

Article

Physicochemical and Microstructural Properties of Red Muds under Acidic and Alkaline Conditions

Qingke Nie ¹, Youdong Li ¹, Guohui Wang ^{1,2} and Bing Bai ^{2,*}

¹ Hebei Research Institute of Construction and Geotechnical Investigation Co. Ltd., Shijiazhuang 050031, China; nieqingke@126.com (Q.N.); hbjklyd@163.com (Y.L.); 11115269@bjtu.edu.cn (G.W.)

² School of Civil Engineering, Beijing Jiaotong University, Beijing 100044, China

* Correspondence: bbai@bjtu.edu.cn; Tel.: +86-010-51684815

Received: 18 March 2020; Accepted: 22 April 2020; Published: 25 April 2020



Abstract: The main purpose of this study was to characterize the mineral and chemical composition of typical red muds in China. Changes in the physicochemical and microstructural properties of red muds collected from the Shanxi and Shandong provinces were investigated after they were immersed in an alkaline NaOH or an acidic HCl solution for 7, 28, and 120 days. The results showed that red mud has a high cation exchange capacity and active physicochemical properties, which can be closely related to its extremely high alkalinity and complex microstructure. The neutralization of red mud with the HCl solution results in the release of Na⁺ from the red mud particles into the leachate and can effectively decrease the pH value of the filtrate. The neutralization process can result in a significant decrease in the liquid limit, plastic limit and plasticity index, whereas the opposite was observed for the different parameters after the addition of the NaOH solution. In this sense, acid neutralization can significantly improve the cementation property of the red mud. This result will increase the water permeability of the acid-treated soil layer and improve the growth ability of plants. The specific surface area of red mud immersed in the NaOH solution decreased, whereas the specific surface area of red mud immersed in the HCl solution increased. This study contributes to our understanding of red mud properties after the red mud has been subjected to acidic and alkaline treatments, and the results can provide insights into the safe disposal of red mud.

Keywords: red mud; filtrate; physicochemical property; specific surface area; microstructure

1. Introduction

Red mud (bauxite residue) is a highly alkaline ultrafine-grained waste material generated during the industrial production of aluminum oxide from bauxite [1–3]. China is now a world-leading producer of aluminum oxide, accounting for approximately 30% of the total production in the world. In 2019, aluminum oxide production exceeded 70 million tons in China. This production will give rise to the formation of a large quantity of hazardous substances (e.g., heavy metal ions and radioactive elements) in the byproducts (e.g., solid waste materials and leachate), causing serious damage to the environment and human health [4,5]. The disposal of red mud requires a large storage space, and the infiltration of various chemical elements into soils may cause soil salinization and groundwater pollution [6]. Importantly, long-term exposure to these hazardous substances can have devastating consequences on human health. Thus, there is an urgent need for the safe disposal of red mud in China to minimize its negative impacts. Red mud can be utilized for various applications [7–9]. Some useful materials, such as valuable metals, can be recovered from red mud that otherwise would be disposed of as waste [10,11]. Red mud can also be used as raw materials for the production of bricks [12,13], concrete [14], admixtures for subgrade and high-performance concrete, calcium-silicon

compound fertilizer, microporous calcium silicate heat insulation products, ceramic composite materials, thermal insulation and refractory materials [15].

The main pollutants of red mud include heavy metal ions, fluoride, radioactive substances, and sodium and aluminum ions. The extremely high pH of red mud (>12) can be attributed to the presence of a large quantity of highly alkaline chemicals, making it corrosive to various biological and metallic materials (e.g., aluminum and steel materials) and siliceous materials (e.g., glass) [14]. There are considerable concerns about the potential leaching of red mud leachate into groundwater, which can cause an increase in pollutants and the pH value of groundwater [16]. In this regard, it is of practical importance to gain a better understanding of the changes in the physicochemical and mechanical properties of soils subjected to red mud pollution [4,17]. Neutralization of red mud with acids (HCl, HNO₃ and H₂SO₄) before storage can be an effective way to make red mud environmentally benign [18]. Han et al. [7] investigated the effectiveness of bauxite neutralization using atmospheric CO₂ and whether neutralization could be accelerated when Ca²⁺ sources were supplied in solid (flue gas desulfurization gypsum) and aqueous (CaCl₂ solution) forms. Obviously, neutralization of red mud can cause changes in the physicochemical, microstructural, and mechanical properties of red mud. From this perspective, red mud can be utilized to improve the cementation of acid soils, which provides a promising approach to improve their microstructure [9,18]. Bai et al. [19] investigated the effects of flow velocity and the concentration of red mud particles and OH[−] ions on the penetration of red mud filtrate with very fine particles in a porous medium. In recent years, red mud has started to be considered as a potential valuable resource instead of waste, and it has been used for the remediation of soils contaminated by high concentrations of metals/metalloids [9].

In this study, we investigated the changes in the physicochemical and microstructural properties of typical red mud in China subjected to acidic and alkaline treatments, which were compared with those of a typical silty soil. This study can provide some insights into the safe disposal of red mud, which has good engineering significance for soil restoration.

2. Material and Methods

2.1. Components and Physicochemical Properties of Red Mud in China

The chemical composition of red mud depends largely on the nature of the bauxite ore, while the mineral composition is also related to the techniques used for the production of aluminum oxide [5,8,10]. Over 95% of alumina produced globally is produced through the Bayer process. In China, aluminum oxide is mainly produced by an alternative sintering process or a combination of sintering and Bayer processes for low-grade diasporic bauxite that is rich in aluminum and silicon. However, more red mud would be generated during the sintering process than during the Bayer process. The survey of several aluminum oxide manufacturers in Guizhou, Shanxi, Shandong and Henan provinces shows that red mud is composed mainly of aluminum and ferric oxides (Table 1). Table 1 also shows that the red mud produced by the combined method has a low content of alkali components but a high content of calcium oxide. In China, the red mud produced by the Bayer method is rich in ferric and aluminum oxides (Table 2), which are lower in ferric and aluminum oxides than those produced in other countries by the same method. Table 2 shows that there is a significant difference in the main mineral components of red mud produced by the sintering process and the Bayer process in China, which is from a statistical result based on the Chinese literature [3–7]. The red mud is composed of 5% particles of $d > 0.075$ mm, 90% particles of $d = 0.075$ – 0.005 mm, and 5% particles of $d < 0.005$ mm [3,9,20]. The physical properties of typical red mud in China are as follows—specific gravity $G = 2.70$ – 2.89 , void ratio $e = 2.53$ – 2.95 , water content $w = 82.3$ – 105.9% , liquid limit $w_L = 71$ – 100% , plastic limit $w_P = 44.5$ – 81% , and plasticity index $I_P = 10$ – 30 , which are all higher than those of the silty clay and silt; natural unit weight $\gamma = 14.2$ – 15.1 kN/m³ and dry unit weight $\gamma_d = 6.6$ – 8.11 kN/m³, which are both lower than those of the silty clay and silt; the liquid limit index $I_L = 0.92$ – 3.37 , indicating a liquid plastic state; and the saturation degree $S_r = 91.1$ – 99.6% , indicating almost complete saturation.

Table 1. The chemical compositions of typical red muds in China.

Chemical Composition	Sintering Process					Combined Process		
	Guizhou	Shanxi	Shandong	Henan	Average	Shanxi	Henan	Average
SiO ₂	25.9	21.4	22.0	21.4	22.7	20.6	20.5	20.6
TiO ₂	4.4	2.9	3.2	2.6	3.3	2.9	7.3	5.1
Al ₂ O ₃	8.5	8.2	6.4	8.8	8.0	9.2	7.0	8.1
Fe ₂ O ₃	5.0	8.1	9.0	8.6	7.7	8.1	8.1	8.1
NaOH	11.1	8.0	11.7	16.3	11.8	8.1	8.3	8.2
CaO	38.4	46.8	41.9	36.0	40.8	45.6	44.1	44.9
Na ₂ O	3.1	2.6	2.8	3.2	2.9	3.2	2.4	2.8
K ₂ O	0.2	0.2	0.3	0.8	0.4	0.2	0.5	0.4
MgO	1.5	2.0	1.7	1.9	1.8	2.1	2.0	2.0
In total (%)	98.1	100.0	99.0	99.6	99.3	100.0	100.0	100.0

Table 2. The mineral compositions (or compounds) of typical red muds in China.

Sintering Process		Bayer Process	
Mineral Compositions	Mass Percentage (%)	Mineral Compositions	Mass Percentage (%)
Calcite	26.0	Hydrogarnet	46.1
Calcium orthosilicate	25.0	Hematite	17.0
Hydrated calcium	15.0	Perovskite	13.6
Hydrogarnet	9.0	Cancrinite	12.3
Hydrous ferric oxide	7.0	Diaspore	2.0
Nepheline	7.0	Illite	2.0
Sodium silicate hydrate	5.0		
Perovskite	3.0		

The cation exchange capacity is generally high and varies substantially in red mud [9,21]. In China, the cation exchange capacity of red mud can reach a maximum of 578.1 meq/kg and a minimum of 207.9 meq/kg, and it normally falls in the range of 250–300 meq/kg, which is higher than that of kaolin and illite but lower than that of montmorillonite. Clearly, the cation exchange capacity of red mud is not stable, and thus, its physicochemical properties are likely to change by the external environment. In addition, the specific surface area of red mud is large, with a maximum of 186.9 m²/g, and varies substantially. The specific surface area can be indicative of the dispersion and lattice structure of red mud, which is closely related to the high alkalinity and particular microstructure of red mud.

2.2. Test Procedures

Typical red mud samples with a pH > 12.3 ($C_{OH^-} = 2 \times 10^{-2}$ mol/L) were collected in Jiaokou County of Shanxi Province (hereafter referred to as Shanxi red mud) and Shandong Province (hereafter referred to as Shandong red mud), which were gray and red-brown in color, respectively (see the digital photographs in Figure 1). The particle size distributions were measured by laser diffraction (LA-950 Mode, HORIBA, Kyoto, Japan; wet method), which can easily measure the solid particle size of soil in the range of nanometer to millimeter. The particles $d < 0.005$ mm, 0.005 mm $< d < 0.075$ mm, and $d > 0.075$ mm accounted for approximately 5%, 90%, and 5%, respectively, and thus these particles were mainly silts with $d < 0.075$ mm. The liquid limit was $w_L = 56.7\%$ and 55.8% , the plastic limit was $w_P = 45.4\%$ and 45.9% (liquid-plastic limit combined measurement method), and the plasticity index was $I_P = w_L - w_P = 11.3$ and 9.9 (ignoring the percent sign) for the Shanxi Province and Shandong Province red mud, respectively. Silty soil samples with a pH of 7.6 were collected from the shallow surface near the red mud impoundment in Jiaokou County of Shanxi Province (hereafter referred to as Shanxi silty soil) and used for comparison, whose liquid limit was $w_L = 32.9\%$, plastic limit was $w_P = 19.2\%$, and plasticity index was $I_P = 13.7$. The temperature of the laboratory was controlled at $T = 22 \pm 0.2$ °C.

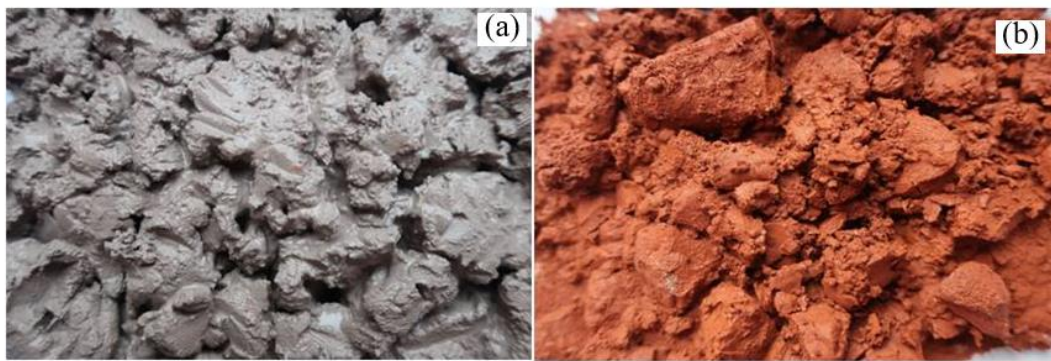


Figure 1. Digital photographs of the raw samples—(a) Shanxi red mud and (b) Shandong red mud.

As a typical acid or alkali substance, HCl (or NaOH) was selected as the neutralization agent or corrosion solution. The red mud particles (or Shanxi silty soil) were completely immersed in an HCl (or NaOH) solution at a solid-liquid ratio of about 60% in weight and stirred for approximately 5 min and then settled in the solution for 7, 28, and 120 days. For each sample, the weight of the air-dried solid particles was 300 g. The selected concentrations were 1 and 4 mol/L, which correspond to high concentration of acid (i.e., $\text{pH} \leq 0$) or alkali (i.e., $\text{pH} \geq 14$). Thus, their limit water content, specific surface area and microstructure were determined. Here, the specific surface area was measured by the nitrogen adsorption method using Autosorb-iQ2 (Quantachrome, Boynton Beach, FL, USA), and the microstructure was observed under a scanning electron microscope (SEM; S4800 Mode, Hitachi, Tokyo Japan). The chemical composition and content of the red mud particles were measured by energy dispersive X-ray spectroscopy (EDX, HORIBA EMAX, Kyoto, Japan). The immersion of the HCl solution into highly alkaline red mud is actually a neutralization process [7,17], and the addition of the NaOH solution can further result in an increase in the pH value of the red mud due to the existence of more OH^- ions. In addition, the NaOH solution can be a corrosion process for the Shanxi silty soil with a pH of 7.6.

3. Physicochemical Properties of Red Mud under Acidic and Alkaline Conditions

3.1. Variation in Limit Water Content

Figure 2 shows the liquid and plastic limits of the Shanxi silty soil, Shanxi red mud and Shandong red mud immersed in the different concentrations of the HCl or NaOH solution for 7 days, where the concentrations of the HCl solution are indicated by negative values and those of the NaOH solution are indicated by positive values for the sake of comparison. Each value was the average of three repeated test results. In Figure 2, “0 mol/L” on the abscissa denotes no acid or alkali added. It is clear that red mud generally has a higher liquid limit and plastic limit but a lower plasticity index ($I_p = 4.8\text{--}18.7$) than silt ($I_p = 4.5\text{--}31.3$) under either acidic or alkaline conditions. As the concentration of the NaOH solution increased, the liquid limit and plastic limit of the Shanxi silt soil tend to increase, whereas that of red mud remained almost unchanged. This outcome can be attributed to the high ionic strength and pH value of pore water in red mud (Table 1), resulting in strong physicochemical interactions between the solid particles and pore water. Thus, the addition of a small quantity of the HCl or NaOH solution can have a negligible effect on the red mud. It is no longer acceptable to classify red mud according to the standards obtained based on common soils with low ion concentrations and neutral pH values.

Figure 3a shows that as the concentration of the NaOH solution increases, the plasticity index of the Shanxi silty soil increases significantly from $I_p = 13.7$ before immersion to $I_p = 25$ after immersion in a 4 mol/l NaOH solution for 7 d. However, the opposite trend is observed with increasing concentration of the HCl solution, and its plasticity index reaches a minimum of $I_p = 4.9$ for the Shanxi silty soil immersed in a 4 mol/l HCl solution for 7 days. It is important to note that this increasing or decreasing trend becomes more pronounced with the increase in immersion time from 7 to 120 days. The liquid

limit and plastic limit of soils are closely related to the ion concentration and pH value of pore water. It can be concluded that the addition of the HCl solution can result in a decrease in the liquid limit, plastic limit and plasticity index, whereas the opposite trend is observed for the addition of the NaOH solution.

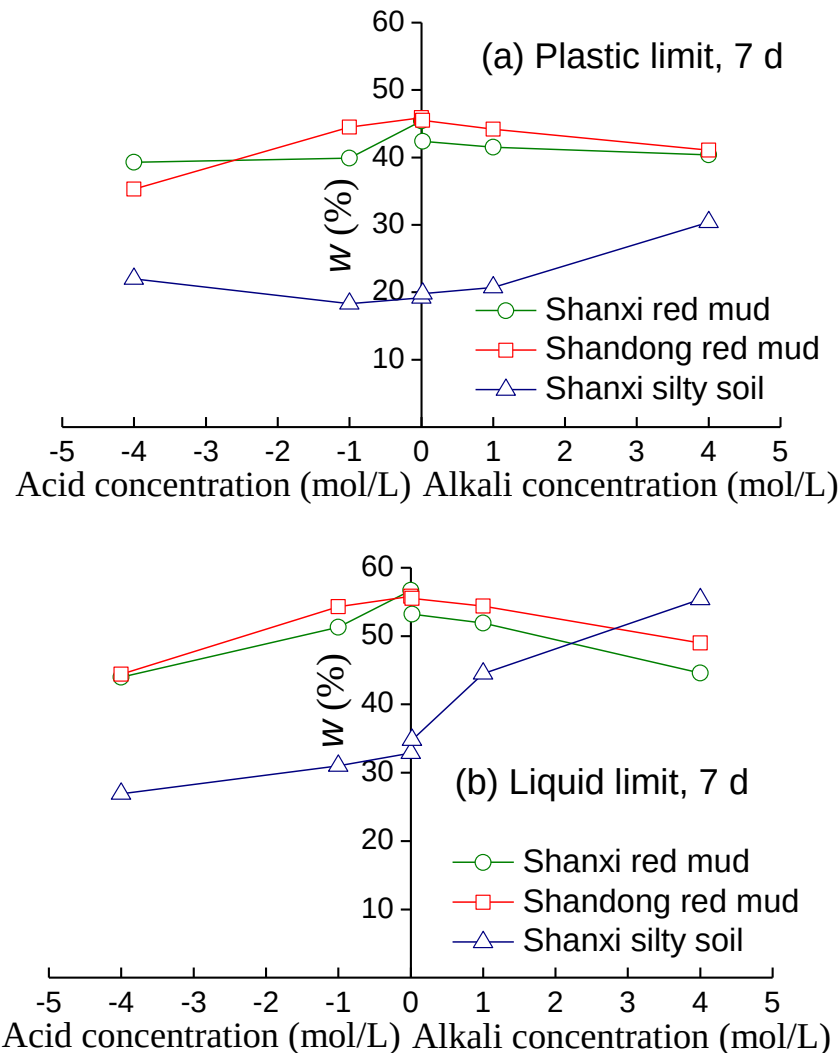


Figure 2. The limit water content as a function of the HCl or NaOH solution concentration—(a) plastic limit, and (b) liquid limit.

Figure 3b shows that for highly alkaline Shanxi red mud, the addition of the NaOH solution within 7 d has no significant effects on the plasticity index, but the addition of the HCl solution can result in a decrease in the plasticity index due to neutralization action. However, the plasticity index of the Shanxi red mud immersed in the NaOH solution also tends to increase over time (e.g., 120 days). Figure 3c shows that the changes in the plasticity index of the Shandong red mud are in good agreement with those for the Shanxi red mud, as shown in Figure 3b.

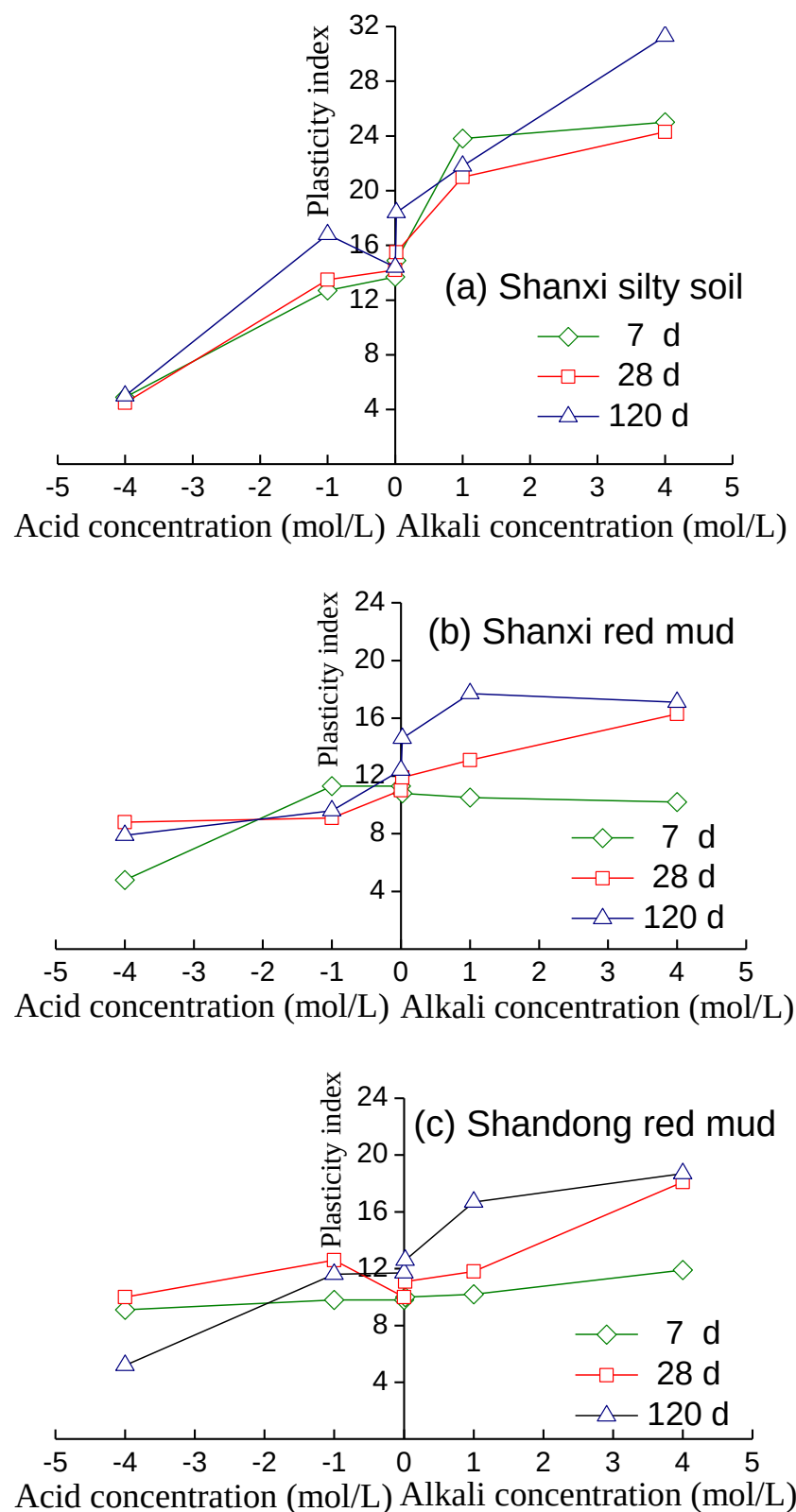


Figure 3. Changes in the plasticity index as a function of the HCl or NaOH solution concentration—(a) Shanxi silty soil, (b) Shanxi red mud, and (c) Shandong red mud.

3.2. Variation in Specific Surface Area

Generally, the specific surface area of the red mud ranges from 10 to 30 m²/g depending on the bauxite grinding [10,18,19]. Table 3 shows the specific surface area of the Shanxi silty soil, Shanxi red mud and Shandong red mud immersed in the HCl or NaOH solution for 120 days, which is measured by the nitrogen adsorption method. The Shanxi silty soil originally had a larger specific surface area (28.432 m²/g) than the Shanxi red mud (8.906 m²/g) and Shandong red mud (22.931 m²/g), but the specific surface area decreases to 1.670 m²/g and 18.89 m²/g after immersion in a 4 mol/L NaOH or HCl solution for 120 days, respectively. However, the specific surface area of the Shanxi and Shandong red muds tends to decrease when immersed in the NaOH solution but increase when immersed in the HCl solution, which appears to be more pronounced for the Shandong red mud. For instance, the specific surface area of the Shandong red mud immersed in the HCl solution increased by 2.64 times from 22.931 to 60.492 m²/g, whereas that of the Shanxi red mud increased by 1.55 times from 8.906 to 13.798 m²/g. Rai et al. [18] also reported that an acid treatment could increase the specific surface area of red mud.

Table 3. The specific surface areas of soil samples immersed in HCl or NaOH solution (m²/g).

Type of Solution	Shanxi Silty Soil	Shanxi Red Mud	Shandong Red Mud
HCl solution (4 mol/L)	18.89	13.798	60.492
Untreated	28.432	8.906	22.931
NaOH solution (4 mol/L)	1.670	5.737	8.530

4. Variation in The Main Metal Elements Under the Acidic and Alkaline Conditions

Table 4 indicates the changes in the main metal elements (i.e., Na, Al, Fe, Ca), and Si and Cl in the weight percentage of the solid particles for the Shanxi silty soil, Shanxi red mud and Shandong red mud immersed in a 4 mol/L HCl or NaOH solution for 120 days (28 days only for the Shandong red mud under alkali action). The measured element contents (EDX method) are actually the contents of some elements of the solid particle sample by the analysis of the dispersive X-ray spectra. In fact, after the acid or alkali treatment, the mineral structure of the solid particles changes obviously and generally exists in the form of compounds or ions due to the addition of acid or alkali solution. Some ions are leached in the filtrate, which causes the difference in the various elements for the same soil to some extent. For clarity, the compositions of the solid particle were expressed in the form of element. Overall, the measured results can explain the difference in the main metal elements of solid particles for the different types of soils (e.g., between the Shanxi silty and Shanxi red mud).

Table 4. The main elements of the solid particle for Shanxi silty soil, Shanxi red mud and Shandong red mud after acid or alkali treatment.

Main Elements	HCL Solution Treatment			Untreated			NaOH Solution Treatment		
	Shanxi Silty Soil	Shanxi Red Mud	Shandong Red Mud	Shanxi Silty Soil	Shanxi Red Mud	Shandong Red Mud	Shanxi Silty Soil	Shanxi Red Mud	Shandong Red Mud (28 Days)
Na	0.52	1.9	0.92	0	7.83	8.87	9.42	14.23	15.88
Al	5.78	9.11	5.52	6.53	10.04	9.63	5.22	8.99	9.64
Fe	4.86	2.71	12.64	7.32	3.59	19.30	6.68	4.55	16.84
Ca	4.14	11.75	1.1	4.94	11.64	0	2.06	10.34	0
Si	18.38	7.01	4.06	19.66	9.09	8.24	19.72	7.67	8.15
Cl	15.96	25.39	6.71	0	0	0	0.82	0	0.83

Table 4 shows that the Shanxi silty soil initially contained 4.94% Ca (i.e., untreated sample) but almost no Na. The immersion in the NaOH solution results in a 9.42% increase in Na. The Si content in the original Shanxi silty soil accounted for 19.66% of the total weight, which is much higher than that in the Shanxi red mud and Shandong red mud (i.e., 9.09% and 8.24%, respectively). However, immersion

in the HCl solution results in almost no increase in Na but a 15.96% increase in Cl for the Shanxi silty soil.

Table 4 also shows that there is a significant difference in the chemical composition between Shanxi and Shandong red mud. For instance, the Shandong red mud contains less Ca (not detected due to its small amount) but more Fe (19.30%) than the Shanxi red mud (11.64% and 3.59%, respectively). This conclusion can also be obtained based on the measurement result after the acid treatment (i.e., 4 mol/L HCl solution) for the Shanxi red mud and Shandong red mud (i.e., Ca: 11.75% and 1.1%; Fe: 2.71% and 12.64%, respectively; see the HCl solution column in Table 4). Hence, the Shandong red mud presents a red-brown color (see Figure 1b) due to the existence of a large number of Fe^{3+} ions. It is important to note that the Al content is still as high as 10.04% and 9.63% for the Shanxi and Shandong red mud after the extraction of aluminum oxide, respectively. Approximately 7.83% and 8.87% of Na was detected in Shanxi red mud and Shandong red mud, respectively, whereas no Na was detected in the Shanxi silty soil (see the untreated column in Table 4), indicating that the presence of Na in the red mud can be mainly attributed to the addition of alkaline substance NaOH during the production of aluminum oxide.

Table 4 indicates that the Shanxi red mud immersed in the NaOH solution shows an increase in Na content from 7.83% to 14.23% of the untreated sample, whereas that immersed in the HCl solution shows an increase in Cl content to 25.39%, and 75.7% was leached out in the Na^+ content of the untreated sample (i.e., from 7.83% to 1.9%) due to the release of Na^+ that formerly existed in the solid matrix of the red mud into the filtrate. In addition, the Fe content is reduced to 75.5% of the untreated sample (i.e., from 3.59% to 2.71%) and that of other contents (e.g., Al and Si) is also significantly reduced. Similarly, the Shandong red mud immersed in the HCl solution also shows a 10.4% decrease in the Na content (i.e., from 8.87% to 0.92%; Table 4). Thus, it can be concluded that Na^+ is the predominant exchangeable cation in the fresh red mud residue.

Sahu et al. [20] investigated the ability of an activated CO_2 -neutralized red mud to remove arsenate (As(V)) from aqueous solutions and showed that the sorption capacity of red mud increases after neutralization. However, it has been reported that red mud treated with an HCl solution has a 30% lower capacity to adsorb metals compared with an untreated red mud [9,18,21]. Rai et al. [18] observed a similar phenomenon by many neutralization methods (e.g., acid neutralization, CO_2 neutralization, sintering, seawater neutralization, and bioremediation), especially for the Na^+ content. Partial dissolution of cancrinite in an acid-treated red mud causes an increase in other phases, e.g., hematite. In particular, there is a higher fraction of water-soluble and exchangeable metals in an acid-treated red mud than in an untreated red mud. Hence, neutralization is a promising method to reduce the adverse environmental impacts resulting from an uncontrolled release from storage, which also has a favorable economy. Obviously, the immersion of red mud in an HCl solution can also have an effect on its physicochemical, microstructural, and mechanical properties.

5. Microstructure of Red Mud under Acidic and Alkaline Conditions

Primary and secondary mineral components of common soils (e.g., silt and clay) are rarely present in red mud. Figure 4a clearly shows that Shanxi red mud particles are composed of andradite (hydrated, $\text{Ca}_3(\text{Fe}_{0.87}\text{Al}_{0.13})_2(\text{SiO}_4)_{1.65}(\text{OH})_{5.4}$, 27.7%), tridymite 2H substructure (SiO_2 , 6.0%), coesite (SiO_2 , 26.3%), sodium aluminum silicate carbonate ($\text{Na}_8(\text{AlSiO}_4)_6(\text{CO}_3)_{1.09}$, 17.6%), calcite ($\text{Ca}(\text{CO}_3)$, 18.0%) and hematite alpha (Fe_2O_3 , 4.4%), as determined by X-ray diffraction (XRD, D8 Advance Mode, Bruker, Karlsruhe, Germany). Figure 4b shows that the Shandong red mud particles are composed of aluminum titanium oxide (Al_2TiO_5 , 17.6%), titanium aluminum oxide ($\text{Ti}_{2.79}\text{Al}_{1.21}\text{O}_{0.024}$, 2.4%), aluminum iron oxide (FeAlO_3 , 17.9%), hydrohematite ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, 23.9%), macaulayite ($\text{Fe}_{24}\text{Si}_4\text{O}_{43}(\text{OH})_2$, 23.2%) and histinerite ($\text{Fe}_2\text{Si}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, 14.9%). Figures 5–7 show the changes in microstructure (SEM images) of the Shanxi silty soil, Shanxi red mud and Shandong red mud immersed in a 4 mol/l HCl or NaOH solution for 120 days, including the untreated samples.

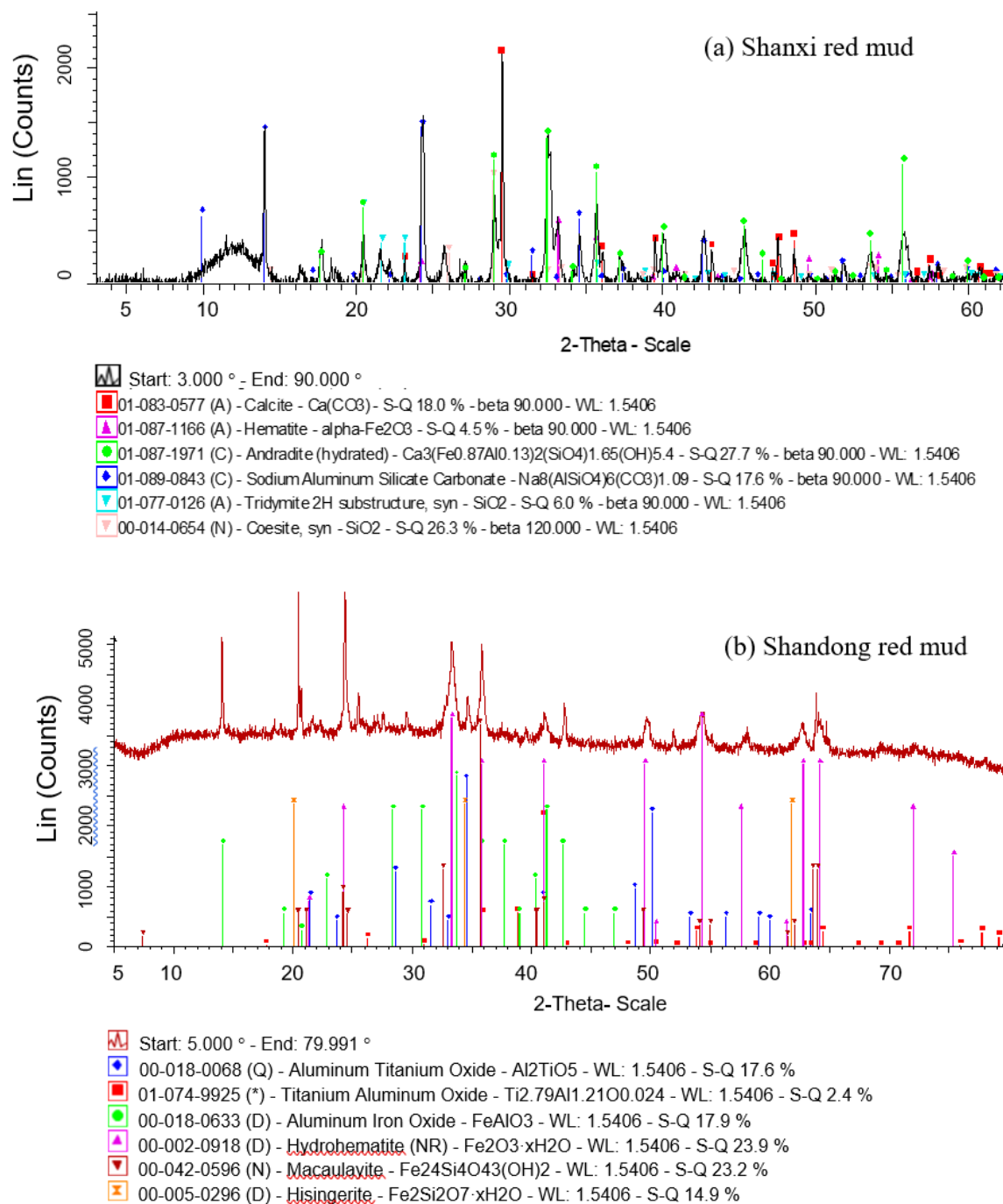


Figure 4. X-ray diffraction (XRD) patterns of the solid particles—(a) Shanxi red mud, and (b) Shandong red mud.

The results show that the two red muds are honeycombs with particles (Figures 6 and 7) that are much smaller ($<10\ \mu\text{m}$) than that of silty soil (Figure 5). For silty soil, even if an acid (HCl) or alkali (NaOH) solution is added, the crystal structures of their mineral particles are still relatively complete. Red mud particles are poorly crystallized and contain amorphous substances in dispersed and disordered states. The fine particles of red mud form a solid mass with very few large pores and low hydraulic conductivity. Obviously, very few plants can survive on red mud due to its low infiltration rate and high water-holding capacity. Red mud is generated after a series of complex physical and chemical processes, especially after dissolution in a highly alkaline NaOH solution. Thus, the structures of primary and secondary mineral components in red mud can be greatly destroyed, indicating that

red mud no longer has the physicochemical and mechanical characteristics of common silty soil or clay soil. For this reason, the interactions between the solid particles and pore water cannot be directly explained by the exchange between the bound water and free water. Thus, physical parameters such as the plasticity index for the classification of silty soil and clay soil no longer apply to red mud, and it is necessary to establish more relevant standards for the classification of red mud based on its particular physicochemical and microstructural properties.

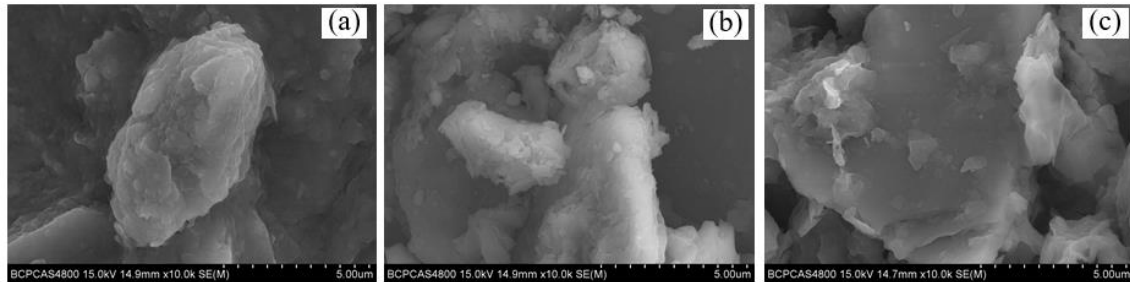


Figure 5. Scanning electron microscope (SEM) images of the Shanxi silty soil—(a) 4 mol/L HCl solution, (b) untreated, and (c) 4 mol/L NaOH solution.

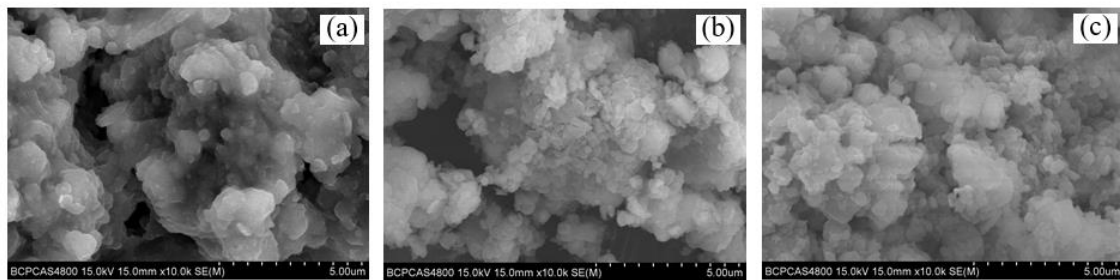


Figure 6. SEM images of the Shanxi red mud—(a) 4 mol/L HCl solution, (b) untreated, and (c) 4 mol/L NaOH solution.

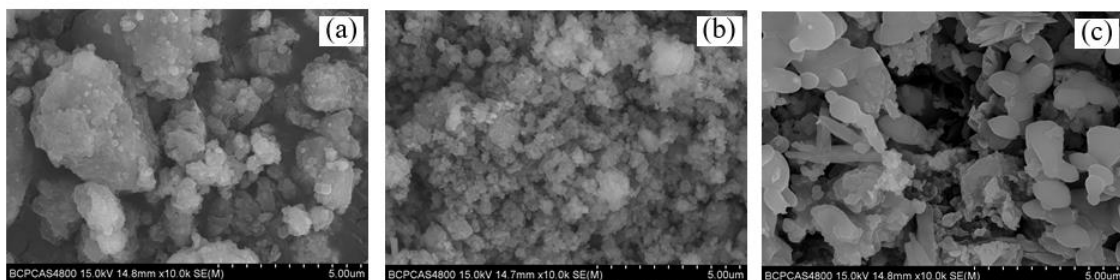


Figure 7. SEM images of the Shandong red mud—(a) 4 mol/L HCl solution, (b) untreated, and (c) 4 mol/L NaOH solution.

Figure 5 shows that there is a dramatic change in the microstructure of the Shanxi silty soil immersed in the HCl or NaOH solution. According to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [22], the addition of acidic substances into soils makes it easier for fine solid particles in soils to form a loose suspended state (Figure 5a), while addition of alkaline substances makes it easier for finer solid particles to be attached to the surface of larger particles (Figure 5c). Under alkaline conditions, the zeta potentials of some materials, such as quartz sands and kaolinite particles, tend to increase with increasing pH value [23]. The potential energy is the sum of the repulsion and the attraction components, indicating an increase in the thickness of the adsorption layer [24]. This increase can be attributed to the increase or decrease in the repulsive force between the solid matrix and fine suspended particles under the actions of the HCl or NaOH solution [25,26]. In general, the solid

particles of silty soil (Figure 5b) are larger than those of red mud (Figures 6 and 7), indicating the presence of a small percentage of fine particles between larger particles.

As mentioned in Section 3.2, there will be an obvious change in the specific surface area of the Shanxi silty soil when it is immersed in the HCl or NaOH solution. This outcome can be attributed to the formation of amorphous substances due to the chemical reaction of silt particles in the HCl, but it is possible that a porous product is simply formed, which are present in a suspended state (Figure 5a). On the contrary, it is obvious that the amorphous substance is recrystallized into well-crystallized compounds in alkali (i.e., NaOH solution; Figure 5c), which is obvious in the Shandong red mud in Figure 7c.

A comparison between Figures 6 and 7 shows a significant difference in microstructures between the Shanxi red mud and Shandong red mud. For the Shandong red mud, the solid particles tend to be smaller and more uniform, whereas those of the Shanxi red mud are slightly larger and filled with finer solid particles. However, solid particles immersed in a 4 mol/L HCl solution become more cloudy compared with those immersed in a 4 mol/L NaOH solution, and the formation of red mud agglomerates under acid neutralization can also be seen from the SEM images (Figures 6 and 7). In fact, the morphological structure of untreated red mud indicates scattered fine particles. The HCl solution results in the occurrence of chemical reactions among the solid particles and between the solid particles and pore water in the red mud and consequently the formation of new amorphous chemical substances and an increase in muddiness.

Overall, acid neutralization results in an increase in the aggregation and uniform distribution of red mud particles, which promote the formation of macroaggregates [20]. This result will increase the water permeability of the acid treated soil layer and improve the growth ability of plants.

6. Conclusions

Typical red mud in China has a high cation exchange capacity and active physicochemical properties, which can be closely related to its extremely high alkalinity and complex microstructure. The neutralization of red mud with the HCl solution results in the release of Na^+ from red mud particles into the leachate, which can effectively decrease the pH value in the filtrate. On the other hand, the migration of the red mud filtrate also causes alkalization damage to common soil (e.g., silty clay).

Red mud generally has a higher liquid limit and plastic limit but a lower plasticity index ($I_P = 4.8\text{--}18.7$) than silt ($I_P = 4.5\text{--}31.3$) under either acidic or alkaline conditions. The acid neutralization of red mud can also result in a significant decrease in the liquid limit, plastic limit and plasticity index, whereas the opposite is observed for the addition of the NaOH solution. In this sense, the neutralization of acid can significantly improve the cementation property of red mud. In addition, the specific surface area of red mud immersed in the NaOH solution decreases, whereas that immersed in the HCl solution increases. For instance, the specific surface area of the Shandong red mud immersed in the HCl solution is increased by 2.64 times, whereas that of the Shanxi red mud is increased by 1.55 times. That is, neutralization can also improve the growth ability of plants, which has good engineering significance for soil restoration.

It is no longer acceptable to classify red mud according to the standards obtained based on common soils with low ion concentrations and neutral pH values, and it is necessary to establish more appropriate standards for the classification of red mud based on its particular physicochemical and microstructural properties.

Author Contributions: Conceptualization, Q.N. and B.B.; methodology, B.B. and Q.N.; investigation, Y.L.; data curation, G.W.; writing—original draft preparation, B.B.; writing—review and editing, B.B.; supervision, Q.N.; project administration, Y.L. and G.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Beijing Natural Science Foundation (No. 8182046) and the National Natural Science Foundation of China (51678043; 51878035).

Conflicts of Interest: The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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