 natural regeneration ( $P<0.05$ ). Macroporosity for macroaggregates and microaggregates of Z3 was  
36 significantly higher than for the residues which had been stacked for less than 10 years ( $P<0.05$ ).  
37 Boundary and interior pores in the residue aggregates were pores which connected or did not connect  
38 to the outside of the whole volume respectively. The numbers of interior pores, boundary pores and  
39 total pores for Z3 were all less than for Z1 and Z2 ( $P<0.05$ ), whilst the fractions of interior and  
40 boundary pores for the three different residues were significantly different ( $P<0.05$ ).

1 Nodal pore size distribution showed that Z3 had the largest porosity within each pore size  
2 diameter (Fig.5). Macro- and microaggregates in residues exhibited the same trend which indicated that  
3 natural regeneration may increase the porosity of residue aggregates. The residue macroaggregates had  
4 the greatest porosity within the 200-300  $\mu\text{m}$  range, whilst residue microaggregates had the greatest  
5 porosity within the 100-300  $\mu\text{m}$  range.

### 6 *3.5 Path length*

7 Path length showed the quantitative distance between the centers of any two adjacent nodal pores in  
8 residue aggregates. Path lengths ranged from 6 to 721, 7 to 658 and 6 to 576  $\mu\text{m}$  in macroaggregates  
9 with increasing disposal age (Z1 –Z3). In microaggregates the path lengths ranged from 8 to 613, 6 to  
10 581 and 8 to 706  $\mu\text{m}$  for Z1, Z2 and Z3 respectively. Significant differences in path lengths were  
11 observed among the residues. Compared to Z1 and Z2, residue aggregates (both macroaggregate and  
12 microaggregate) having been disposed for 20 years had a lower number of paths, but a higher average  
13 length of paths. With increasing disposal age, the average length of paths in aggregates increased  
14 significantly.

### 15 *3.6 Path tortuosity*

16 Following natural regeneration, the average tortuosity of paths increased significantly from 1.85 to  
17 2.03 in macroaggregates, and varied from 1.90 to 2.02 in microaggregates (Table 2). The relative  
18 frequency of path tortuosity increased with increasing tortuosity up to 1.7-2.0, and then decreased with  
19 increasing tortuosity (Fig. 6). The relative frequencies in Z3 were lower than in Z1 and Z2, in both  
20 macro- and microaggregates. The maximum tortuosity values were 2.6, 2.9, 3.4 for residue  
21 macroaggregates with increasing disposal age respectively, whilst for the residue microaggregates, the  
22 maximum tortuosity values were 2.8, 3.1, 3.5 respectively.

### 23 *3.7 Pore throats*

24 Except for pore size and path tortuosity, throats of interconnected pores is another indicator to affect  
25 fluid flowing within the pore system. Throats of the pore system in residue aggregates were extracted  
26 to separate the interconnected pores, and their surface areas were calculated (Fig. 7). For 20 year old  
27 residue (Z3), the total number of pore throats was significantly lower than for Z1 and Z2 (Table 2).  
28 Compared to path tortuosity, the pore surface area distribution in aggregates showed the same trend.  
29 For macroaggregates, the largest throat surface areas in Z1 and Z2 were  $9.21 \times 10^{-3} \text{ mm}^2$ , and  $7.86 \times 10^{-3}$   
30  $\text{mm}^2$  respectively, whilst the largest throat surface area in Z3 was  $0.01 \text{ mm}^2$ . For microaggregates, the  
31 largest throat surface areas in Z1 and Z2 were  $4.97 \times 10^{-3} \text{ mm}^2$  and  $7.13 \times 10^{-3} \text{ mm}^2$  respectively, whilst  
32 the largest throat surface area in Z3 was  $0.01 \text{ mm}^2$ .

## 33 **4. Discussion**

### 34 *4.1 Effects on residue aggregation and aggregate micromorphology*

35 The relative rates of natural weathering processes and improvement in residue properties will  
36 influence soil-formation at the disposal area. Rainfall leaching will dissolve soluble alkaline minerals  
37 such as sodalite and calcite which will buffer pH and salinity (Santini and Fey, 2013), whereas wind  
38 erosion will affect the redistribution of aggregate sizes at the residue surface (Amézketa, 1999).  
39 Following natural regeneration, residue particles became coarser, pH and EC decreased, and with  
40 improving physicochemical properties, a more agreeable environment for microorganism and

1 herbaceous plant colonization developed, as evidenced by the encroachment of plants on residues  
2 which had been stacked for 20 years. Microorganism activity binds clay with polysaccharides in  
3 microaggregates which thus improve particle aggregation (John et al., 2005). Plant roots are also  
4 considered as temporary binding agents which may affect soil aggregation (Bronick and Lal, 2005).  
5 With no external organic carbon additions, major sources in bauxite residue may be due to microbial  
6 activity and pioneer plant tissues (Bradshaw, 2000). Gräfe and Klauber (2011) suggested that in order  
7 to support the development of ecosystems on disposal areas, residue pH should be between 5.5 - 9.0,  
8 EC reduced to <4 mS/cm, whilst ESP should be less than 9.5%. Weathering had therefore ameliorated  
9 the residues to the extent that it was now capable of supporting plant growth. The residues in Z3 had a  
10 low EC (0.36 mS/cm) which was lower than 4 mS/cm. Nevertheless residue pH (9.45) and ESP  
11 (28.99%) were higher than the suggested rehabilitation objectives and a vegetation cover still  
12 established. Introduction of appropriate halophytes and alkaliphilic microbes may be selected to  
13 stimulate aggregation. Halophytes for example will exude organic acids, provide H<sup>+</sup>, increase the  
14 partial pressure of CO<sub>2</sub> in rooting zones and stimulate microbial communities. Microbial activity may  
15 further reduce pH and remove excess Na<sup>+</sup> (Xue et al., 2016). Establishment of pioneer plant  
16 communities may further support the improvement of residue properties to encourage establishment of  
17 sustainable ecosystems on disposal areas.

18 Mechanisms of soil aggregation involve a variety of interactions with binding agents, including  
19 organic carbon and polyvalent ions (Six and Paustian, 2014). Accumulation of organic carbon and  
20 exchangeable Ca content were beneficial to aggregate stability in bauxite residue as organic carbon and  
21 Ca were effective binding agents in particle aggregation (Courtney et al. 2009; Courtney et al., 2013).  
22 According to residue micromorphology, aggregate size became coarser following natural regeneration.  
23 The dynamic changes of Ca and Na contents on the surface of the aggregates by energy-dispersive  
24 X-ray analysis showed that the increase in Ca content had a positive correlation with the improvement  
25 of aggregate structure in the residues. Polyvalent ions such as Ca<sup>2+</sup> may have bridged clay particles and  
26 organic carbon to enhance particle aggregation, or Ca<sup>2+</sup> carbonates may precipitate to form secondary  
27 carbonate coatings which may bind primary particles together to inhibit clay dispersion (Jiang et al.,  
28 2012). Compared to macroaggregates, a higher Ca content existed on the surface of microaggregates  
29 which verified the hierarchical order of particle aggregation: the lowest hierarchical order was the  
30 formation of microaggregates, including clay particles, organic molecules (OM) and polyvalent cations  
31 (P) (Clay-P-OM) (Tisdall and Oades, 1982). Calcium ions are regarded as ion bridges forming  
32 microaggregates which result in a higher content of Ca<sup>2+</sup> in residue microaggregates than in  
33 macroaggregates. The accumulation of organic carbon had a positive effect on aggregate stability in  
34 residues. Addition of organic waste had been considered as an effective method to improve related  
35 properties of bauxite residue and provide organic materials to plant growth. Jones et al. (2011) added  
36 organic waste into residue sand and found that organic materials improved aggregate stability of  
37 bauxite residue. Following natural processes, the microstructure of residue aggregates improved from a  
38 dense massive microstructure to a porous microstructure (Fig. 3 and Fig. 4).

#### 39 4.2 Effects on residue aggregate microstructure

40 Soil structure is a key factor that influences various functions of soil and reflects the dynamic  
41 behavior of recycling and energy flow in soil (Barbosa et al., 2015). High resolution tomography  
42 facilities such as synchrotron-based  $\mu$ -CT have become available to permit quantitative studies of soil  
43 aggregate microstructure formation. The residue which had been stacked for 20 years supported plant

1 growth and showed that it could be regarded as a soil-like medium. In this study, the indicator kriging  
2 method was used to determine aggregate microstructure and pore characterization in bauxite residue.  
3 Although pore-size distribution is one of the most important parameters, as it is expressed in terms of  
4 the frequency distribution of logarithmic effective radii, shape parameters such as throat area, path  
5 length and path tortuosity have been selected to describe the detailed aggregate microstructure in the  
6 residues (Schlüter et al., 2011).

7 The scanning images indicated that although the total number of pores in macro- or  
8 microaggregates decreased, the porosity (including macroporosity and mesoporosity) increased  
9 significantly compared to Z1 and Z2, whilst a greater quantity of large and long pores existed in Z3.  
10 The 3D pore systems for Z1 exhibited similar honeycomb patterns, while in Z2 and Z3, more  
11 continuous longer channels were found. The larger pore structure were beneficial to infiltration and  
12 substance exchanges between water, nutrients, gas and thermal conduction (Ayoubi et al., 2012). The  
13 accumulation of large pores resulted in a relatively loose physical structure which led to rapid moisture  
14 movement which effectively supply plant root absorption (Bui et al., 1989). Specific surface area of  
15 soil aggregates is a critical indicator of soil structure. The increase in specific surface area showed  
16 improvement in aggregate structure (Arthur et al., 2013). With increasing disposal age, specific surface  
17 area significantly increased, indicating that aggregate structure had improved.

18 The pore morphological parameters, such as pore throat area, path length, and tortuosity, revealed  
19 the aggregate structural differences between the different disposal ages. Z3 had a lower path number,  
20 but the longest paths and average path, compared to Z1 and Z2. The continuous longest paths are  
21 usually formed by plant roots or soil fauna which is beneficial to soil water flow (Peth et al., 2008).  
22 Compared to Z1 and Z2, the existence of plant roots may lead to longer pore paths in Z3. The residues  
23 (Z3) had a higher path tortuosity which showed that there was a large volume of irregular pores in  
24 residue aggregates. Zhou et al. (2013) found that soil aggregates had a higher path tortuosity with  
25 addition of organic waste, which was in agreement with our results. Natural regeneration significantly  
26 decreased the number of pore throats but increased their throat surface area which suggested that  
27 natural weathering processes may improve water, gas and nutrient fluxes in bauxite residue. The results  
28 demonstrate that shape parameters are also capable of differentiating macro- and microaggregate  
29 microstructures in bauxite residues.

30 All of these quantitative results, together with the 2D and 3D observations, have indicated that  
31 with increasing disposal age, and without human disturbance, both macro- and microaggregate  
32 structure, and aggregate stability and pore characterization have improved thereby supporting plant  
33 growth. These results confirm our hypothesis that natural regeneration may not only ameliorate  
34 physicochemical properties, but also promote residue aggregation and aggregate microstructure  
35 formation. Synchrotron-based X-ray micro-computed tomography and image analysis provided an  
36 improved understanding of aggregate microstructure and soil-formation process at the bauxite residue  
37 disposal area. Pore size distribution and shape parameters in residue aggregates may provide specific  
38 characterization of aggregation following natural regeneration. As soil formation is crucial for  
39 successful plant cover on the disposal area, high resolution tomography and image analysis may be  
40 regarded as an effective tool to evaluate aggregation and soil development processes for the  
41 rehabilitation of bauxite residue disposal areas.

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1 **5. Conclusions**

2 Natural regeneration ameliorated the physicochemical properties and aggregate stability of bauxite  
3 residues. With increasing disposal age, aggregate structure improved and became more stable.  $\text{Ca}^{2+}$   
4 content increased whilst  $\text{Na}^+$  content decreased on the surface of residue aggregates which indicated  
5 improvement in their structure. The total number of pores, number of interior pores, number of  
6 boundary pores, total number of throats, and total number of paths decreased significantly following  
7 natural regeneration, whilst porosity, specific surface area, average length of paths and average  
8 tortuosity of paths increased. The results indicated that long-term natural regeneration promoted  
9 aggregation and altered the three-dimensional microstructure of macro- and microaggregates. It  
10 verified our hypothesis that natural weathering processes may not only ameliorate the related  
11 physicochemical properties of bauxite residue, but also improve residue microstructure. Our future  
12 studies will investigate the improvement of microstructure and pore-size characterization in bauxite  
13 residue following addition of gypsum and organic waste.

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