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Research Paper

Basic characteristics and resource utilization of red mud

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ABSTRACT

Red mud is the solid waste produced during the production of aluminum oxides. China is a major producer of aluminum oxides. At present, China has a low utilization of the resource of red mud. Large piles of red mud have posed numerous negative effects on the environment. It is of great significance to explore the effective ways to deal with red mud and construct ecological environment. In this study, the physical properties, hazardous properties, radioactivity and stress-strain relations of red mud are introduced. Based on previous researches, the resource utilization in remediation of heavy metal contaminated soil, treatment of heavy metal wastewater, extraction of valuable metals and preparation of building materials are reviewed. Experiments have proven the feasibility of the red mud to replace part of the cement in the preparation of road base material, which provides some guidance for the utilization of red mud.

Key words: Red mud, resource utilization, solid waste.

INTRODUCTION

Red mud is a solid waste discharged from aluminum oxide production by aluminum plants. China has accumulated 400 million tons of red mud that exceed any other country. At present, most of the red mud is treated by open storage (Qi, 2007), which does not only occupies or consumes large amounts of land, but also causes environmental problems such as dust and groundwater contamination (Smith, 2009; Nan, 2009; Rout et al., 2013; Olszewska et al., 2016).

In recent years, red mud has been studied by both domestic and foreign scholars. Chen et al. (2004) explored the relationship between red mud structural properties and its strength-deformation properties through a consolidated drainage triaxial shear test, and proposed structural quantitative parameters. Wang et al. (2005) believed that the hydration of red mud mainly produces hydrated dicalcium silicate and calcium carbonate, and its strength is mainly dependent on the hydration of mineral components such as dicalcium silicate and the carbonization of hydroxides. Liu et al. (2016) analyzed the influence of water content on the mechanical properties of red mud based on unconfined compressive strength test, consolidated drainage triaxial shear test, and the cyclic experiment hydraulic characteristics. They found that Bayer red mud is very sensitive to water and is significantly reduced in its strength. It is even disintegrated and may lose its bearing capacity. Xue et al. (2017) described the research progress of alkaline regulation of red mud from the perspective of chemistry and biology, summarized the mechanism of alkaline conversion of red mud, and proposed the development direction for alkali removal of red mud. Liu and Wu (2012) reviewed the composition and basic characteristics of red mud, emphasized the importance of red mud storage yard design and operation safety, and proposed that using red mud as a building material and filling material is an effective means of dealing with red mud. The prospects of red mud as an environmental restoration material are anticipated.

Combining the results of previous studies and the author's research, this article introduces the physical properties, hazardous characteristics, radioactivity and stress-strain relations of red mud, and reviewed the resource utilization in remediation of heavy metal-contaminated soil, treatment of heavy metal wastewater, extraction of valuable metals, and preparation of building materials. Experiments prove

Table 1: Basic physical indexes of red mud.

Parameter	Specific gravity of soil G_s	Liquid limit ω_L(%)	Plastic limit ω_P (%)	Plasticity index I_p	Cohesion c (kPa)	Internal friction angleφ(°)
Red mud	2.70	27.2	17.2	10.0	10.7~29	7.2

Table2: Main chemical compositions of red mud.

Chemical constituents	SiO_2	Al_2O_3	CaO	Na_2O	Fe_2O_3	TiO_2	MgO	Others
Percentage content (%)	26.80	24.03	15.58	7.15	6.96	3.42	1.22	14.84

Table 3: Leaching toxicity of excess heavy metals in red mud.

Heavy metal ions	Pb	Cr	Cd	Ni	Be	As	F^-
Contents in the red mud (mg kg^{-1})	86	240	6	64	4.97	8.88	1275
Leach concentration limit (mg L^{-1})	5	15	1	5	0.02	5	100
Leaching concentration (mg L^{-1})	0.0018	0.0134	0.000166	0.000326	0.000084	0.023	7.86

the feasibility of the red mud to replace part of the cement in the preparation of road base material. It has certain reference significance for the comprehensive utilization of red mud.

THE BASIC CHARACTERISTICS OF RED MUD

The physical properties of red mud

The basic physical parameters of the samples extracted from the red mud storage yard of an aluminum company in Lvliang, Shanxi, are shown in Table 1. The mechanical properties are close to the silt. The chemical composition is shown in Table 2. It can be seen that the red mud contains more Al_2O_3, SiO_2, and CaO and belongs to the Bayer process.

The hazardous properties of red mud

As a type of solid waste, the hazards of red mud including toxicity, corrosion, flammability, reactivity, and infectivity should be identified according to the "Identification standards for hazardous wastes General specifications"(GB 5085.7-2007):

(**1) Toxicity:** according to the "Solid waste-Extraction procedure for leaching toxicity-Sulphuric acid and nitric acid method" （HJ/T 299-2007, the leachate of the red mud was collected and detected by an inductively coupled plasma spectrometer to obtain leaching concentrations of super-elements such as Pb, Cr, Cd, Ni, Be, As, and F- in the red mud (Table 3). It can be seen that the above elements in the red mud leachate are far from the concentration limits specified in the "Identification standards for hazardous wastes-Identification for extraction of toxicity" (GB 5085.3-2007), indicating no leaching toxicity.

(2) Corrosion: According to the "Identification standards for hazardous wastes-Identification for corrosivity"(GB 5085.1-2007), the pH value of the red mud leachate was 10.1, which is less than the pH value of 12.5. This indicates that it is not corrosive, according to the "Solid waste-Glass electrode test-Method of corrosively" (GB/T 15555.12-1995) .

(3) Other **aspects:** Red mud obviously has no dangerous characteristics such as flammability, reactivity and infectivity. Therefore, although the red mud used in this test is industrial solid waste, it is not an hazardous waste.

Radioactivity of red mud

According to the "Standard test method for leachability of low and intermediate level solidified radioactive waste forms"(GB/T 7023-2011), the external exposure index of the red mud is 2.72 which is less than 2.8. According to the "Limits of radionuclides in building materials"(GB 6566-2010), it belongs to decoration materials Class C and can be used for exterior decoration of buildings and for outdoor purposes.

Stress-strain relationship of red mud

The stress-strain curve of a red mud specimen with a size of Φ×H=50 mm × 50 mm can be divided into three stages shown in Figure 1. In the initial stage, with the increase of displacement, the magnitude of load increase is relatively

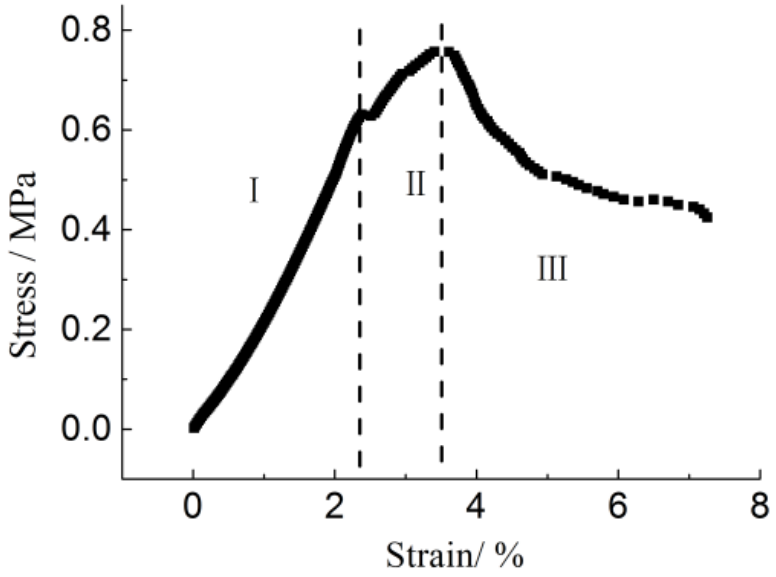

Figure 1: Stress-strain curve of red mud.

slow, and the specimen is gradually compacted to approach the elastic deformation. During the continuous loading stage, as the displacement increases, the load increases rapidly, small cracks appear in some weak parts of the sample, the porosity in the sample decreases, the density increases. Thus the crack continues to expand when the load reaches maximum gradually. At the softening stage, the cracks in the specimen continue to expand and its crack width gradually increases. The structure of the specimen is destroyed, the load decreases rapidly with increase in displacement, and has obvious strain softening characteristics.

RESOURCE UTILIZATION OF RED MUD

Restoration of heavy metal contaminated soil

With the rapid development of industry, the phenomenon of excessive acidification and heavy metal content in soil is very common in China. Curing/stabilization technology is a more commonly used method for the treatment of contaminated soils. The solidification of the contaminated sites with red mud in combination with lime, fly ash, zeolite, and other materials has achieved significant results. Yang et al. (2013) analyzed the curing progress of heavy metal ion in detail and compared the absorption of red mud to different heavy metal ions with that of other adsorbents. The results showed that red mud had better adsorption performance, as is shown in Table 4. Wang et al. (2016) used microwave hole-making techniques to modify the red mud, and analyzed the micro-characteristics before and after modification by scanning electron microscopy and X-ray diffraction. The results showed that the activated red mud has more pores and better adsorption. Gray et al. (2006) studied the effect of red mud and lime on the concentration of different heavy metal ions in the soil, and found that red mud had a significant adsorption effect on Zn, Cd, Ni and other ions when the amount of red mud was 5%. Zhu et al. (2016) studied the adsorption of cadmium ions in solidified contaminated soils of red mud and zeolite mixed materials. The results showed that the best curing effect of cadmium ions can be achieved when the amount of red mud mixed is 5%. Lv (2015) used red mud and cement to solidify arsenic slag. The study showed that as the cement content and the amount of red mud increased, the As leaching concentration of the solidified body decreased, and the solidification effect of the red mud-cement on As was the best when the red mud content was 30%. Gray et al. (2006) conducted a pot experiment and a study on the solidification of heavy metal contaminated sites with red mud and lime. The results showed that red mud and lime can be used to restore the acidic soils with heavy metal pollution. The restored land can re-grow vegetation. Therefore, the addition of red mud can effectively reduce the leaching concentration of heavy metals in the soil and is conducive to the growth of vegetation. It also reduces the risk of pollution of groundwater by heavy metal ions at contaminated sites and is conducive to environmental protection and personal safety.

Treatment of heavy metal industrial wastewater

Water pollution is harmful and difficult to treat for a long time. Its main sources are industrial and agricultural

Table 4: Adsorption capacities of red mud and other adsorbents on heavy metals.

Heavy metal ions	Adsorbent	Adsorption (mg/g)	Heavy metal ions	Adsorbent	Adsorption (mg/g)
	Red mud	105		Red mud	389.6
	Fly ash	0.089		Fly ash	18
Cd(Ⅱ)	Clay	39.5	Pb(Ⅱ)	Clay	19.5
	Corn stalk	39.56		Rice shell	120.48
	Peanut shell	36.96		Sawdust	9.78
	Red mud	63		Red mud	160.55
	Fly ash	7		Fly ash	0.031
Cu(Ⅱ)	Clay	31.2	Zn(Ⅱ)	Clay	13.4
	Sawdust	13.95		Peanut shell	15.6
	Peanut shell	24.32		Sawdust	17.09

wastewater and domestic sewage. The pollution components mainly include anions, heavy metal cations and organic compounds. Many researches have shown that red mud can effectively absorb heavy metals such as Pb^{2+}、Cr^{6+}、Cr^{3+}、Cd^{2+}、and Cu^{2+} in aqueous solution. Gupta et al., (2011) used hydrogen peroxide to treat the red mud, and then studied the effect of activated red mud on the removal of Pb^{2+} and Cr^{6+} heavy metal ions. The results showed that activated red mud can effectively remove Pb^{2+} and Cr^{6+}, and the adsorption effect on Cr^{6+} is better. Nadaroglu et al. (2010) evaluated the ability of red mud to adsorb copper ions in aqueous solution. The results showed that red mud had better adsorption of copper ions. In a study, Chen et al. (2015) used red mud to treat Mn^{2+} and NH^{4+} in wastewater, and explored the effects of pH, temperature, red mud content, and adsorption time on the red mud sorption efficiency. The results showed that the effect of red mud absorbing Mn^{2+} and NH^{4+} is enhanced with the increase of temperature, red mud content and adsorption time. Luo et al. (2014) studied the red mud treatment of wastewater containing cadmium, and reached the following conclusion: red mud can effectively adsorb cadmium ions in sewage, and the higher the temperature, the higher the pH of the solution, the better the adsorption effect of red mud. Li and Li (2014) studied the effect of red mud on the adsorption of copper ions. The results showed that with increase in adsorption time, increase in pH, and the increase in amount of red mud, the adsorption capacity of red mud to copper ions will increase. In summary, the addition of red mud can effectively remove heavy metals and organics from wastewater. However, special activation treatment is generally required for the addition of red mud and the process is complicated.

Extraction of metal elements

Red mud contains many elements such as aluminum, iron, titanium, vanadium, and niobium. These elements can be extracted after a certain process, which can effectively improve resource utilization, and is an important way in the production of additional products of red mud. Sun (2008) employed the dealkalization of lime to reduce the alkalinity of red mud, and then extracted germanium and titanium from the red mud. The extraction rate was up to 90 and 95%. Smirnov and Molchanova (1997) used a composite resin material to recover elements such as antimony and uranium from red mud slurry, developed ion exchange technology in red mud, and looked forward to its industrial development prospects. Agatzini-Leonardou et al. (2008) found that the efficiency of recovery of titanium from red mud reached 64.5%. Ujaczki et al. (2017) studied the efficiency of extraction of rare earth elements from red mud under different extractant conditions. Based on the sum of economic values of the extraction, the highest rare earth efficiency will be generated under hydrochloric acid conditions, and it is suggested that red mud can be the second sources to be used as a key raw material. However, the extraction of valuable metals from red mud is limited due to its complicated process and high cost.

Manufacturing building materials

The effect of red mud on the performance of ordinary portland cement was studied by Sutar et al. (2016), and the mechanism of red mud was analyzed by scanning electron microscope and X ray photoelectron spectroscopy. The results showed that the incorporation of red mud could promote the hydration process of cement, improve the strength of concrete. Also, they pointed out that red mud could be used as filling material instead of ordinary portland cement. The replacement rate was 20%. Nevin and Vahdettin (2000) used sintered red mud to produce ceramic glazed tiles, which changed the traditional ceramic raw materials, reduced the cost for the production of glazed tiles, and also achieved the goal of environmental protection. Senff et al. (2014) used red mud to prepare cement, explored the performance and durability of cement and found that the exothermic peak was lower than that of

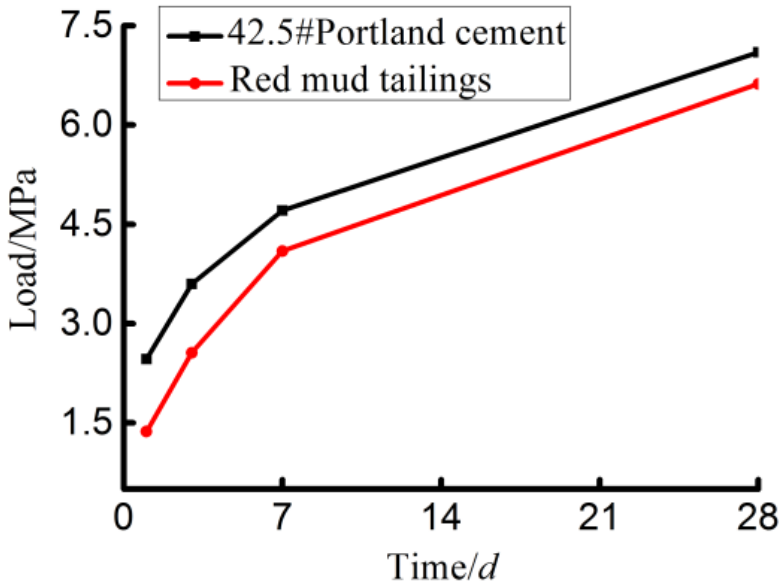

Figure 2: Change in strength of the hardened samples with curing time.

cement. Zhu et al. (2010) prepared filler materials based on red mud and found that they have higher strength and good mechanical properties. Figure 2 shows the compressive strength of cementitious materials replaced by Portland cement and red mud. There is little difference, therefore red mud can be used instead of cement as a cementitious material. Yang et al. (2006) conducted researches on red mud used in non-fired bricks and compared cement bricks made from red mud, fly ash, and ore slag as the main raw materials. The results show that the red mud bricks can meet the requirements of the national standard MU15. According to the test results shown in Figure 2, the red mud building materials belong to the Class C, which can be applied to the exterior of buildings and can be used for outdoor purposes.

Preparation of road base materials

The use of red mud to replace part of the cement to form a road base layer has the obvious advantages of reducing costs and consuming large amounts of industrial solid waste. Using the above-mentioned red mud, loess, and 42.5# ordinary Portland cement as raw materials, with the ratio of red mud, cement, loess of 0:5:100 and 15:5:100 respectively, the samples of Φ×H=50mm×50mm are produced. After demoulding, they are kept in the curing tanks for 6, 13 and 27 days, respectively. The unconfined compressive strength is tested after they are taken out and soaked in the water tank for a day.

Figure 3 shows the variation curve of the unconfined compressive strength of solidified soil with different red mud contents with curing age. It can be seen that with the increase of age, the unconfined compressive strength of solidified soil shows an increasing trend. The changing process of the unconfined compressive strength of solidified soil with curing age is divided into two stages, namely t<14 d, which is the first stage. At this time, with the increase in curing age, the unconfined compressive strength of the solidified soil increases rapidly. t> 14 d is the second stage. At this stage, as the curing age increases, the unconstrained compressive strength of solidified soil increases slowly, but it still maintains the increase of strength. This shows that as the age increases, the red mud cement generates more hydrates and fills the pores between the soil particles, which increases the density of the soil and the strength.

At the same time, it can be seen that when 15% red mud is incorporated, the unconfined compressive strength of the solidified soil is significantly higher than that of the solidified soil without red mud. At 7 days, the unconfined compressive strength of the solidified soil without red mud is only 1.6 MPa, and the unconfined compressive strength of the solidified soil mixed with 15% of red mud reaches 2.7 MPa, which fully satisfies the requirements of road base material strength. At 28 days, the unconfined compressive strength of the solidified soil without red mud is 2.6 MPa, and the unconfined compressive strength of the solidified soil mixed with 15% of red mud reaches 3.5. This shows that the incorporation of red mud effectively increases the strength of the solidified soil, and reduces the use of cement, thereby reducing costs.

Conclusions

(1) The physical properties of red mud are close to those of silt, and the stress-strain relationship is softened. Red mud

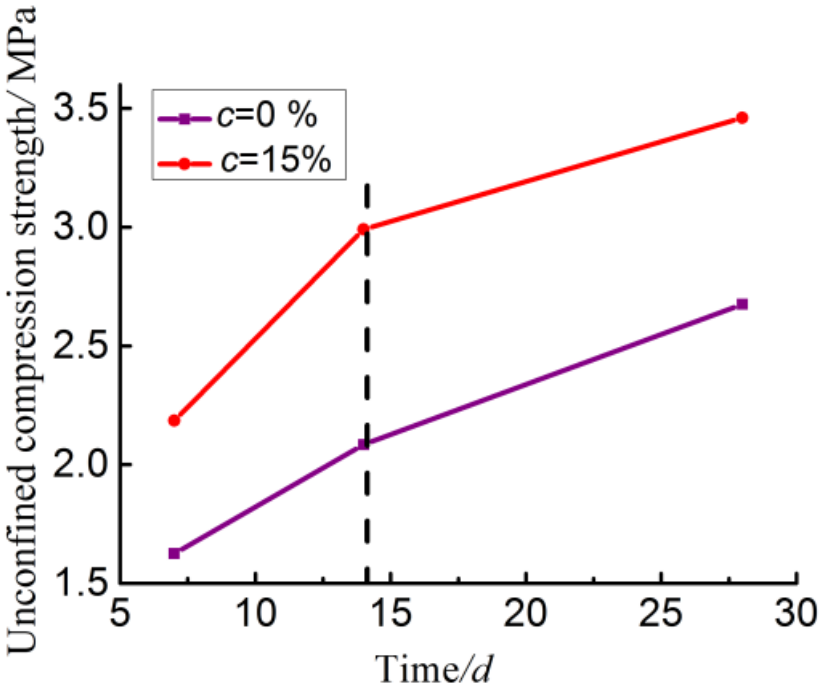

Figure 3: Unconfined compressive strength of stabilized soil with different curing time.

does not have the dangerous characteristics such as leaching toxicity, corrosiveness, flammability, reactivity and infectivity; therefore, its building materials are decoration materials Class C, which can be used for exterior decoration of buildings and for other outdoor uses.

(2) As a solid waste of industry, red mud can be used as a resource to treat waste. It is mainly used to restore heavy metal contaminated soil, treat heavy metal industrial wastewater, extract valuable metals, make building materials and so on. It has a great prospect. The development in the technology of dealing with red mud will be an important research direction in the future.

(3) The addition of red mud can effectively improve the unconfined compressive strength of the cement solidified soil, fully meet the requirements of the base of the road, and reduce the use of cement, thus lowering the cost of the project.

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