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Performance and Heavy Metal Leaching Behavior of Bituminous Fly Ash-Based Geopolymer in Aggressive Environments

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ABSTRACT

This article investigates the performance of a geopolymer synthesized from bituminous fly ash (BFA) activated with sodium hydroxide. The BFA-based geopolymer (BFAG) exhibited high mechanical strength and a densified microstructure. The optimal SiO_2/Al_2O_3 and Na_2O/SiO_2 molar ratios were found to be 3:1 and 0.2, respectively, yielding a 28-day compressive strength of 9.65 MPa. The inclusion of 30wt.% of a PS material containing heavy metals led to a substantial reduction in strength by 56% and 73% compared to samples with the SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1, respectively, at 28 days. The ability of the BFAG matrix to contain 30wt.% PS was evaluated using a waste extraction test (WET). The leaching behavior of heavy metals from the BFAG matrix was assessed with three aggressive leachants: sodium citrate, sodium acetate, and synthetic acid rain. Results showed that, under exposure to these leachants, the leached concentrations of Cr, Fe, and Zn from samples with the SiO_2/Al_2O_3 ratio of 3:1 were lower than those from samples with the 2:1 ratio, with concentrations ranging from 0.32-1.73, 3.07-6.67, and 152-284 mg/L, respectively. Despite exposure to harsh conditions, the BFAG matrix effectively immobilized over 99% for Cr and Fe and Zn, except when exposed to sodium citrate which only retained 98.5% of Zn. BFAG can be used to treat heavy metal and heavy metal-contaminated sludge. This matrix reduces environmental exposure, thereby decreasing heavy metal leaching into the environment before safe disposal in landfills. BFAG can also be used as a cement substitute in the solidified process, which lowers treatment costs and reduces cement consumption. It can decrease carbon dioxide emissions from cement production.

1. INTRODUCTION

Geopolymers are green polymeric materials formed by the polycondensation of silica and alumina precursors. Geopolymerization reactions under alkali activation of solid aluminosilicate materials produce amorphous to semi-crystalline three-dimensional aluminosilicate networks, having cementitious properties and a strength level comparable to those of traditional cement. Moreover, the advantage of a small impact on climate change has caused these geopolymeric materials to receive considerable attention as substitute cementitious binders for cement in different applications including construction materials and waste treatment.

In environmental work, the geopolymer matrix has become widely used to immobilize heavy metal containing wastes. Most heavy metals are toxic and having amphoteric characteristics. They are readily soluble and widely distributed in the environment, causing problems due to mismanagement worldwide. To prevent the release of these toxic metals, the most common treatment method is to stabilize the toxicity

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and mobility of these metals and then contain them within an impermeable solidified matrix prior to disposal in the landfills. With increasing concern regarding sustainable development, geopolymers have been introduced as solidification binders with potential properties to control the release of toxic metals into the environment (Teixeira et al., 2011; Lombi et al., 2010; Tian et al., 2022).

Several studies have investigated the mechanical, physical, chemical, and microstructure of geopolymers related to the immobilization of heavy metal-containing waste (Provis and Deventer, 2009; Waijarean et al., 2017; Xia et al., 2020; Sun et al., 2022). Compressive strength of geopolymer under different conditions around 25-105 MPa at 28 days (Cong and Cheng, 2021). In terms of microstructure, the ^{27}Al spectra indicate a mixture of four-, five-, and six-fold coordinated Al-O units. (Van Jaarsveld and Van Deventer, 1999; Waijarean et al., 2017) Aluminosilicate materials from industrial by-products or residues have also been reported to be used as heavy metal-immobilizing agents. These waste-derived starting materials include coal fly ash (Silva et al., 2007; Duxson et al., 2005; Xia et al., 2020; Castillo et al., 2022; Su et al., 2023), water treatment residue (Aly et al., 2008; Lombi et al., 2010; Waijarean et al., 2017), metakaolin (Cheng et al., 2015), and red mud (Sun et al., 2022). The performance of heavy metal immobilization varies to a large extent on the chemical compositions (Si/Al) of the starting raw materials, types and compositions of alkali (Na_2O/SiO_2) activators, curing conditions, speciation of heavy metals, types of leaching solutions and leaching conditions (Zhang et al., 2008; Zheng et al., 2010; Waijarean et al., 2017; Xia et al., 2020; Sun et al., 2022).

The effects of alkaline dosage and the Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymers have been explored (Van Jaarsveld and Van Deventer, 1999). A geopolymer with the highest strength and the lowest leachable fraction of Cr, Cu, and Zn was obtained at an intermediate alkaline activator dosage of Na/municipal solid wastes incineration (MSWI) fly ash = 2.8 mol/kg and Si/Al molar ratio = 2.0. For the effect of Si/Al, the leachable fraction of Cr and Cu decreased with an increasing Si/Al ratio, while Zn had its lowest point at an intermediate Si/Al ratio. Various studies have shown that geopolymers exhibit better immobilization performance on MSWI fly ash than Portland cement. This is because active aluminosilicates in MSWI fly ash participate in the geopolymerization reaction, generating new phases such as Friedel's salts ($3CaO·Al_2O_3·CaCl_2·10H_2O$) and hydrocalumite ($Ca_2Al(OH)_6Cl_2H_2O$). Consequently, fly ash-based geopolymers effectively encapsulate heavy metals and chloride ions. In addition, studies on the eluviation and leaching behavior of broken, fly-ash-based porous geopolymers have shown that grain size, pH, and solid-liquid ratio significantly affect the leaching of heavy metals, in that order. Thus, heavy metal leaching from fly-ash-based geopolymers can be controlled (Fan et al., 2021; Shi et al., 2021). BFA better than Ordinary Portland cement (OPC) material. Because, the C-A-S-H gel and N-A-S-H gels offer longer chain lengths and denser cross-linking structure than the C-S-H gel of OPC. Moreover, the C-A-S-H gel is more sensitive to chemical attack than the N-A-S-H gel because of the higher Ca/Si ratio (Valencia-Saavedra et al., 2020; Yang et al., 2022). Previous research has studied the use of water treatment residue (WTR) as an immobilizing agent for an electroplating sludge containing Zn, Fe and Cr as the major heavy metals. WTR with an initial SiO_2/Al_2O_3 ratio of 1.78 was pretreated by calcining at 800°C for 1 h. The performance of the WTR-based geopolymer matrix to immobilize 30wt.% electroplating sludge showed strength and metal leaching results which are acceptable for disposal in landfills (Waijarean et al., 2017). Furthermore, these three heavy metals (Zn, Fe and Cr) were synthesized in the form of hydroxides and solutions of nitrates to study the interaction of heavy metals and the microstructure of WTR-based geopolymers (Waijarean et al., 2017). It is suggested that the presence of metal hydroxides as charge-balancing cations in the geopolymer structure affected the strength rather than the incorporation and can immobilize the three heavy metals for disposal in the landfill.

The aim of this research is to investigate the potential of bituminous fly ash (BFA) as the immobilizing agent for an plating sludge. BFA is a waste-derived aluminosiliceous material generated from power plants. The source of bituminous fly ash in Thailand is from bituminous coal-fired power plants in the northeastern region. The toxicity of fly ash is influenced by factors like the type of coal burned and the combustion technology used. However, BFA is not classified as hazardous waste because the toxic levels found are lower than the permissible limit. Therefore, BFA can be used as a material for geopolymer production. The quantity of fly ash produced is related to the country's energy production from coal. With increasing energy demands, fly ash generation is on the rise. In 2023, approximately 6.05 million tons of bituminous coal were imported, according to the Department of Primary Industries and Mines. In the present research, factors affecting the effectiveness of the BFAG to contain heavy metals present in the plating sludge were studied. Molar ratios of SiO_2/Al_2O_3 between 2 and 3, an alkali activator using NaOH at molar ratios of Na_2O/SiO_2 between 0.15 and 0.30 and various types of leachant were examined. The leaching test was applied from a waste extraction test (WET) using sodium citrate, sodium acetate and synthesis acid rain as leaching solutions. Strengths, microstructures and the ability of the BFAG solidified PS to contain heavy metals were evaluated.

2. METHODOLOGY

2.1 Materials

Bituminous fly ash (BFA) was obtained from the BLCP Power Station in Rayong Province. Si waste which was used to adjust the SiO_2/Al_2O_3 ratio for the BFAG mixtures was obtained from AGC Automotive (Thailand) Co., Ltd. located in Cholburi Province. The starting materials were analysed by X-ray fluorescence (XRF), and the chemical compositions of the elemental oxides are reported in Table 1. In addition, commercial grade NaOH was used as an alkali activator for geopolymerization reactions.

Plating sludge (PS) was generated from the wastewater treatment plant of an electroplating industry in Bangkok, Thailand. The sludge was then oven-dried at 105°C before particle size reduction to less than 50 mm. The PS was subjected to microwave digestion, and the concentration of heavy metals present in the sludge was measured by atomic absorption spectrophotometry. The main heavy metals present in PS were Zn, Fe, and Cr at the concentrations of 690, 163.5, and 37.5 g/kg dry wt. PS, respectively.

2.2 Sample preparation

The geopolymer was synthesized from BFA and activated with a commercial-grade NaOH solution. The molar ratio of BFA was adjusted to have a SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1 through the addition of Si waste. The proportion of each mixture is shown in Table 2. The NaOH solution was added to the solid mixture to gain the required alkali dosage of Na_2O/SiO_2 between 0.15 and 0.3, then mixed for 10 min to obtain a homogeneous mix. The mixtures were then transferred to cylindrical PVC moulds with a diameter of 35 mm and a height of 70 mm, then vibrated for 2 min to remove entrapped air bubbles. The sample specimens were wrapped with cling film to prevent carbonation and water evaporation during curing under ambient temperature (30±2°C). The optimum alkali dosage of NaOH was determined by means of strength development after curing for 7, 28, and 60 days. The solidified PS was prepared by mixing BFA with 30wt.% PS and the solution of NaOH to gain an optimum alkali dosage. All mix proportions were prepared in a similar manner to that of the control (without PS).

Table 1. Chemical compositions of the starting materials

Materials	Chemical composition (wt.%)						
	SiO_2	Al_2O_3	Na_2O	CaO	MgO	Fe_2O_3	K_2O
BFA	60.10	28.70	0.38	1.45	0.47	4.70	1.25
Si-waste	68.10	4.85	0.16	9.53	3.98	0.96	0.55

Table 2. Mix proportions of geopolymer with and without PS

Samples	SiO_2/Al_2O_3 molar ratio	Synthesis geopolymer (% by wt.)				
		BFA	Si-waste	NaOH	PS	Total
BFA geopolymer	2:1	86	-	14	-	100
	3:1	58	28	14	-	100
BFA geopolymer +30wt.%PS	2:1	60	-	10	30	100
	3:1	40	20	10	30	100

2.3 Compressive strength test

The compressive strength of the cylindrical specimens was determined according to the ASTM D 1633-17 test method. The compaction test was done on the smooth surface samples at the age of 7, 28, and 60 days. Six samples for each mix proportion were analysed and the strength value was averaged with 95% confidence to ensure the reproducibility of the results.

2.4 Microstructure characterization

The crystalline phases of the BFAG with and without PS were examined at the age of 28 days using X-ray diffraction (XRD). A Bruker AXS series D8 Discover with Cu Kα radiation with an average wavelength of 1.54184° was used. The powder sample was scanned from 4° to 80° 2θ at a rate of 0.01 s per step. Scanning electron microscopy (SEM) was carried out using a JEOL series JSM-6400 operated at 15 kV. The fragmented samples from the 28-day strength test were used for SEM analysis and coated with gold. The solid-state MAS NMR spectra was used to characterize ^{27}Al resonance. A Bruker Avance III 500 spectrometer operating at an ^{27}Al frequency of 130.24 MHz at a magnetic field of 11.7 T was used, and the spectra were referenced with respect to $Al(H2O)_6^{+3}$.

2.5 Leaching test

A waste extraction test (WET) was used according to the Ministry of Industry, Thailand, standard for assesses the leaching of heavy metals from PS, which was solidified within the BFAG matrix. Three solutions were used as leachants for these tests to simulate the leaching performance under severe and normal scenarios that the solidified PS might encounter during placing in the landfill. These three leachants were sodium citrate, sodium acetate and synthetic acid rain. Sodium citrate and sodium acetate solutions were prepared by adjusting the pH of critic acid and acetic acid with 4 N NaOH to a pH of 5.0±0.1 and 4.93±0.05 whereas the synthetic acid rain was prepared from 80 %v/v sulfuric acid and 20%v/v nitric acid and diluted to a pH of 5.0 with deionized water. The BFAG samples with and without 30wt.% of PS at the age of 28 days were dried in a hot air oven at 105 °C for 1 h. The dried samples were crushed until the particle sizes were less than 2 mm or able to pass through a sieve (No. 10). The crushed samples were then contacted with an amount of leachant which is equal to 10 times that of the sample weight. The closed plastic vessels containing the mixtures were rotated at 300 rpm for 48 h. The leachates were then filtered through a 0.45 µm membrane filter to remove suspended solids. The filtrates were used for pH measurements and heavy metals concentration determination by ICP-AES. Each leachate was analysed in triplicate, and the mean value was reported.

3. RESULTS AND DISCUSSION

3.1 Effect of alkali dosage

Variation in the Na_2O/SiO_2 molar ratio from 0.15 to 0.3 on strength development of BFA-based resulted in a geopolymer with the highest strength of 4.8 and 11.1 MPa from BFA with the starting SiO_2/Al_2O_3 molar ratio of 2 at the age of 28 and 60 days, respectively (Figure 1). NaOH plays an important role in the mechanical strength of the geopolymer matrix in that it activates the surface dissolution of Si and Al from a solid aluminosilicate source of BFA, resulting in the gelation of aluminosilicate species, and helps charge balancing during the polymerization of the aluminosilicate network (Duxson et al., 2005; Castillo et al., 2021). At lower alkali dosage (Na_2O/SiO_2 molar ratio of 0.15), the dissolution rate of Si and Al was low, thus resulting in a lower degree of geopolymerization reactions which is accountable for the lower strength development.

When the Na_2O/SiO_2 molar ratio increased to 0.25 and 0.30, the highly alkali environment increases the rate of surface dissolution of Si and Al from BFA which is responsible for a supersaturation of silicate and aluminate species in the system. A rapid formation of aluminosilicate gel and precipitation on the surface of solid particles at the beginning obstructs further dissolution of Si and Al from the surface of the BFA. Another explanation for this phenomenon could be caused by an increased viscosity of the alkali solution at increasing Na_2O/SiO_2 molar ratio, thus delaying the transportation of silicate and aluminate species after dissolution from BFA. The accumulation of silicate and aluminate species nearby the BFA surface hinders the release of these two species into the solution due to the rise of speciation equilibrium. The excess alkaline therefore negatively affected the strength development of the BFAG. Similar observations have been reported: a very high alkali dosage will dissolve too many fly ash particles, leading to structural disruption of the aluminosilicate phases and a reduction on strength (Zheng et al., 2010; Cheng et al., 2015). Several research have reported the optimal concentrations of sodium hydroxide ranging between 7 and 12 M, with the Na_2O/SiO_2 molar ratio from 0.2

to 4.0 (Amran et al., 2021; Elmesalami and Celik, 2022). The maximum compressive strength of BFAG was found at a Na_2O/SiO_2 ratio of 0.20 that was selected to study effect of SiO_2/Al_2O_3 molar ratio.

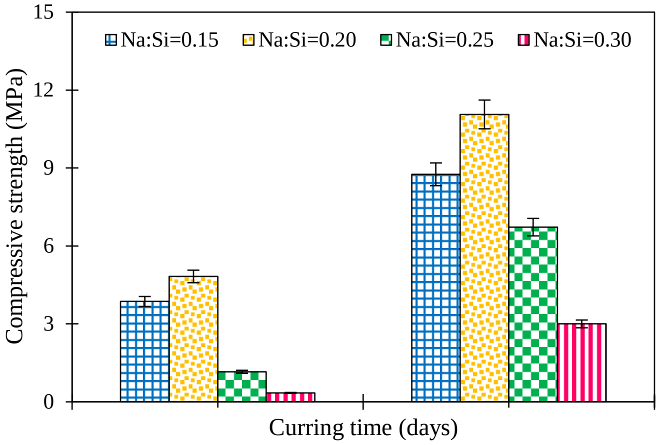

Figure 1. Strength development of BFAG under various alkali dosage

3.2 Effect of SiO_2/Al_2O_3 molar ratio of BFA

Previous research reported that a SiO_2/Al_2O_3 molar ratio of 1:1 resulted in a small amount of N-A-S-H gel, and these mechanisms did not contribute to the development of compressive strength. Conversely, at a SiO_2/Al_2O_3 molar ratio of 4:1, N-A-S-H gel was not observed, and it formed a large pore structure, leading to lower strength and it formed a large pore structure, leading to lower strength. A SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1 was found to promote the formation of a well-dispersed N-A-S-H gel within the geopolymer binder (Aly et al., 2008; Castillo et al., 2022). As these ratios influence compressive strength development, they were chosen for further study in this topic. Higher strength development was obtained from BFA-based geopolymers with a SiO_2/Al_2O_3 molar ratio of 3:1 and a Na_2O/SiO_2 ratio of 0.20 at all curing durations (Figure 2). It is generally known that the structure of geopolymers formed varies from polysialate (-Si-O-Al-O-), to poly sialate-siloxo (-Si-O-Al-O-Si-O-), and poly sialate-disiloxo (-Si-O-Al-O-Si-O-Si-O-) when the SiO_2/Al_2O_3 molar ratios increase from 1:1, 2:1, and 3:1, respectively (Amran et al., 2021; Luhar and Luhar, 2022). In this research, Si-waste was used to adjust the SiO_2/Al_2O_3 molar ratio from an initial value of approximately 2:1 (2.09) to 3:1. It could be possible that the presence of CaO and Al_2O_3 in Si-waste at 9.53 and 4.85wt.% is beneficial for strength development from the formation of CSH gel (calcium silicate hydrate) and additional geopolymer products. CSH gel is formed by the reaction between CaO from Si-waste and silicate species from both Si-waste and BFA which can transform into a solid and harden (Castillo et al., 2021; Su et al., 2023). However, there are several factors affecting strength gain of geopolymers including the availability of the solid aluminosilicate source from the starting materials.

3.3 Effect of plating sludge on strength

A significant reduction in mechanical strength of BFAG containing 30wt.% of PS at the SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1 activating with alkali at a Na_2O/SiO_2 ratio of 0.20 was gained from samples at all curing durations (Figure 3). The strengths of geopolymers at 7 days were 0.38 and 0.55 MPa at the SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1, respectively, while at 28 days, the strengths of geopolymers at the SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1 increased to 1.87 and 2.57 MPa, respectively. The strengths of geopolymers with a SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1 reduced by 56% and 73% compared with control geopolymer. This observation agrees with several publications which were reported to be caused by the interferences of heavy metals on the geopolymerization reactions (Zhang et al., 2008). These heavy metals could be immobilized through physical encapsulation or chemical mechanisms depending on their chemical forms. It was found that the presence of heavy metals as hydroxides affected the strength of geopolymers synthesized by the alkali activation of water treatment residue greater than their presence in the form of soluble nitrates (Waijarean et al., 2017).

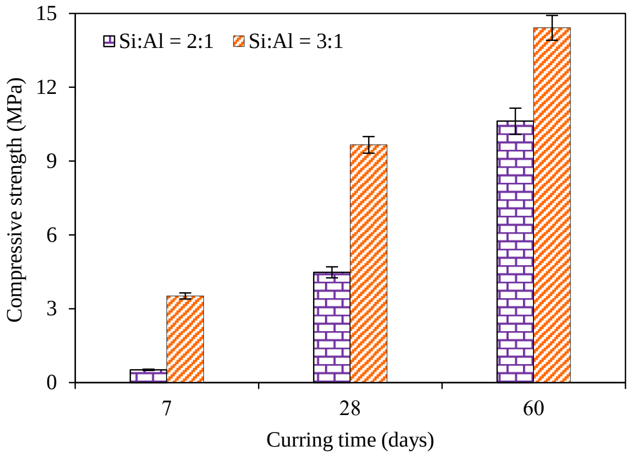

Figure 2. Strength development of BFAG at SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1

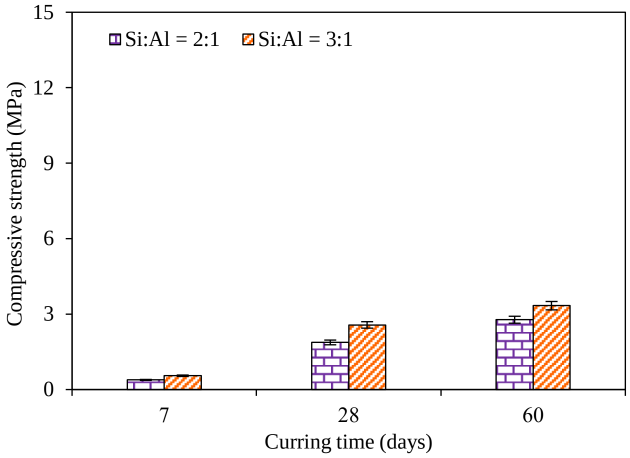

Figure 3. Strength development of BFAG containing 30wt.% PS

Reduction of compressive strength of geopolymer solidified PS results from physical encapsulation and chemical mechanisms. Physical encapsulation adsorbing heavy metal ions on pore structure with Van der Waals force (Zhang et al., 2008; Tian et al., 2022). The chemical mechanisms such as sorption, precipitation, and substitution can be found in geopolymer matrix. Previous research reported that the interfering effects caused by both synthesized metal hydroxides such as $Zn(OH)_2$, $Cr(OH)_3$, and Fe $(OH)_3$, and electroplating sludges. The metal hydroxide ion was adsorbed with chemical bond and high alkalinity can precipitated ion on surface of BFAG that impede geopolymerization reactions. In addition, adsorbed and precipitated metal hydroxide ion reacted and incorporate with alumino-silicious materials and form to metal silicate or metal oxide which reduce SiO in the metrix (Asavapisit and Macphee, 2007; Waijarean et al., 2017). In addition, the negative charge of Al tetrahedrons can bind to metal oxide ions, which replace Na^+ or K^+ in the geopolymer structure (Castillo et al., 2021; Tian et al., 2022). The samples were higher than the minimum requirement of the standard criteria regulated by U.S.EPA 1992 and the ministry of industry (Thailand) standard (0.34 MPa).

3.4 Microstructures of BFAG

In this research, ^{27}Al MAS NMR spectroscopy was used to investigate the structure of the Al-O units. The ^{27}Al MAS NMR spectra of BFA and BFAG with SiO_2/Al_2O_3 molar ratios of 2:1 and 3:1 are shown in Figure 4. The ^{27}Al spectrum of BFA contained broad resonances at 59.4, 54.3, and 1.5 ppm (Figure 4(a)), corresponding to four- and six-fold coordinated Al-O units, respectively. The investigation of the reacted samples of the BFAG at SiO_2/Al_2O_3 molar ratios of 2:1 and 3:1 exhibit the appearance of different aluminium spectra comprising four-, five-, and six-fold coordinated Al. The single sharp tetrahedral Al resonance at 61.0 ppm (Figure 4(b)), and 60.2 ppm (Figure 4(c)) indicates a higher degree of structural order. The reaction products produced from alkali activation of BFA, which corresponds to the strength gain of the BFAG could be associated with a well-formed geopolymer. When alkali solution was mixed with BFA and forms geopolymer, the material exhibits typical characteristics of a well-reacted geopolymer, evidenced by a sharp tetrahedral ^{27}Al resonance at 61.0 ppm (Figure 4(b)), and 60.2 ppm (Figure 4(c)) indicates a higher degree of structural order. Previous studies showed that the ^{27}Al spectra indicate a mixture of four- and six-fold coordinated Al, the peaks in the spectra of the samples shift of 58.5 and 2.2 ppm (Van Jaarsveld and Van Deventer, 1999). While the ^{27}Al spectrum of the water treatment residue-based geopolymers is typical of dehydroxylated kaolinite-type minerals, containing Al resonances at 59.0, 27.7, and 3.2 ppm, corresponding to four-, five- and six-fold coordinated Al-O units, respectively (Waijarean et al., 2017) The reaction products produced BFAG, and the strength gain of the BFAG could be associated with the formation of a well-formed geopolymer.

SEM micrographs of BFAG with a SiO_2/Al_2O_3 molar ratio of 2:1 and curing for 28 days indicated the presence of unreacted or partially reacted spherical BFA with a variation in particle sizes (Figure 5(a)). The gel-like aluminosilicate materials or geopolymer products were deposited everywhere on the surface of the BFA particles alongside small and large pores or voids scattered throughout the sample. By increasing the SiO_2/Al_2O_3 molar ratio to 3:1, the appearance of a dense microstructure of the geopolymer products were obtained with less pores and voids (Figure 5(b)). This evidence is in-line with the mechanical strength performance of the BFAG (Askarian et al., 2019; Cong and Cheng, 2021; Luhar and Luhar, 2022)

When the PS was added to the BFAG at 30wt.% (Figure 6(a)-(b)), a microstructure consisting of gel-like agglomerations in a less homogenous manner was developed compared to the control (without PS). The formation of these complex mixtures of gel-like products could have arisen from the chemical mechanisms of metal hydroxides present in the PS. These metal hydroxides are very soluble under the highly alkali environment of the system and transport into the aqueous phase of the mixture. This affects the speciation equilibrium during the transformation of the silicate and aluminate species into gel-like products and subsequently hindering the polymerization process. As a result, a less homogenous microstructure containing large pores is responsible for a reduction in mechanical strength (Duxson et al., 2005; Su et al., 2023). The matrix has high porosity and contains unreacted fly ash that may be caused from interfering effect of metal hydroxide ion from PS (Asavapisit and Macphee, 2007; Zheng et al., 2010).

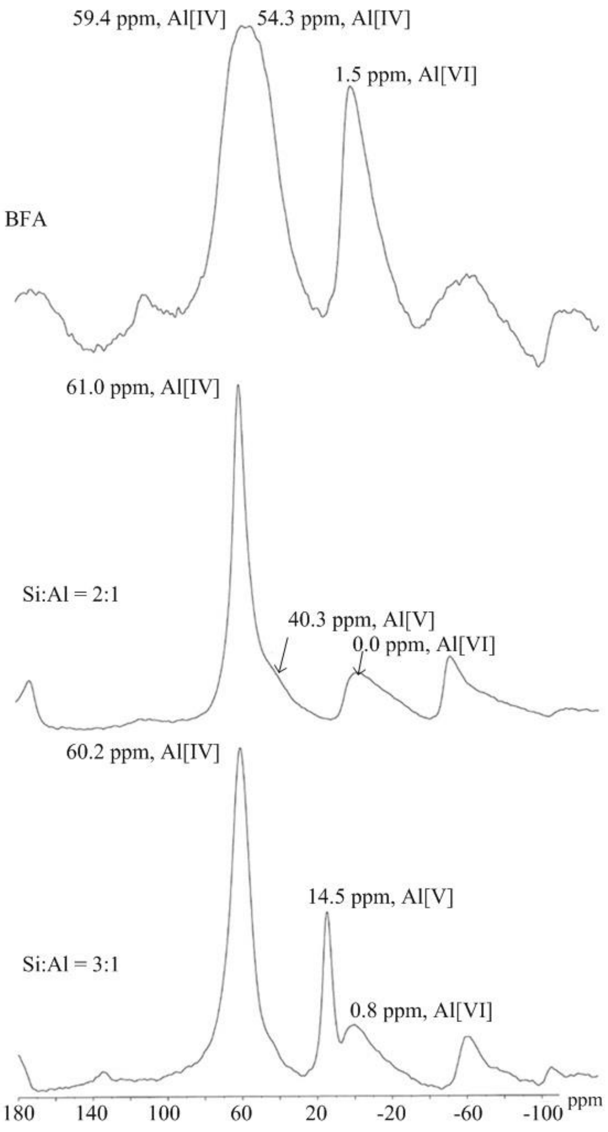

Figure 4. ^{27}Al MAS NMR of BFA, BFAG at SiO_2/Al_2O_3 molar ratio of 2:1 and 3:1

The XRD patterns of BFA and BFAG with SiO_2/Al_2O_3 molar ratios of 2:1 and 3:1 with and without PS are shown in Figure 7 (a)-(c). Quartz and mullite are the two major crystalline phases detected from the BFA sample (Figure 7(a)). The presence of a broad hump in the 2 theta values between 18 and 25 degrees indicates the presence of amorphous materials. In addition to quartz and mullite, the peaks of the sodium aluminium silicate hydrate (NASH) were observed from the BFAG with SiO_2/Al_2O_3 molar ratios of 2:1 and 3:1 (Figure 7(b)). The broad hump in the 2 theta values from approximately 20 to 40 degrees with low and dispersed intensity diffractograms could be described as semi-crystalline phases including gel-like silicate and aluminate precursors (Van Jaarsveld and Van Deventer, 1999; Silva et al., 2007; Luhar and Luhar, 2022). The addition of the PS at 30wt.% to the alkali activated BFA resulted in the transformation of the original metal hydroxides into different crystalline phases such as zinc silicate ($ZnSiO_4$), maghemite (Fe_2O_3), zinc iron oxide ($ZnFe_2O_4$), aluminium iron oxide ($FeAlO_3$), and chromium oxide (CrO) as shown in Figure 7(c). Previous research reported that the immobilization of heavy metal in fly ash binders activated alkali solutions may be included in the gepolymer matrix in metal silicate hydrate (MSH) form that does not contribute to strength development. (Zheng et al., 2010; Waijarean et al., 2017). Under a highly alkali environment, it could be possible that heavy metals in the original form of hydroxide were solubilized and interacted with other ion species within the system and transformed into other insoluble compounds including zinc silicate. Zinc was present in the PS at the highest concentration among other heavy metals, which was equal to 690 g/kg dry weight. This results in the insufficient silicate anions that can undergo geopolymerization reactions leading to significant a mechanical strength reduction.

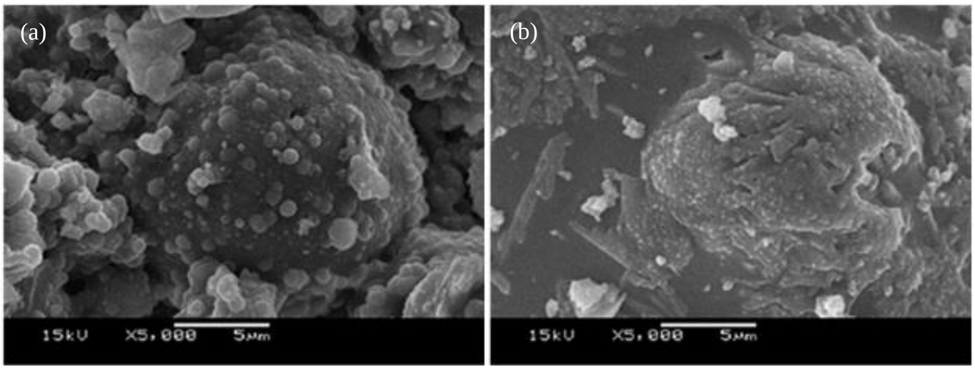

Figure 5. SEM micrographs of BFAG; (a) SiO_2/Al_2O_3 = 2:1, (b) SiO_2/Al_2O_3 = 3:1

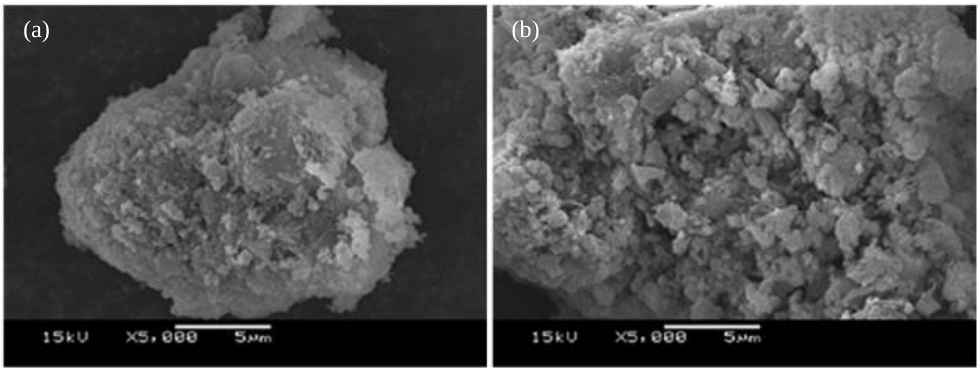

Figure 6. SEM micrograph of BFAG containing 30wt.% PS; (a) SiO_2/Al_2O_3 = 2:1, (b) SiO_2/Al_2O_3 = 3:1

3.5 Effect of various leachants on the heavy metal containment

A waste extraction test was applied to evaluate the leaching performance of heavy metals from BFAG containing 30wt.% PS using different leachants (Table 3). After the solidified PS samples with a SiO_2/Al_2O_3 molar ratio of 2:1 was extracted with the leachants for 48 h, the leachate pH values made with sodium citrate, sodium acetate and synthetic acid rain increased from the initial pH values of 5±0.1 to 7.13, 7.59, and 11.39, respectively. Sodium citrate and sodium acetate are acidic buffer solutions and therefore can resist changes in pH upon contact with a highly alkali solidified sample better than synthetic acid rain. Similar variation in leachate pH values were observed from solidified samples with a SiO_2/Al_2O_3 molar ratio of 3:1.

PS contains Zn, Fe, and Cr at concentrations of 690, 163.5, and 37.5 g/kg dry weight, respectively. The concentration of Zn in the leachates from all samples upon contact with various leachants were the highest followed by Fe and Cr (Table 3). The leaching process occurs when leachant into the solidified samples through micro-cracking, connected pores and voids. This interrupts the chemical equilibrium within the solidified matrix, resulting in the solubilization of heavy metals immobilized within the geopolymer network. The soluble heavy metals were then transported out of the solidified sample into the leachant via diffusion, a process controlled by the concentration gradient between the solid and solution (Asavapisit and Macphee, 2007; Amran et al., 2021; Tian et al., 2022).

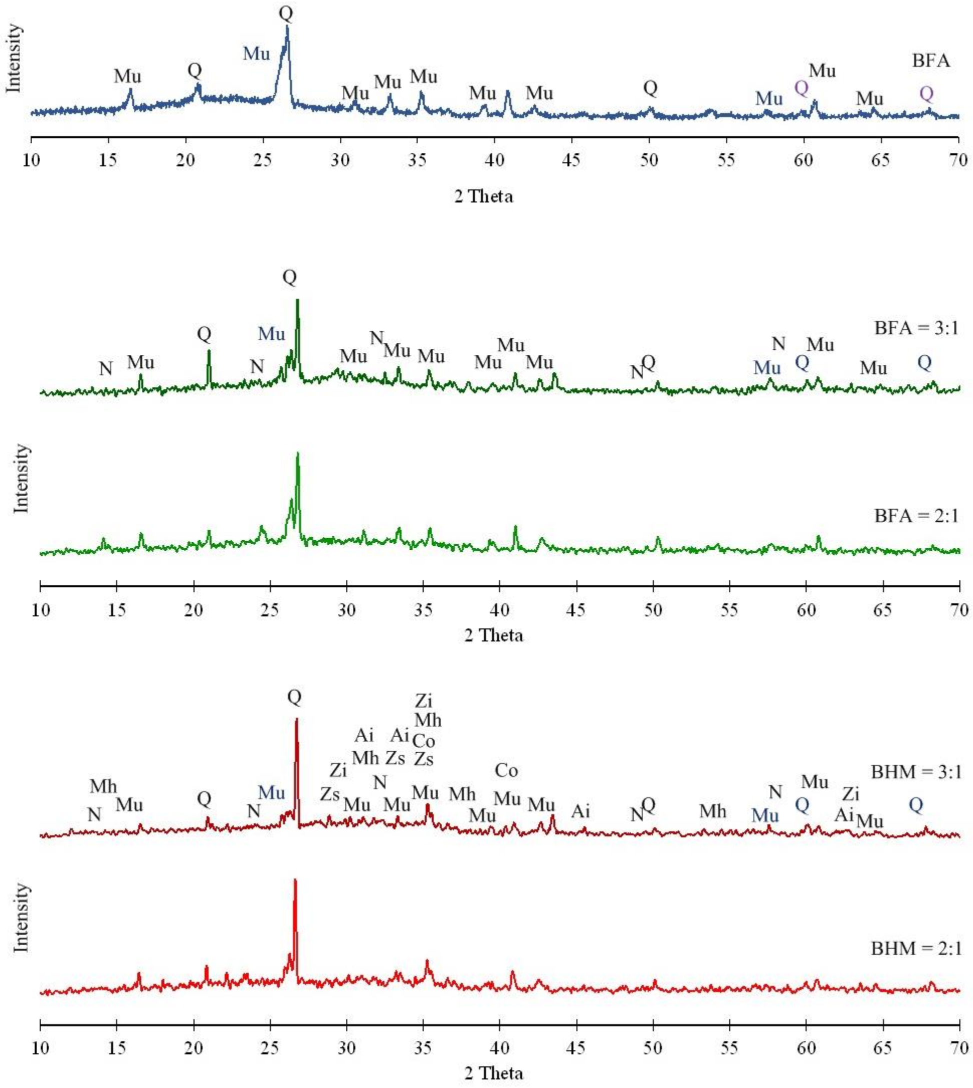

Figure 7. XRD patterns of (a) BFA, (b) BFAG at SiO_2/Al_2O_3 = 2:1 and 3:1 and (c) BFAG containing 30wt.% PS, (Q=Quartz, Mu=Mullite, N=NASH-Sodium aluminum silicate hydrate, Ma=Maghemite, Zs=Zinc Silicate, Co= Chromium Oxide, Zi=Zinc Iron Oxide, Ai=Aluminium Iron Oxide)

The highest concentration of Zn, Fe, and Cr were found in sodium citrate solution. This is because sodium citrate is more aggressive than sodium acetate and synthetic acid rain. Both sodium citrate and sodium acetate are leachants made with organic acids (citric and acetic) which can act as chelators by bonding to Zn, Fe, and Cr resulting in the formation of complexes with these metal ions. Citric and acetic acids are weak carboxylic acids and can partially dissociate in water to generate hydronium (H_3O^+) and carboxylate ($RCOO^-$) ions. Sodium citrate which is a tricarboxylic acid can generate hydronium ions greater than sodium acetate, which is a monocarboxylic acid and as a result, could lead to a higher solubility of heavy metals (Asavapisit and Macphee, 2007; Zhang et al., 2008; Tian et al., 2022). In addition, pKa of sodium citrate (pKa=3.13) is lower than pKa of sodium acetate (pKa=4.76), which can donate a proton very easily and destroy the geopolymer matrix easily.

On the other hand, synthetic acid rain consists of nitric and sulfuric acids, which are strong mineral acids. But during the preparation of synthetic acid rain, the nitric and sulfuric acids may be dissociated in the second and third rounds in water, resulting in a lower pKa value compared to the citrate and acetate acids. It is rapidly neutralized by hydroxide ions (OH^-) from the highly alkali solidified sample which caused the leachate pH values of all samples to increase from an initial value of 5 to 11.3. The hydrolysis of the amphoteric metal oxides or hydroxides in the leachate comprising excess OH^-, lead to the formation of complex ions with heavy metals which are soluble (Asavapisit and Macphee, 2007; Zhang et al., 2008; Tian et al., 2022). Although Zn was found to have the highest concentration in all leachates, the ability of the BFAG matrix to contain all heavy metals of interest was higher than 98%.

Table 3. Concentration of heavy metals in leachate extracted using waste extraction test and contacted with various types of leachant.

Types of leachant	Initial pH	Leachate pH	Concentration of heavy metals (mg/L)			%Containment		
			Cr*	Fe	Zn*	Cr	Fe	Zn
The ministry of industry (Thailand) Standard*			5	-	250			
SiO_2/Al_2O_3 = 2:1								
sodium citrate	4.93	7.13	4.97	12.44	408.40	99.52	99.72	97.84
sodium acetate	5.00	7.59	2.06	3.84	218.60	99.80	99.91	98.84
synthetic acid rain	5.00	11.39	1.54	4.95	224.10	99.86	99.90	98.92
SiO_2/Al_2O_3 = 3:1								
sodium citrate	4.93	7.65	1.73	6.67	284.20	99.83	99.85	98.50
sodium acetate	5.00	7.11	0.50	3.07	152.10	99.95	99.93	99.19
synthetic acid rain	5.00	11.30	0.32	4.53	154.20	99.97	99.91	99.26

4. CONCLUSIONS

BFA, a waste-derived aluminosiliceous material from power plants is suitable to be used for the synthesis of geopolymers by alkali activation. Geopolymers produced with a Na_2O/SiO_2 molar ratio of 0.2 and a SiO_2/Al_2O_3 molar ratio of 3:1 were capable of immobilizing heavy metal-containing PS. SEM and XRD results indicate that the addition of 30wt.% PS significantly affected the mechanical strength and structure of the BFAG. This arises because the heavy metals present in the PS as hydroxides were transformed into different insoluble crystalline phases and physically encapsulated within the matrix instead of being incorporated as charge-balancing cations in the geopolymer network. A leaching test suggested that the BFAG with a SiO_2/Al_2O_3 molar ratio of 3:1 achieved the best immobilization of the PS. The leaching behaviour of heavy metals is dependent on both the chemical forms of heavy metals and the types of leachant. BFAG can substitute ordinary Portland cement (OPC) as solidified binder for treat metals hydroxide from PS before landfilling. This substitution offers two benefits: reducing cement usage and CO_2 emissions from cement production. Furthermore, it aligns with the bio-circular-green process by utilizing industrial waste for beneficial purposes. It provides the additional advantage of reducing waste through the repurposing of fly ash, serving as a guideline for studying waste utilization to sustainability in the industry.

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