**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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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 ($\text{pH} = 3.0$) and deionized water ($\text{pH} = 7.0$) 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.

39 Graphic Abstract

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43 **Key Words:** Geopolymers, Red mud, Fly ash, Sulfuric acid resistance, Leaching

44 behavior, FTIR, Chemical Bonds, Mineralogy.

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1. Introduction

Geopolymer is a type of aluminosilicates with an amorphous or semi-crystalline framework. The geopolymeric structures are constituted with three basic repeated units: poly-sialate (PS, $-\text{Si-O-Al}-$), poly-sialate-siloxo (PSS, $-\text{Si-O-Si-O-Al}-$), and poly-sialate-disiloxo (PSDS, $-\text{Si-O-Si-O-Si-O-Al}-$) [1], which are formed via the polymerization of silicate and aluminate tetrahedrons. The molecular structure of geopolymer is simplified as $M_n\{(SiO_2)_z - AlO_2 -\}_n$, 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 (Na^+) and potassium (K^+), which balances the negative charge of the geopolymeric network introduced by $\text{Al}(\text{OH})_4^{-1}$ [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 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 ± 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 SiO_2 , Al_2O_3 , Fe_2O_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 SiO_2 , Al_2O_3 , and Fe_2O_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 $\text{Si/Al}=2.0$ and $\text{Na/Al}=0.6\text{-}0.8$ 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 0.001M sulfuric acid ($\text{pH} = 2.75$). Allahverdi, 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 Na_2O 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 to 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 with X-ray diffractometer (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) to examine the changes in their mineralogy, microstructure, and chemical bonds, respectively. The concentration of heavy metals leached from both cylindrical and powder RFFG samples in the sulfuric acid solution and deionized water was determined using an atomic absorption spectrophotometer (AA). Furthermore, RFFG samples were cured at room temperature and 80°C to investigate the effect of curing temperature on the leaching behavior of heavy metals. As a promising alternative to Portland cement and soil stabilizer, RFFG can be frequently exposed to various soils, and thus the leached concentrations of the heavy metals in RFFG samples were compared with the corresponding limits specified in the US EPA regulations for soil contamination.

2. Materials and Methodology

2.1. Materials

FFA from Headwater Resources Inc. and RM from Alcoa World Alumina L.L.C. were mixed in a mass ratio of 4:1 to synthesize geopolymers. The soil-like RM was first dried in an oven at 100°C to remove the remaining moisture, and then ground with a kitchen mill until all the particles passed a No. 100 mesh (i.e., the opening size of 152µm) to facilitate the geopolymerization. The particle size distribution curves of RM and FFA are shown in **Figure 1**, with their median particle sizes being 1.9µm and 16.0µm respectively, and their chemical compositions are summarized in **Table 1**. The major chemical constituents in RM are SiO₂, Al₂O₃, Fe₂O₃ and CaO, and in FFA are SiO₂ and Al₂O₃. A 50 wt.% sodium hydroxide solution from Fisher Science Inc. USA, 2M sodium trisilicate solution and deionized water were mixed at a proportion of 3:7:3 to prepare the activator solution. The 2M sodium trisilicate solution was prepared by dissolving sodium trisilicate pellets from Sigma Aldrich Inc. USA in deionized water. A sulfuric acid solution of pH 3.0 was prepared by diluting 17.8 M sulfuric acid with deionized water to soak the RFFG samples in durability tests and leaching tests. Deionized water of pH 7.0 was used as another soaking solution to investigate the influence of pH value on the leaching behavior of heavy metals in RFFG samples. OPC samples were also prepared with type II cement, whose chemical composition is given in **Table 1**, as a control group to provide reference mechanical properties and sulfuric acid resistance.

2.2. Geopolymer Sample Preparation

Based on the authors' previous study, RFFG samples were synthesized at Si/Al and Na/Al molar ratios of 2.0 and 0.6, respectively, for achieving good mechanical properties [14]. Si/Al and Na/Al molar ratios were calculated with the contents of Si, Al and Na in the activator solutions and the solid raw materials. Two groups of RFFG samples were prepared using two types of molds for mechanical properties and durability testing: a cylindrical mold with an inner diameter of 40.0mm and a height of 100.0mm for unconfined compressive strength (UCS) tests and a rectangular mold with dimensions 100.0mm(L)×25.4mm(W)×17.7mm(H) for three-point bending tests. RM and FFA were mixed with the alkali activator solution for 30 minutes, casted into the molds, vibrated for 5 minutes to remove the air bubbles introduced during the mixing and cured at room temperature (~23°C) and at a relative humidity of 40%-50% for 28 days. The control OPC cylindrical samples were prepared at a cement/water ratio of 0.35 and cured at room temperature at 100% relative humidity for 28 days. For leaching tests, small cylindrical samples with a diameter of 25.4mm and a height of 63.5mm were prepared. These samples were prepared in the same way as the durability testing counterparts, and cured at room temperature and at 80°C to investigate the effect of curing temperature on the leaching behavior of heavy metals in the sulfuric acid. For the samples cured at 80°C, they were sealed in plastic bags immediately after vibration and put in an oven at 80°C for one day, and then cured at room temperature with a RH of 40%-50% for another 27 days. In addition, powder samples with a particle size less than 45 µm were prepared by grinding the cured cylindrical samples for leaching tests to examine the influence of sample size on the leaching behavior of heavy metals.

2.3. Sulfuric Acid Exposure

For the durability test, the RFFG samples were soaked in a sulfuric acid solution (pH=3.0) and deionized water (pH=7.0) at a solid/liquid volumetric ratio of 1/4 for 1, 7, 28, 56, 90 and 120 days before testing their mechanical properties. The OPC control samples were soaked in the same solutions for 1 and 7 days as short-term exposure and 120 days as long-term exposure. A pH meter was used to monitor pH values of the soaking leachate during the course of soaking. The soaking solutions were refreshed every day in the first 3 days of soaking when their pH value increased quickly, and every 7 days from the 7th day to the end of the soaking. The dimensions and weight of the soaked samples were measured to monitor their physical change during acid exposure when the solutions were refreshed. The solution on the surface of the soaked samples was wiped out with paper towels before the testing. Three replicates were used for each soaking period.

2.4. Mechanical Property Testing, SEM, FTIR, and XRD

Unconfined compression tests were conducted on the cylindrical samples (40.0mm×100.0mm) after soaking for various time periods using an Instron loading frame at a constant loading rate of 0.5 in./min for determining their UCS, failure strain and Young's modulus. The top surface of the samples was covered with a piece of cardboard to reduce the end effect on the testing results. The flexural strength of prismatic RFFG samples was measured using a three-point bending test according to the ASTM C78 [50].

The microstructures of the geopolymer samples were examined with a JEOL JSM-7000F field emission SEM in secondary electron mode. After unconfined compression tests, small pieces of the crushed geopolymer samples were selected for the SEM test. The external surfaces of the cylindrical samples, which were exposed to air and might be carbonated, were avoided for microstructure evaluation [51].

FTIR and XRD experiments were conducted on the RFFG samples after being soaked in sulfuric acids and deionized water to investigate changes in their chemical bonds and mineralogy. Chunks of the samples after the mechanical property tests were ground to powder with an agate mortar and pestle until particle sizes were less than 45 μ m. The FTIR spectra were obtained with a BrukerOptics Vetex70 FTIR spectrometer using transmittance mode in the range of 500-1600 cm^{-1} at a resolution of 2.0 cm^{-1} . The powder samples were scanned with a Rigaku Geigerflex X-ray powder diffractometer using a $\text{CuK}\alpha$ radiation with a voltage of 37.5 kV and a current of 25 mA at 1 sec/step to obtain the XRD spectra. The XRD data were collected from 6° to 70° 2 θ at 0.02 °/step and analyzed with MDI Jade 5.0.

2.5. Leaching Tests

Two types of RFFG samples were used for leaching tests: (i) small cylindrical samples (25.4mm $\times$ 63.5mm); and (ii) powder samples with a particle size less than 45 μ m, which were ground from the cured small cylindrical samples following the same procedure as the FTIR and XRD samples. The samples were soaked in the sulfuric acid and deionized water at the volumetric ratio of 1:20 [52] for 4 hours, 8 hours, 12 hours, 16 hours, 24 hours, 3 days, 7 days, and 14 days, respectively. While the powder samples

were soaked in a 50mL glass vial and rotated in a centrifuge to expedite the leaching of heavy metals, the cylinders were soaked statically to mimic practical scenarios when RFFG are used in civil engineering projects. Two replicates were used for each sample set. The leachate was collected and pressure filtered through a 0.45 μ m filter paper, and then the concentration of Cu, Pb, Cr, Cd, As, Al and Fe in the collected leachate was measured with atomic absorption spectroscopy (AA) test.

3. Results and Discussion

3.1. Changes in Physical and Mechanical Properties of Durability Testing Samples

The normalized weight of cylindrical RFFG and OPC samples with respect to the respective original values prior to soaking is plotted as a function of the soaking time, as shown in **Figure 2**. The weight of the RFFG samples increased appreciably after the first day of soaking, due to a large amount of solution adsorbed by the pores in the samples. During the soaking period of 2 to 21 days, the weight started to decrease gradually from ~1.08 times to ~1.05 times of the respective initial weight, due to the partial dissolution of geopolymers (including geopolymer gels, unreacted materials, nonreactive materials and crystals), yet no apparent visual degradation on the samples was observed. After 21 days, the weight of the RFFG samples stayed nearly constant throughout the rest of soaking period up to 120 days, implying that no further dissolution of geopolymers happened. On the other hand, the weight change of the OPC samples soaked in the sulfuric acid is different from that in the deionized water, as plotted in **Figure 2**. During the first 14 days of soaking in the acid and water, the weight of the OPC samples barely

changed. During longer soaking (i.e., >20 days), the weight of OPCs in the sulfuric acid reduced by ~2% while the OPCs in the deionized water gained about 2% weight.

UCS, Young's modulus, failure strain and bulk density of the RFFG samples after soaking for up to 120 days are presented in **Figure 3**. As shown in **Figure 3** (a), the average UCS values of the RFFGs did not decrease after soaking for one day, while the average UCS of the OPC samples reduced by about 30% and 10% after one day of soaking in deionized water and the sulfuric acid, respectively. The UCS of the RFFG samples decreased from 10 ± 1.6 MPa to 6.7 ± 1.9 MPa after soaking in the acid solution for 7 days, and maintained around 10.8 ± 0.6 MPa after soaking in the water for the same time period, where 1.6, 1.9 and 0.6 are the respective standard deviations. The UCS of the OPC samples reduced from 9.3 ± 2.8 MPa to 8.5 ± 2.8 MPa and 6.3 ± 4.6 MPa after soaking in the acid and water for 7 days, respectively. After soaking for 28, 56 and 120 days, the UCSs of RFFG samples maintained around 6-7 MPa statistically, regardless of the leachants used. This is consistent with the observation that the weight of the RFFG samples barely had further change after soaking for longer than 21 days (**Figure 2**). After the long-term soaking of 120 days in the acid, the UCS of the RFFG samples reduced by up to 30% statistically, whereas the statistical UCS loss of OPC was about 14% (from 9.3 ± 2.8 MPa to 7.3 ± 1.2 MPa). The slightly higher UCS of OPC after the long-term exposure than that after the short-term soaking might be due to low permeability of OPC, which prevented the samples from further absorbing the liquid or acid, and allowed the further development of strength during the extended curing. It should be noted that the sustained UCS values of the RFFG and OPC samples are statistically similar, although a larger strength loss occurred in the RFFG samples after exposed to the acid and deionized

water. The failure strain of both the RFFG and OPC samples increased after soaking, as demonstrated in **Figure 3** (b). The failure strain of RFFG samples increased from 2.2% to ~3.5-4.0% after soaking in the sulfuric acid for 1, 7 and 28 days, and further increased to ~5% after soaking for longer than 56 days. The change in the failure strain of the RFFG samples soaked in the deionized water was similar except that the samples soaked for 28 and 56 days had a lower failure strain. The failure strain of OPC samples increased by ~1% after one-day soaking (from 3.6% to 4.4% and 4.8% in the acid and water, respectively) and did not have any statistically significant changes after soaking for longer periods. Both the RFFG and OPC samples show an apparent decrease in Young's modulus after soaking in the acid and water, illustrating that the stiffness is affected by the acid attack more significantly compared to strength and ductility. The bulk density of the RFFG samples increased from 1.7g/cm³ to 1.9g/cm³ after one-day soaking in the sulfuric acid and deionized water due to the absorption of liquids, and decreased to 1.8g/cm³ after longer soaking. The OPC samples had a higher initial density than the RFFGs and barely showed any change after soaking, regardless of the pH values of the leachants and soaking periods. As illustrated by the unconfined compression testing results, the RFFG samples had similar durability to the control OPC samples after soaking in both the low pH sulfuric acid solution and deionized water.

The flexural strength of the prismatic RFFG samples before and after soaking in the sulfuric acid and deionized water is plotted against the soaking time in **Figure 4**. The flexural strength of the samples decreased from ~7MPa to ~4MPa after soaking for 1 day and barely reduced further statistically after soaking for longer time periods. The loss of flexural strength in the RFFG samples after 120 days of soaking is about 45%, higher

than the UCS loss (~30%), illustrating that the flexural strength of the RFFG samples is more adversely affected by the attack of acid or deionized water. This is due to the different failure mechanisms and induced stresses between three-point bending test and UCS test. For RFFG samples, their flexural strength is mainly governed by the tensile strength. Compared to compressive strength, tensile strength depends more on the binding strength of geopolymer gels. Therefore, although the deterioration of both the flexural strength and UCS of the RFFG samples during the soaking is largely attributed to the partial dissolution of geopolymer gels, the decrease in the flexural strength was larger than the UCS. In addition, the pH values of the leachants for the RFFG and OPC after one-day soaking were both greater than 11. Since residual alkaline solution remained in the samples that were easily dissolved in the soaking solutions, the dissolution of alkali from the RFFG samples can be another reason for the reduction of mechanical strength and Young's Modulus of the RFFG samples after one day's soaking. It also should be noted that the large moisture adsorption of the OPC and RFFG samples during the soaking can be another cause for the decrease of compressive strength, flexure strength and Young's modulus, since mechanical properties of the cementitious materials were inversely related to the moisture content [53-55].

3.2. Changes in Microstructure and Mineralogy of Durability Testing Samples

The SEM images of the RFFG samples before and after soaking in the sulfuric acid solution and deionized water were compared to reveal the change in their microstructure. **Figure 5** shows the SEM images of the RFFG samples soaked for 1 day because the mechanical strength decreased the most during this soaking period, and the

micro-morphologies of the RFFG samples soaked longer did not change much afterwards. In the unsoaked sample, the unreacted particles are wrapped and bound with geopolymer gels, where the pores and cavities are observed in the geopolymer matrix, as shown in **Figure 5** (a). In the samples soaked for 1 day, the particles are still bound with the gels, while those close to the cavities are loosely compacted, as the fly ash circled in **Figure 5** (b) and (c). The “geopolymer gel wrapping” appears less apparent in the soaked samples, which qualitatively implies that the leachant might have intruded in the samples through the capillary pores and dissolved the surrounding geopolymer gels. Unfortunately, a quantitative conclusion on the dissolution of geopolymer gels cannot be obtained, since neither an EDX analysis that can quantitatively distinguish geopolymer gels from fly ash nor a quantitative characterization method was available. Other than these, no apparent morphological difference is observed between the unsoaked and soaked samples.

The mineralogical change of the RFFG samples before and after soaking in sulfuric acid solution and deionized water was characterized with XRD. Since no apparent mineralogical change is observed between the RFFG samples at short soaking time intervals, only comparison among the XRD spectra of those soaked for 0, 1, 56 and 120 days is shown in **Figure 6** and **Figure 7**. The peaks of minerals in the RFFG samples did not change after the soaking, indicating that the crystalline phases in the geopolymer were not dissolved by the leachants. However, the hump between 17° - 38° 2θ , which is the characteristic XRD pattern of amorphous geopolymer gels, shifted to 15° - 32° 2θ after the first day of soaking. This shift implies the partial dissolution of geopolymer gels in the sulfuric acid. This hump gradually narrowed to 15° - 30° 2θ after 56 days of soaking, and showed a decrease in intensity after soaking for 120 days, as illustrated by the

enlarged view in **Figure 6** (b). The XRD spectra of the RFFG samples soaked in the deionized water followed a similar pattern to that in **Figure 6**. However, the intensity weakening of the hump from 56 days to 120 days in **Figure 7** (b) is less apparent than that in **Figure 6** (b). This elucidates that the partial dissolution of geopolymer gels in the sulfuric acid is slightly more significant than the deionized water. Nonetheless, the slightly higher dissolution of geopolymer gels by the acid did not result in a higher mechanical deterioration for the RFFG samples (**Figure 3** and **Figure 4**).

The partial dissolution of geopolymer gels by the leachants was also confirmed with FTIR characterization, as the FTIR spectra of the RFFG soaked in the sulfuric acid and deionized water for 0, 1, 56 and 120 days shown in **Figure 8**. The asymmetric stretching vibration band of Si-O-T (T is Si or Al), which is often assigned to geopolymer gels, was observed in the unsoaked RFFG samples. The center of this band shifted from 972 cm^{-1} to a higher wavenumber in the range of $987\text{-}993\text{ cm}^{-1}$ and $987\text{-}989\text{ cm}^{-1}$ after the samples were soaked in the sulfuric acid and deionized water, respectively. This shift is caused by the dealumination and depolymerization of the leachant attack to the RFFG samples [27, 47]. Bakharev [27], Ahamari and Zhang [47] found the similar FTIR patterns in their studies on the resistance of fly ash based geopolymers to sulfuric acids and the leaching tests of mine tailings based geopolymers with an acid of pH 3.0, respectively. The wavenumber of Si-O-T band did not further increase as the soaking time increased, illustrating that no further dissolution of this geopolymeric structure occurred when the soaking for longer than 1 day. The appearance of another small peak around 870 cm^{-1} in the samples soaked for more than 56 days is attributed to the dissolution of geopolymer gels [27].

The XRD and FTIR characterization results are consistent with the changes in mechanical properties of the RFFG samples after soaking in the sulfuric acid and deionized water. The deteriorating effect of the leachants on geopolymer gels and mechanical properties of soaked RFFG samples is summarized as follows: (i) the decreasing mechanical strength (e.g., UCS and flexural strength) and Young's modulus of the RFFG samples can be attributed to the partial dissolution of geopolymer gels by the leachants; (ii) the dissolution of alkali and the large amount of water absorption (verified with the weight increase in **Figure 2**) can be other causes for the decrease of the strengths and Young's modulus of the RFFG samples; (iii) neither further dissolution of geopolymer gels was observed during the soaking longer than 1 day, nor did the mechanical strengths showed further appreciable decrease; and (iv) the deteriorating effect of the sulfuric acid on the mechanical properties of the RFFG samples is similar to that of deionized water during the 120 days of soaking based on the mechanical and analytical results in this study.

3.3. Leaching Behavior of Al in RFFG Samples

The leaching behavior of Al in RFFG samples was also investigated to shed light on the dissolution of geopolymer gels in the sulfuric acid and deionized water. The concentrations of Al in the collected leachates were obtained with AA tests, as shown in **Figure 9**, where P and C in the legends indicate the RFFG samples in powder and cylindrical forms, respectively. More Al was leached out at a faster rate from the powder samples than their cylindrical counterparts in the respective leachants, as shown in **Figure 9 (a) and (b)**. Note that Al might have not reached the theoretical maximum level,

which should be the concentration of Al in the RFFG samples from the raw materials (see **Table 1**), based on the increasing trend of the leaching curve in **Figure 9** (a). For the samples cured at room temperature, the leaching behavior of Al in the sulfuric acid and deionized water was similar, regardless of the form of the samples (e.g., powder or cylinder). For the samples cured at 80°C, no clear trend was observed in the leaching behavior of Al in the different leachants used. Specifically, for the powder samples cured at 80°C, the maximum concentration of leached Al is much higher in the sulfuric acid than the deionized water, while for the cylindrical samples cured at 80°C, the maximum concentration of leached Al is less affected by the different leachants. This is consistent with the observation that no apparent difference was observed in the mechanical deterioration from the durability tests between the samples soaked in these two leachants (**Figure 3** and **Figure 4**).

3.4. Leaching Behavior of Heavy Metals in RFFG Samples

The concentrations of leached Fe, As, Cu, Cr and Cd were detected with AA tests as well. Similar to Al, the leached concentration of As from the powder and cylindrical samples soaked in sulfuric acid and deionized water increased with the leaching time, as illustrated in **Figure 10**. Note the concentration of As at 168 hours (7 days) in the curve T23-7.0-P and the concentration at 336 hours (14 days) in the curve T80-3.0-P appear abnormally lower than the concentrations of Al leached in shorter periods, which might be resulted from the testing bias and should be considered as outliers. The initial leaching of Arsenic (As) from the powder samples was fast (see **Figure 10** (a)), with its concentration after 4 hours of soaking in the range of 1-1.5ppm and showing little

dependence on the curing temperature of the RFFG samples or the pH value of the leachants. After the first 24 hours, the concentration of As leached from the 80°C cured powder samples in deionized water barely changed, and As was increasingly leached from the other powder samples. For the cylindrical samples, the initial leaching rate (during the first 72 hours) of As was much lower than the powder samples (see **Figure 10** (a) and (b)). As the soaking continued, more arsenic was leached from the cylindrical samples and reached a similar level to that from the powder samples. Leached As from the cylindrical samples cured at room temperature was less than 0.7 ppm when the soaking time was shorter than 24 hours, while the concentration increased gradually to 1.5-2.0 ppm during the rest of soaking period. As was undetectable in the leachate of the cylindrical samples cured at 80°C during the initial soaking period, as shown in **Figure 10 (b)**, especially in the deionized water, in which the concentration of As was undetectable until soaking more than 7 days.

Iron (Fe) leached from the powder samples followed a similar trend to Al during the soaking time, but at much lower concentrations (<4 ppm), while Fe leached from the cylindrical samples was negligible (<0.015 ppm). The concentration of other heavy metals: Cu, Cr and Cd, leached from both powder and cylindrical RFFG samples was very low and did not show any change during the soaking. Therefore, the leaching behavior of heavy metals Fe, Cu, Cr and Cd is not presented herein for the sake of conciseness.

The maximum concentration of heavy metals detected in the leachate during the soaking is presented in **Figure 11**. The maximum concentrations of Fe leached from the powder samples are much higher than those from the cylindrical samples, while the

highest concentrations of As leached from these two forms of samples are similar. The dependence of the leaching behavior on the samples' forms varied with the type of metals. The concentration of Fe leached from the cylindrical RFFG samples was undetectable, while the counterpart from the powder samples was close to 4ppm after the soaking of 14 days. On the other hand, the concentration of As leached from neither the powder samples nor cylindrical samples showed much further increase after it reached 2 ppm, as shown in **Figure 10**. The findings about As agree with those of Arioz, et al. [45], who found that As was immobilized better than the other metals by the FFA based geopolymer. The maximum concentrations of Cu, Cr and Cd leached from the powder samples are similar to those from the respective cylindrical counterparts, which are all at trace levels (<0.15 ppm). As illustrated in **Figure 11**, more heavy metals were leached by the sulfuric acid than the deionized water. The maximum concentrations of Cu, Cr, Cd, and As leached from the RFFG samples are much lower than their respective contamination limits in soils set by US EPA, which are 45, 212, 2 and 5.6 ppm, respectively [56].

4. Conclusions

The durability and leaching behavior of heavy metals of RFFG exposed to a sulfuric acid of pH 3.0 and deionized water of pH 7.0 were investigated in this study. UCS, Young's modulus and flexural strength of the RFFG samples decreased by ~30%, ~70% and 45% after soaking in the sulfuric acid for 120 days, respectively, which are comparable to the deterioration of respective mechanical properties of the control OPC samples.

The deterioration of the mechanical properties of the RFFG samples is attributed mainly to the partial dissolution of geopolymer gels, which is verified by the SEM, XRD and FTIR characterization results. The extended soaking (>7 days) did not cause further dissolution of geopolymer gels, as indicated by the qualitative comparison of the XRD and FTIR spectra among the RFFG samples soaked for different time periods. Furthermore, the change in the mechanical, physical and microstructural properties of the RFFG samples during the soaking in the sulfuric acid is similar to that in the deionized water, although the dealumination effect of the sulfuric acid on the powder samples is more intense than the water.

The concentrations of As, Cu, Cr and Cd detected in the leachate of the RFFG samples were all much lower than the respective contamination limits in soils set by the US EPA standard, even for the leachate of the powder RFFG samples. In addition, the curing temperature did not have much influence on the leaching behavior of heavy metals in the RFFG samples soaked in sulfuric acid or deionized water.

Based on current study, the resistance of RFFGs against a low pH value sulfuric acid and deionized water was found comparable to OPC. Mechanical properties and durability of RFFG can be further improved by optimizing the synthesis procedure, chemical composition of the raw materials and curing conditions. Furthermore, the use of RFFG in civil engineering projects that may be exposed to a sulfuric acidic environment will not introduce heavy metals at a level exceeding the respective EPA limits to the surrounding soils. Therefore, red mud-fly ash based geopolymerization technology not only produces a more economical and 'greener' alternative to OPC, but also lends itself to recycle and reuse two abundant industrial wastes: red mud and fly ash.

501

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Figure 10. Concentration of As leached from RFFG (a) powder samples and (b) cylindrical samples cured at room temperature and 80°C soaked in sulfuric acid (pH=3.0) and deionized water (pH=7.0) for 4 to 336 hours (14 days). Note that the samples are designated by curing temperature (T23: 23°C, room temperature or T80: 80°C)-pH value of the leachant (3.0: sulfuric acid or 7.0: deionized water)-sample size (C: cylinder or P: powder).

Figure 11. Maximum concentrations of the detectable heavy metals leached from the powder and cylindrical RFFG samples cured at room temperature and 80°C. Note that the samples are designated by curing temperature (T23: 23°C, room temperature or T80: 80°C)-pH value of the leachant (3.0: sulfuric acid or 7.0: deionized water)-sample size (C: cylinder and P: powder).

716 **Table 1. Chemical compositions of RM, FFA and cement (heavy metals at trace**
717 **levels were not detectible)**

Chemical Composition	Red Mud (wt.%)	Class F Fly Ash (wt.%)	Type II (MH) Portland cement
SiO ₂	22.82	57.91	19.80
Al ₂ O ₃	15.06	27.44	4.80
Fe ₂ O ₃	17.34	6.32	3.00
CaO	12.24	1.30	61.90
MgO	0.27	--	3.80
Na ₂ O	4.37	--	0.61
K ₂ O	1.19	--	--
SO ₃	--	0.21	3.00
MnO	0.36	--	--
P ₂ O ₅	2.43	--	--
TiO ₂	3.43	--	--
Loss in ignition	15.75	2.15	2.24

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Figure 1. Particle size distributions of red mud and class F fly ash used for geopolymer synthesis.

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756 **Figure 7. XRD spectra of (a) RFFG samples before and after soaking in the**
 757 **deionized water (pH=7.0) for 1, 56 and 120 days with the spectra between 10° and 45°**
 758 **2θ; and enlarged in (b). (Q: Quartz and M: Mullite).**

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762 **Figure 8. FTIR spectra of unsoaked RFFG sample and RFFG samples soaked in (a)**
 763 **sulfuric acid (pH=3.0) and (b) deionized water (pH=7.0) for 1, 56 and 120 days. The**
 764 **vertical dotted lines indicate the position of the asymmetric stretching vibration**
 765 **band of Si-O-T for geopolymer gels.**

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769 **Figure 9. Concentration of Al leached from RFFG (a) powder samples and (b)**
 770 **cylindrical samples, cured at room temperature and 80°C soaked in sulfuric acid**
 771 **(pH=3.0) and deionized water (pH=7.0) for 4 to 336 hours (14 days). Note that the**
 772 **samples are designated by curing temperature (T23: 23°C, room temperature or**
 773 **T80: 80°C)-pH value of the leachant (3.0: sulfuric acid or 7.0: deionized water)-**
 774 **sample size (C: cylinder or P: powder).**

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Figure 10. Concentration of As leached from RFFG (a) powder samples and (b) cylindrical samples cured at room temperature and 80°C soaked in sulfuric acid (pH=3.0) and deionized water (pH=7.0) for 4 to 336 hours (14 days). Note that the samples are designated by curing temperature (T23: 23°C, room temperature or T80: 80°C)-pH value of the leachant (3.0: sulfuric acid or 7.0: deionized water)-sample size (C: cylinder or P: powder).

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