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Strength properties of geopolymers derived from original and desulfurized red mud cured at ambient temperature

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HIGHLIGHTS

- Utilizing original and desulfurized red mud for geopolymer preparation was explored.
- The high alkalinity of original red mud contributes to the formation of geopolymer.
- Na_2SO_4 could increase the pH value and accelerate the dissolution of fly ash.
- A potential synergy among alumina, power plant, and geopolymer industries exists.

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ABSTRACT

This study investigated the feasibility of using red mud derived from the Bayer process in alumina industry to make geopolymer cured at ambient temperature. Two types of red mud were used: the original one and the one after desulfurization of flue gas from coal-burning power plant. The red mud and class C fly ash were mixed at a constant ratio of 50:50 with additional alkaline solution, cured at ambient temperature, and tested for the strength properties at different ages. The geopolymers derived from red mud before and after flue gas desulfurization (FGD) obtained a compressive strength of 15.2 MPa (2.5 M NaOH) and 20.3 MPa (3.5 M NaOH), respectively. The high alkalinity of original red mud was found to contribute to the formation of geopolymer, but additional NaOH solution was needed to achieve a desirable strength. The higher strength of geopolymer made with red mud after FGD was attributed to the effect of Na_2SO_4, which was the reaction product of NaOH and flue gas. As an activator, Na_2SO_4 could increase the pH value, accelerate the dissolution of fly ash under alkaline environment. The results from this study indicate a potential synergy among alumina, power plant, and geopolymer industries.

1. Introduction

Red mud, the industrial waste from the alumina/aluminum industry, has been continuously produced since the inception of the aluminum industry in the late nineteenth century. It is estimated that the global red mud residue reached 2.7 billion tons in 2007 with an annual increase of 120 million tons [1]. The huge amount of red mud has raised significant environmental concerns, making it urgent to develop and implement improved means of storage and remediation, and to pursue large-volume utilization options of red mud as a toxic industrial waste product. Until now, most of red mud has been simply stored into huge ponds as a waste by-product. However, due to an excessive amount of alkaline solution used for the extraction of alumina by the Bayer process, red mud is characterized by high alkalinity, leading to potentially environmental problems in soil and groundwater pollution. One previous research investigated the mineralogical changes due to long-term carbonation of the red mud slurry, and it was found that the carbonation is indeed a slow process and the high alkalinity can remain on the time scale of decades [2]. One potential and promising way of reducing alkalinity is to utilize red mud for flue-gas desulfurization (FGD), a pollution control process required for the removal of sulfur oxides in coal-fired power plants to reduce air pollution [3,4]. After FGD, the high alkalinity of red mud is neutralized by the acidic flue-gas, alleviating the

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potentially hazardous environmental issues. But still, large-volume utilizations such as in civil engineering applications are necessary to exploit any potential benefits of the red mud after the desulfurization.

Recently, an innovative material, geopolymer, may reveal the direction for the large-volume utilization of red mud. Geopolymer is a special cementitious material that has the potential to be an alternative to the Ordinary Portland cement (OPC). Unlike the mechanism of hydraulic reaction of OPC, geopolymer requires an alumina silicate material (such as fly ash, slag) and an alkaline reagent (such as sodium or potassium hydroxide) as source materials to react and form an inorganic polymer-like structure, which can serve as a binding material [5]. The rising interest in geopolymer is mainly due to the ongoing emphasis on sustainability: Production of OPC is energy-intensive and releases a significant volume of carbon dioxide (CO_2) to the atmosphere, whereas the production of geopolymer may only create one fifth to half volume of CO_2 comparing to the same production of Portland cement [6]. Geopolymers also have many advantages over OPC such as high strength, high temperature resistance and acid resistance. However, previous studies demonstrate that a temperature threshold may exist for the Class F fly ash based geopolymers [7], and a widely accepted temperature range for the successful curing of geopolymer is between 50 and 80 °C, which is much higher than ambient temperature and thus may impede the utilization of geopolymer as a construction material [6].

An economic evaluation reveals that the most costly factor in geopolymer production is the supply of alkaline reagent. Since red mud is highly alkaline and contains both alkalis and aluminates, it has the potential to be utilized into geopolymer production. Several researchers have attempted to use red mud for geopolymer materials in many ways, including red mud with thermal pretreatment, mixing red mud with rice husk ash or fly ash, etc. [8–14]. The product after FGD was also used as a source material for geopolymer preparation in previous study [4].

The objective of this paper is to explore the possibility of utilizing red mud before and after FGD as a source material for the production of geopolymers cured at ambient temperature. The setting time, compressive strength and failure strain of the geopolymer materials were tested in the laboratory, and the composition and microstructure were characterized by X-ray diffraction (XRD), electron microprobe (EMP) and scanning electron microscopy (SEM). The mix proportions of geopolymer materials were optimized and evaluated based on the test results.

2. Materials and background

2.1. Flue gas desulfurization using red mud

The red mud both before and after the process of FGD were used as a source material for making geopolymer in this study. Among the key properties of red mud produced as a waste by-product from the Bayer process, its high alkalinity provides the potential for flue-gas desulfurization applications, a pollution control process required for the removal of sulfur oxides in coal-fired power plants to reduce air pollution. Giving that the aluminum industry consumes a large amount of electricity, which is typically generated on site in aluminum production facilities, it is beneficial to use alkaline red mud waste as an acid-absorbing agent in the desulfurization of flue gas produced from coal-burning power plant.

In a separate study by the authors, the reactivity of red mud with sulfur dioxide (SO_2) as the primary contaminant of flue gas from coal combustion was characterized with both kinetic and stoichiometric testing in laboratory-scale reactors under specific process conditions including pH, red mud concentration, and SO_2 loading. Red mud slurry was used in FGD. After 20 cycles of FGD, the red mud was dried and prepared as a source material for geopolymer as shown in Table 1.

2.2. Materials

Both dried red mud before and after FGD (named RM1and RM2, respectively, in the study) from Xinfa Group, Shandong, China, were used as raw materials for geopolymer synthesis. Class C fly ash (named FC) and Class F fly ash (named FF) were also used as another raw material (Charah, Inc.). Sodium hydroxide (NaOH) (Sigma-Aldrich Co.) and deionized water were used to make the alkaline reagents with varying concentrations. Both types of red mud were pulverized and passed a No. 50 sieve to minimize the influence of compositional variation.

2.3. Methods

A previous study reveals that the geopolymers with a higher red mud/fly ash ratio tend to be weaker than those with a lower ratio (80:20, 50:50 and 20:80) [9]. However, large-volume utilization of red mud is the purpose of this study. Basing on previous researches, the raw materials, red mud (RM1 or RM2) and fly ash (FC or FF), were mixed at a predetermined weight ratio of 50:50 for 10 min. Then the alkaline solution was added to the powder mixture and stirred for another 10 min. In this study, seven different concentrations of alkaline solution from 0 to 6.5 mol were employed in making geopolymer to determine the optimal concentration. In general, a lower solution/solid ratio results in a higher strength and less volume change for the formed geopolymer. It is also beneficial on the economic aspect because the alkaline solution costs the most. However, a very low solution/solid ratio may cause issues in mixing uniformity and workability. Different solution/solid ratios were tried and a fixed solution/solid ratio of 0.5 was selected due to the workability of red mud for all the geopolymer in the study. The geopolymer mix was then poured into plastic molds with an inner diameter of 2.5 cm and a height of 5 cm, followed by curing at an ambient temperature of 20 °C for 24 h. After that the specimens were demolded and continued to cure in the same environment. The geopolymer specimens were tested for unconfined compressive strength at 3, 7, 14, 21, and 28 days at a constant loading rate of 0.5%/min using a Material Testing System (MTS).

In order to investigate the effects of chemical compositions and microstructure of geopolymer on its strength, X-ray diffraction (XRD), scanning electron microscope (SEM) and electron micro-

Table 1
Chemical Constituents of raw materials, wt%.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	SO_3
FC	44.41	18.79	10.01	18.59	0.89	3.03	1.44	1.81
FF	43.16	22.80	23.60	3.29	0.75	0.73	1.62	1.20
RM1	25.58	26.40	23.26	1.33	14.98	0.15	0.21	0.80
RM2	26.15	27.23	23.98	1.13	11.45	0.17	0.23	2.73