



# Durability of red mud-fly ash based geopolymer and leaching behavior of heavy metals in sulfuric acid solutions and deionized water



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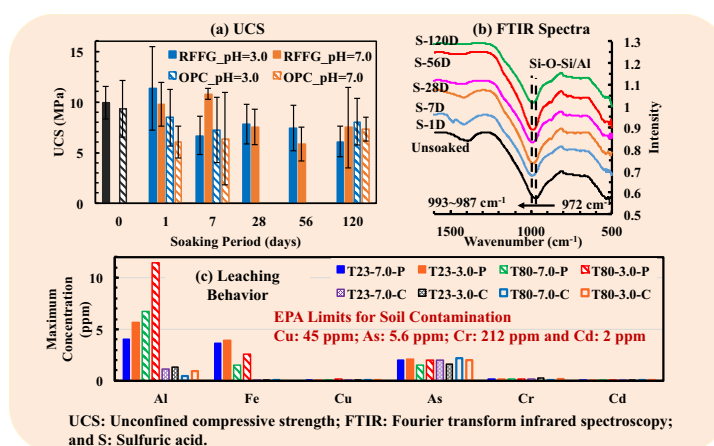
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## HIGHLIGHTS

- RFFG showed comparable resistance against low pH sulfuric acid to OPC.
- Depolymerization and dealumination were the main reasons for RFFG's mechanical deterioration.
- The concentrations of leached heavy metals in RFFG were lower than respective EPA limits.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The durability and heavy metal leaching behavior of red mud-class F fly ash based geopolymers (RFFG) were investigated in this study. RFFG specimens were soaked in sulfuric acid solutions (pH = 3.0) and deionized water (pH = 7.0) for 1–120 days, and then their remaining mechanical properties and the change in the microstructures were characterized with unconfined compression tests, three-point bending tests, scanning electron microscopy, X-ray diffractometer and Fourier transform infrared spectroscopy, respectively. The leaching behavior of heavy metals in RFFG samples after soaking up to 14 days was also examined with atomic absorption spectroscopy. The RFFG samples' resistance against sulfuric acid was comparable to the ordinary Portland cement (OPC), and their mechanical degradation was mainly attributed to the depolymerization and dealumination of geopolymer gels. The highest concentrations of the heavy metals leached by the sulfuric acid from the RFFG samples were much lower than the respective US EPA limits for soil contamination.

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## 1. Introduction

Geopolymer is a type of aluminosilicates with an amorphous or semi-crystalline framework. The geopolymeric structures are con-

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stituted with three basic repeated units: poly-sialate (PS,  $-\text{Si}-\text{O}-\text{Al}-$ ), poly-sialate-siloxo (PSS,  $-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Al}-$ ), and poly-sialate-disiloxo (PSDS,  $-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Al}-$ ) [1], which are formed via the polymerization of silicate and aluminate tetrahedrons. The molecular structure of geopolymer is simplified as  $M_n\{(\text{SiO}_2)_z - \text{AlO}_2-\}_n$ , where  $z$  is the Si to Al ratio, ranging from 1 to 3 for cementitious geopolymer,  $n$  is the degree of polycondensation and  $M$  is an alkali cation, such as sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ), which balances the negative charge of the geopolymeric network introduced by  $\text{Al}(\text{OH})_4^-$  [1].

Geopolymers are synthesized by activating Si- and Al-rich raw materials with alkali hydroxide and/or alkali silicate solutions at ambient or slightly elevated temperatures. In recent years, geopolymers have been successfully synthesized with many silicate and aluminate rich materials, including metakaolin [2–4], natural aluminosilicate minerals [5,6], fly ash [7–10], granulated blast furnace slag [11,12], red mud [13,14], rice husk ash [13] and palm oil fuel ash [15,16], most of which are industrial wastes. Because of their high mechanical strength, low energy consumption and low  $\text{CO}_2$  emission during the production process, geopolymer becomes a promising sustainable alternative to ordinary Portland cement (OPC). Given the massive demand for cement in the construction industry, geopolymerization technology also provides an effective way to recycle and reuse various industrial by-products (e.g., fly ash, red mud, etc.).

Red mud (RM), also known as bauxite residue, is the main byproduct of the Bayer process for extracting aluminum from bauxite ores. The inventory of RM was staggering 2.7 billion tons by 2011 and is growing at a rate of 120 million tons per year [17]. The NaOH solution used in the Bayer process results in a high water content and a high alkalinity for RM, which has a pH value of  $11.3 \pm 1.0$ . In addition, RM is known to contain substantially elevated levels of several trace and toxic metals native to many bauxite ores, including iron, manganese, copper, zinc, cadmium, lead, chromium, and nickel [17]. These characteristics make it difficult for alumina refineries to safely dispose of and treat RM. So far few safe and economical large-scale applications of RM have been available. Currently, RM is disposed of into on-site waste lakes for further dewatering, consolidation and storage, which is very costly due to mandatory environmental monitoring and long-term maintenance. On the other hand, high Si and Al contents in RM make it a suitable raw material for geopolymerization. Due to its high alkalinity, RM can partially replace alkali hydroxide, one of the most expensive raw materials used in geopolymer synthesis.

Fly ash is one of the main byproducts from coal-fired power plants, which is classified as class F and C fly ashes according to the ASTM C618 [18,19]. Class F fly ash (FFA) is produced by the combustion of bituminous coals or anthracites. Its main chemical constituents are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , with their total amount around 70 wt%, while CaO is less than 20 wt%. Class C fly ash (CFA), containing 50–70 wt% of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  and more than 20 wt% CaO, is the residue from burning sub-bituminous coals and lignites. Both FFA and CFA contain trace amount of heavy metals, such as As, Cd, Co, Cr, Pb, Sb and Zn [20]. The annual production of fly ash is 900 million tons globally [21] that makes its disposal a great challenge. Because of its high content of amorphous silicates and aluminates, fly ash is one of the most widely used raw materials for synthesizing geopolymer. More recently, geopolymer with comparable strengths to OPC has been successfully synthesized with a mixture of fly ash and RM [14,22,23]. In a previous study by the authors, the effect of the chemical composition of raw materials and curing conditions (e.g., temperature, humidity, and time) on the mechanical properties and microstructure of RM-FFA based geopolymers (RFFG) was systematically studied [14]. Based on the authors' previous work [14], the RFFGs with a

high mechanical strength were synthesized from FFA and RM at nominal molar ratios of  $\text{Si}/\text{Al} = 2.0$  and  $\text{Na}/\text{Al} = 0.6\text{--}0.8$  and cured at ambient conditions (e.g., temperature of  $\sim 23^\circ\text{C}$  and relative humidity of 40%–50%).

The durability of geopolymer has been evaluated to ensure its long-term performance in engineering applications, such as the resistance to acid attack [24–28], alkaline silicate reaction [29–31], and freeze and thaw cycles [32,33]. Particularly, the resistance of geopolymers to sulfuric acid has been examined due to the frequent exposure of concretes to acid rain [34], sewage [35,36] and sulfur-rich soils [37]. Palomo et al. [38] and Ariffin et al. [39] found that metakaolin- and blended ash-based geopolymers had better acid resistance than OPC, based on their remaining compressive and flexural strength after soaking in 2% and 0.001 M sulfuric acid (pH = 2.75). Allahverdi and Skvara [25,26] and Bakharev [27] examined the deterioration mechanisms of fly ash based geopolymers in sulfuric acid by measuring mass, microstructural, and mechanical change after soaking in various pH value conditions. Thokchom et al. [28,40] assessed the effect of  $\text{Na}_2\text{O}$  concentration on the resistance of fly ash based geopolymers to sulfuric acid. The aforementioned studies indicated that the depolymerization and dealumination of geopolymer gels are the primary reasons for the degradation of mechanical properties after sulfuric acid attack. Nonetheless, the majority of these studies were conducted on metakaolin and fly ash based geopolymers. With the participation of RM in the geopolymerization, the durability of the derived geopolymers may be different, and thus the resistance of RFFG to sulfuric acid requires a systematic investigation.

In addition, to assess the contamination risk of geopolymer to surrounding soils and its suitability of immobilizing toxic metals, the leaching behavior of geopolymers synthesized from different raw materials was investigated [41–46]. Álvarez-Ayuso et al. [44] studied the leaching behavior of fly ash based geopolymer in deionized water, and found the leaching ability of metals depended on the type of chemical elements, feature of the geopolymer samples (ground or monolithic) and fly ash sources. Aly et al. [41] examined the leaching ability of Cs, Sr, Na and Al from metakaolin based geopolymer powder in deionized water, where a small amount of Cs and Sr were added in the geopolymers. They found that Cs and Sr were well and partly bound with geopolymers, respectively; and the leaching ability of Na was much higher than Al, which was leached from both geopolymer gel and residual alkali solution. By conducting the leaching tests on fly ash-slag based geopolymer in deionized water, Izquierdo et al. [43] found that geopolymers can provide an efficient encapsulation for heavy metals once the dosage, synthesis and curing conditions were well tailored for the synthesis of geopolymers. Ahmari and Zhang [47] found that heavy metals can be efficiently immobilized by mine tailings based geopolymer. Based on the microstructural analysis, they attributed the leaching of metals by the acid and alkali partially to the dissolution of geopolymers.

Due to the heavy metals present in RM and FFA, it is important to study their leaching behavior in RFFG samples while being exposed to sulfuric acids. Since there is no unified definition for heavy metals, only those specified in the US EPA regulations and present in the raw materials of RFFG samples, including Cu, Pb, Cr, Cd, As, and Fe, were considered in this study. In addition, the leaching behavior of Al was monitored to shed light on the underlying mechanisms of dissolution of geopolymer gels in water and sulfuric acid. In this study, RFFG samples were soaked in a sulfuric acid solution of pH 3.0 and deionized water of pH 7.0 for 1–120 days. Unconfined compressive strength, Young's modulus, failure strain and flexural strength of the soaked samples were measured and compared with the unsoaked counterparts and the OPC control samples. The soaked samples were also characterized

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