

Scientific paper

Development of Foamed Geopolymer with Addition of Municipal Solid Waste Incineration Fly Ash

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Received 23 January 2021, accepted 29 June 2021

doi:10.3151/jact.19.830

Abstract

In order to develop a safe technology for recycling municipal solid waste incineration fly ash (MSWI-FA), the authors have attempted to produce foamed geopolymers with addition of MSWI-FA, and have investigated their various properties, including bulk density, strength, thermal conductivity, and leaching concentration of heavy metals and chlorine, etc. The polymerization reaction products, crystalline compounds and microstructure were also examined through X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analyses. It was found that it is possible to produce foamed geopolymer with a bulk density of less than 0.5 and a uniform distribution of air voids, by adding metallic aluminum powder as foaming agent and using less than 20% MSWI-FA and suitable alkali activator having low NaOH mole concentration. $\text{CaCl}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, CaO and KCl , initially included in the MSWI-FA, were not found in the foamed geopolymers. The geopolymers, which used ground granulated blast furnace slag (BFS), coal fly ash and MSWI-FA as precursors, were mainly composed of C-A-S-H gels, incompletely reacted precursors and a small amount of N-A-S-H gels. The foamed geopolymer had very high immobilization capacity of heavy metals (Cd, Cr, Cu, Mn, Pb, Zn), not varying with the pH of leachate. The immobilization efficiency of As changed with the pH of leachate and BFS content. When the BFS content was not less than 60%, the leaching concentrations of all the traced heavy metals including As were low, satisfying the environmental criteria of Japan for recycled construction materials without direct contact with water. The chlorine immobilization capacity of the foamed geopolymers is expected to exceed 70% in long-term age.

1. Introduction

The incineration is considered as the most effective method for reducing the mass and volume of municipal solid waste and the conservation of landfill space (MEJ 2020). At the same time, municipal solid waste incineration (MSWI) generates larger quantities of bottom ash (BA) and fly ash. The BA accounts nearly 90% and the remaining 10% are fly ash collected from the air pollution control systems (Kamada 2016). In addition to the MSWI, fly ash is also generated during the melting process of incinerator fly ash. Heavy metals, such as Cd, Pb, As, Cr, Zn and Se, are concentrated in the two kinds of fly ash, here collectively referred to as MSWI-FA. Leaching of pollutants from MSWI-FA is potentially harmful to the environment and has become an environmental concern with respect to its disposal and/or reuse. In particular, leaching of toxic metals has been shown to be highly variable and may occur over a long period. Therefore, MSWI-FA is classified as a hazardous

waste, which is designated as general waste required to be specially managed and must be pre-treated before final disposal in Japan.

MSWI-FA has the potential to be used as a mineral additive in cement products. However, its high content of chlorine that is mainly originated from plastic wastes restricts its application in construction materials because chlorine is detrimental to the passivation of embedded rebars. In order to solve this problem, the pre-treatment methods, such as water washing and thermal treatment, have been proposed (Ferone *et al.* 2013; Tahara *et al.* 2002). These pre-treatments certainly eliminate the chloride in MSWI-FA, but generate new waste and increase the energy requirement and cost of MSWI-FA recycling.

A number of methods have been suggested to reduce the leaching of toxic elements from this kind of hazardous waste before disposal or reuse (Quina *et al.* 2008). The government of Japan recommends four pre-treatment methods of MSWI-FA in Notification No. 194 of the Ministry of Health, Labour and Welfare, which are (1) cement solidification, (2) chemical stabilization, (3) thermal treatment (melting) and (4) separation treatment (solvent extraction). Cement solidification, using Portland cement as a binder, is a pre-landfill treatment method most commonly used worldwide (Polettini *et al.* 2001). This method solidifies MSWI-FA into a monolithic or granular material, ensuring easy handling and transportation to landfill sites, but excluding any kind of reuse. However, the cement solidification method typically uses around 300 to 400 kg of cement for treating per

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ton of MSWI-FA. Along with the added water, this method causes a significant increase in the volume and mass to be landfilled (Benassi *et al.* 2016). Additionally, the hardened cement monolithic seems to be unable to strongly immobilize the heavy metals when they are exposed to an aqueous solution for a long time (Zhao *et al.* 2002). Recently, another issue that has recently attracted attention is the large amount of CO₂ emissions from the Portland cement production process.

In the chemical stabilization method, inorganic heavy metal immobilizers such as silica fume, phosphate, silicate and calcium hydroxide, and organic ones such as sixthio guanidine acid, tetrathio bicarbamic acid, thio-urea and ethylene diaminetetracetic acid (EDTA), are uniformly mixed with MSWI-FA to change the heavy metals into insoluble heavy metal chelate compounds before final disposal as landfills. The addition of heavy metal immobilizer is always performed together with the cement use for increasing the immobilization efficiency and ensuring easy transportation to landfill sites (Ma *et al.* 2019). However, the chemical stabilization method still needs landfill to dispose the MSWI-FA like the cement solidification method. Furthermore, the use of heavy metal immobilizers is costly.

Thermal treatment method can immobilize some toxic heavy metals in the slag by melting (>1200°C) and cooling processes. The slag produced can be used as construction materials such as road materials (e.g. asphalt mixture, roadbed etc.) or as aggregates for concrete (Fujiyoshi 2005). However, the melting leads to the evaporation of some heavy metals, the off-gas needs to be strictly treated to ensure the safety of the vaporized metal compounds and the method involves significant energy consumption.

The metal separation method, such as water-extraction, acid-extraction, alkali-extraction and biological-extraction (Hong *et al.* 2000), can extract heavy metals, but the treatment process is complex and the residues are still potentially harmful to the environment because some heavy metals remain in the treated MSWI-FA. In conclusion, some of the shortcomings of the conventional stabilization technologies must be solved, including low long-term stabilization, landfill consuming and high cost of chemical immobilizer.

In recent years, alkali-activated materials (AAM), also called geopolymers (GP) have attracted attention as eco-friendly binder materials and potential alternative to Portland cement (OPC) in specific applications since it produces 75 to 90% less CO₂ than OPC (Davidovits 2013). When two types of concrete have almost the same slump (15.0 cm) and compressive strength (30 MPa), the CO₂ emissions of GP concrete are 35% or 55% of OPC concrete, depending on the source of NaCO₃ (natural or artificial), which is one of the raw materials of sodium silicate (Na₂SiO₃) used as a component of alkali activator (Li 2016). Generally speaking, the carbon footprint of GP concrete is 40 to 60% of that of concrete using only OPC as binder (McLellan *et al.* 2011). Geopolymer is a mix-

ture of amorphous aluminosilicate precursors with excellent Si⁴⁺ and Al³⁺ dissolving ability and at least one type of aqueous alkaline solutions of sodium or potassium silicate, sodium carbonate and hydroxide. Typical precursors from industrial waste are coal fly ash (CFA) and ground granulated blast furnace slag (BFS). Compared with OPC, GP has high acid and fire resistance, and in addition, resistance to alkali-silica reaction. The GP gels, generated through the dissolution and polycondensation process of Si(OH)₄ and Al(OH)₄, have a three-dimensional structure similar to zeolite or quasi-feldspar, which accommodates harmful heavy metal elements by about 90% or more (Davidovits 2015). Besides this physical encapsulation of GP gels, GP is also responsible for immobilizing heavy metals, such as Zn²⁺, Pb²⁺, Cd²⁺, Ni²⁺, etc., in the geopolymer matrices through ion adsorption (Kara *et al.* 2017; Zheng *et al.* 2015). It was reported that little arsenic (As) was incorporated in the pore system and the reaction products of CFA or metakaolin-based geopolymer matrices, but it was apparently associated with iron from dissolved precursors (Fernandez-Jiminez *et al.* 2004, 2005). However, Friedel's salt has a strong fixing capacity for As and heavy metals such as Cr, Pb, Zn and Cd through ion exchange, especially for the anion of AsO₄³⁻ and the cation of Zn²⁺ (Zhang *et al.* 2011; Liu *et al.* 2011). The high content of chlorine in MSWI-FA may be favorable for the formation of Friedel's salt. In addition, geopolymer has a high ability to immobilize radioactive elements such as Ra, U, Sr and Cs, which is very advantageous for disposal of radioactive wastes (Davidovits 1994; Li *et al.* 2016, 2018).

The new pre-treatment methods of MSWI-FA were investigated by taking advantage of the excellent ability of geopolymer to immobilize harmful metals, As and other heavy metals were confirmed to be effectively immobilized (Liu *et al.* 2019, 2021; Tome *et al.* 2018).

The flue gas produced during waste incineration contains much hydrogen chloride (HCl), sulfur oxides (SO_x) and nitrogen oxides (NO_x). Slaked lime [Ca(OH)₂] always is blown into the flue to remove HCl and SO_x, before the MSWI-FA is separated from the flue gas and collected by an electrical dust collector or by a bag filter (Yamashita 2003). Thus, MSWI-FA is highly alkaline (pH>12.0) and contains much CaCl₂, CaSO₄, NaCl, CaCl(OH) and unreacted slaked lime, etc. besides high concentrations of heavy metals and metallic aluminum (Al). It is considered that the metallic aluminum is derived from the aluminum foil paper contained in the garbage.

If the alkali activator (AA) contains sodium silicate, which is used in the preparation of geopolymer with MSWI-FA, the sodium silicate will react rapidly with the unreacted slaked lime and CaSO₄ in the MSWI-FA and causes the geopolymer to solidify early. In addition, in a strong alkaline environment of GP, the metallic aluminum in MSWI-FA generates hydrogen gas and Al(OH)₃ (2Al+6H₂O→2Al(OH)₃+3H₂↑). The formation of

Table 1 Chemical compositions of BFS, CFA and GF (mass %).

Fillers	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Trace elements	Total
BFS	32.68	0.63	13.71	0.37	0.20	45.14	4.92	nd	0.30	0.04	1.80	nd	0.21	100.00
CFA	58.65	1.18	24.66	6.13	0.08	3.61	1.16	1.10	1.62	0.89	0.45	nd	0.47	100.00
GF	7.59	1.42	1.57	1.29	0.12	37.85	0.36	1.52	6.08	2.27	8.39	30.10	1.56	100.12

[Notes] nd: Not detected; GF represents MSWI-FA.

Table 2 Trace elements of BFS, CFA and GF (mass %).

Fillers	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb
BFS	nd	nd	nd	0.0035	nd	nd	nd	nd	nd	nd	nd	0.0600	0.0086	0.0273	nd	nd	0.0736	-
CFA	0.0400	0.0083	0.0065	0.0149	0.0125	0.0174	0.0068	0.0023	nd	nd	0.0083	0.1229	nd	0.0410	0.0024	nd	0.0726	0.0123
GF	nd	0.0160	nd	nd	0.0890	0.7759	nd	nd	0.0070	0.1227	0.0024	0.0467	nd	0.0058	nd	0.0317	nd	0.1956

[Notes] nd: Not detected; GF represents MSWI-FA.

Al(OH)₃ promotes the polycondensation reaction of geopolymer. Therefore, the setting of geopolymer using MSWI-FA is fast (<15 minutes). If the GP with MSWI-FA is not used as a recycling material, only disposed of in landfills, fast setting is desirable. However, recycling the GP with MSWI-FA as construction material requires a suitable setting time for casting and finishing. Moreover, the foaming reaction and hydrogen generation of metallic aluminum in the GP with MSWI-FA will result in high porosity and low strength of GP. Porosity and high specific surface area of MSWI-FA requires much alkali activator (thus large liquid-solid ratio) for preparing GP, which reduces the strength of GP (Tome *et al.* 2018). Moreover, the chloride in MSWI-FA would lower the strength of GP by causing structural discontinuity within the geopolymer gels (Lee *et al.* 2020). For these reasons, it is not easy to produce strong geopolymer products with MSWI-FA.

On the basis of the characteristics of MSWI-FA stated above, for practically recycling geopolymer with MSWI-FA as construction materials, the authors developed porous lightweight geopolymer with addition of MSWI-FA by utilizing its foaming feature in this study without manifesting the problem of the rapid reaction of MSWI-FA with AA since even if MSWI-FA is not added in GP, the setting time of general GP is still very short when foamed by metallic aluminum (Al) or hydrogen peroxide (H₂O₂). The mixtures of GP with MSWI-FA were first examined, then their mechanical and physical properties were measured and the reaction products and microstructure of the foamed geopolymers were investigated by X-ray Diffraction (XRD) and Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) analyses. Finally, the leaching of chloride and heavy metals were discussed for the foamed geopolymers at different ages in acid, neutral and alkaline environments.

2. Materials and methods

2.1 MSWI-FA and other precursors

MSWI-FA used in this study was collected from a municipal solid waste incineration facility in April 2018, as

shown in **Fig. 1**. The MSWI-FA sample is referred to herein as GF. The GF was used in a dry state and has a density of 2.42 g/cm³ and a specific surface area (Blaine value) of 9051 cm²/g, respectively. The porous and rough surface of GF may contribute to this large Blaine value. The chemical compositions of GF obtained by X-ray fluorescence (XRF) analysis are shown in **Tables 1 and 2**. The major components include CaO, SiO₂ and Chlorine, which exceed half of the total mass of GF. The content of heavy metal ranges from 0.007% to 0.776%, the order of content is Zn>Pb>Cu>Cr>As. Though not detected by the XRF analysis due to low content, GF contains a certain amount of metallic aluminum, which foams in alkaline environment.

As shown in **Fig. 2**, the XRD pattern of GF has not obvious broad hump, suggesting that the GF does not almost contain glassy or amorphous phase. Main crystalline phases identified includes sylvite (KCl), halite (NaCl), lime (CaO), portlandite [Ca(OH)₂], calcite (CaCO₃), anhydrite (CaSO₄) and calcium chloride hydroxide [CaCl(OH)], etc. Compared to other mineral materials, GF is characterized by the presence of massive chlorine and lime besides heavy metals and metallic aluminum. This is because the plastics mixed in municipal solid waste are rich in chlorides to generate HCl during the incineration process and the lime blow treatment for neutralizing the acid gas (HCl, etc.) and adsorbing the SO_x in the exhaust fume. It is believed that the CaClOH is formed by the reaction between CaO and



Fig. 1 Municipal solid waste incineration fly ash (MSWI-FA).

HCl. Because of the presence of CaO, Ca(OH)₂ and CaSO₄, the hardening of geopolymer is faster when the alkaline activator consists of sodium silicate. In addition, the foaming reaction of metallic aluminum is very faster in the strongly alkaline environment of geopolymer, as mentioned above.

Geopolymer using MSWI-FA alone has small strength. Therefore, Japanese Industrial Standard (JIS) Class 4000 BFS with density of 2.90 g/cm³ and Blaine value of 4279 cm²/g was mixed. When a large amount of GF are used, the geopolymer would set too quickly due to the CaO, Ca(OH)₂ and CaSO₄ contained in GF, and because of the large specific surface area of GF, a great liquid-solid ratio is required, which makes the cost of geopolymer high. Hence the geopolymer was prepared by replacing a part of coal fly ash (CFA) with GF. The quality of CFA used met with JIS II type, having density of 2.31 g/cm³ and Blaine value of 4392 cm²/g, respectively. The chemical compositions of CFA and BFS, determined by the XRF, are shown in **Tables 1** and **2**. The CaO content of CFA was only 3.61%.

2.2 Alkali activator (AA)

In this study, two kind of AA were used as alkali activator, which were denoted as Aa1 and Aa2 and composed of sodium hydroxide solution (NH) and sodium silicate solution (WG). The WG was prepared by diluting JIS No. 1 sodium silicate (specific gravity: 1.55, mole ratio of SiO₂/Na₂O: 2.07) with tap water at a volume ratio of 1:1, which had specific gravity of 1.27. In case of Aa1, the volume ratio of WG to NH was 7:3 and the NH was a commercial product having molar concentration of 14.3 M, mass concentration of 40% and specific gravity of 1.43. However, for the Aa2, the volume ratio of WG to NH was 1:1, and the NH used had molar concentration of 10 M, mass concentration of 30% and specific gravity of 1.33. The volume ratios of the two AAs were determined to ensure the foamed geopolymer to have a small bulk density, based on the results of parameter studies performed in advance (Hayashi 2020).

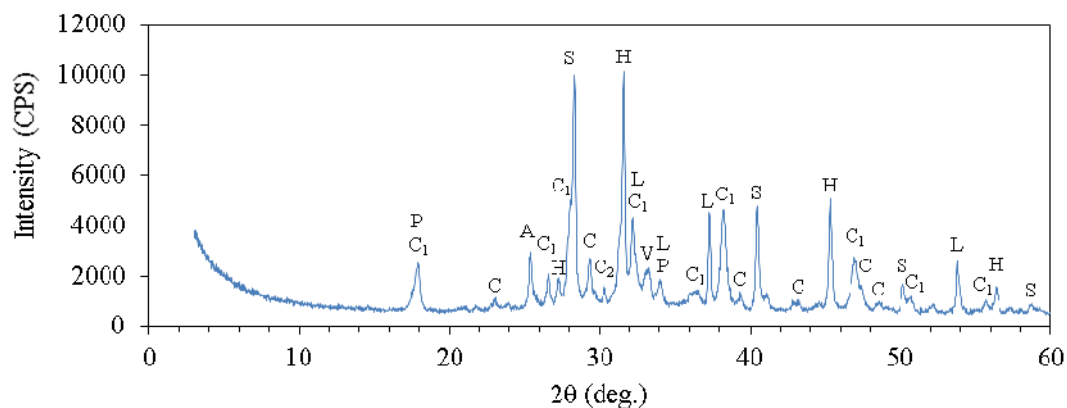
2.3 Additives

Hydrogen or oxygen bubbles are produced when a foaming agent encounters alkaline or alkaline earth binders. Well-known foaming agents include metallic aluminum, metallic silicon and hydrogen peroxide. Compared to metallic aluminum and hydrogen peroxide, the foaming reaction of metallic silicon powder is slow. It is difficult to use metallic silicon powder in the geopolymer with the addition of GF due to rapid setting. However, the foaming reaction of hydrogen peroxide is too rapid to mold geopolymer, and the oxygen produced may accelerate the corrosion of reinforcing steel bars in foamed geopolymer. Therefore, in this study, the metallic aluminum powder (Al) was used as foaming agent. More than 80% of the Al particles were in the size range of 53 to 150 μm.

In a strongly alkaline environment, rapid foaming reaction of Al leads to large bubbles and uneven size distribution of bubbles. Large bubbles may escape from GP during foaming, thus increasing the bulk density, reducing the strength and increasing the thermal conductivity of the foamed GP due to thermal convection. Therefore, the authors compared the performances of foamed geopolymers with and without the foam stabilizer that was zinc stearate {[CH₃(CH₂)₁₆COO]₂Zn} powder with maximum size of 50 μm.

2.4 Mix proportions and specimen preparation

It is not difficult to foam geopolymer by adding foaming agent, but in order to make the foamed geopolymer to have small density, uniform size distribution of voids and desirably high strength, the authors did a lot of exploratory experiments to investigate the effects of many factors on the density of foamed geopolymer (Hayashi *et al.* 2020), including mixing ratio of BFS and GF, AA compositions, dosage of foaming agent, liquid (AA)-solid (BFS+CFA+GF) ratio, temperature, etc. In addition, for investigating the effect of the foam stabilizer on the performances of the foamed geopolymer, in the Mixture 2, the aforementioned foam stabilizer was used. The addition of powder-type foam stabilizer increased the



[Notes] P: Portlandite, Ca(OH)₂; L: Lime, CaO; A: Anhydrite, CaSO₄; C₁: Calcium Chloride Hydroxide, CaCl(OH); C: Calcite, CaCO₃; V: Vaterite, CaCO₃; C₂: Wollastonite, CaSiO₃; H: Halite, NaCl; S: Sylvite, KCl.

Fig. 2 XRD pattern of GF.

Table 3 Mix proportions of foamed geopolymers.
(All the ratios are mass-based).

Mixture	AA	AA/S	BFS/S	CFA/S	GF/S	Al/S	ZS/S
1	Aa1	0.5	0.3	0.6	0.1	0.02	0
2		0.6					0.03
3	Aa2	0.7	0.6	0.2	0.2	0.03	0.02
4							
5			0.03				

[Notes] AA: Alkali activator; S: Filler materials including BFS, CFA and GF; Al: Metallic aluminum powder; ZS: Zinc stearate powder.

viscosity of freshly mixed geopolymer and makes foaming expansion difficult, thus the liquid-solid ratio of Mixture 2 was increased. The mix proportions of five mixtures are shown in **Table 3**, which were determined based on the aforementioned prior investigations to ensure the foamed geopolymer to have a density of less than about 0.6. High AA requirement was resulted from the higher specific surface area of GF.

Two types of test specimens were prepared: 4×4×16 cm prismatic specimen and 30×15×6 cm plate specimen. After mixing the dried GF, BFS and CFA until uniform, the AA solution was added and mixed for 1 minute. The foaming agent was then added and mixed again for 1 minute. When mixing Mixtures 2 to 5, the zinc stearate powder was first mixed with the precursors. After cured at 80°C for 24 hours, the specimens were stored in the 20°C, 60% RH room. This curing method is called heat curing here. Demolding was performed after the 80°C curing. The specimens were sealed with plastic wrap in the entire curing period to prevent moisture evaporation.

2.5 Test methods

At the specified curing ages (7, 28 days), three-point bending test was first performed for each group of prismatic specimens, using an Amsler universal testing machine. Next, compressive strength was measured, using the fractured pieces after the bending test. The flexural and compressive loads were applied on the sides of the prismatic specimens' perpendicular to the casting direction. The flexural strength was an average of three test specimens, but the compressive strength was an average of six fractured pieces. The bulk density was calculated from the mass and volume of the prismatic specimen dried in an oven at 105±5° for over 18 hours.

Thermal conductivity of the foamed geopolymers was measured by the hot wire method, using the plate specimens. In the case of Mixture 1 and 2, the sizes and distribution of the voids were uneven and different between the plate specimens. Therefore, four specimens were used to measure the thermal conductivity for each mixture and two positions were measured for each of the specimens. The thermal conductivity was an average of the 8 measured values for each mixture. However, in the case of Mixtures 3 to 5, the voids were small and their distribution was uniform, thus there was small difference between the plate specimens. Therefore, two plate

specimens were used for each mixture and three positions were measured for each plate specimen. The average of the 6 measured values was taken as the thermal conductivity.

At 28 days of age, the samples of Mixture 1 and 2 were analyzed by the XRD. The analysis conditions were 40 kV and 30 mA of X-ray power, 2 degrees/minute of scanning speed, 0.02-degree step width and continuous scanning angle range of 3 to 60 degrees (2θ). The XRD patterns of BFS, CFA and zinc stearate were also measured under the same conditions.

Raw GF particles were observed by the SEM. In order to evaluate the microstructure and the reaction products of foamed geopolymer, 7 or 28-day-old geopolymers were observed by the SEM and the EDS analysis was conducted for several points. Geopolymer samples were impregnated by embedding with Epofix resin after drying thoroughly and then were polished flat after hardening at room temperature.

To evaluate the potential release of heavy metals from the raw GF and the foamed geopolymers with the addition of GF, leaching tests were conducted. At 7, 28, 91 days after the strength test in the case of Mixture 1 and 7 days for Mixtures 3 to 5, the fractured specimens were crushed (after dried in case of Mixtures 3 to 5) and then sieved out 0.6 to 4.75 mm particles. For each kind of foamed geopolymer and each age, geopolymer sample with a certain mass was taken and put into a polypropylene beaker with leachate in a liquid-solid ratio of 20 (mL/g) and the top of the beaker was then sealed with plastic wrap. Three kinds of leachate were used in this study, which were phthalate pH standard solution (pH 4.01), neutral phosphate pH standard solution (pH 6.86) and caustic soda solution (pH 12.5), respectively. The beaker was placed in an ultrasonic device with deionized water and oscillated with 28 kHz ultrasonic wave for 10 minutes at the ambient temperature (about 20°C). Then, the solution was filtered to get the extraction liquid with the filter paper that had the maximum opening size of 15 μm, meeting with JIS P3801, Class 3. The necessary amount of extraction liquid was taken to do the ICP-AES (induction coupled plasma atomic emission spectrometry) analysis under the axial model to determine the amounts of toxic elements in each undiluted extraction liquid. Although only one extraction liquid was prepared for each foamed geopolymer and for each age, the ICP analysis results were credible because a relatively large GP sample was used to prepare the extraction liquid and the GP matrix was homogeneous in compositions.

The above leaching test was conducted, referring to the rapid analysis method (ultrasonic pretreatment) suggested by the Bureau of Environment, Tokyo Metropolitan Government in 2009 (TMEB 2009), here called ultrasonic oscillation method. The liquid-solid ratio for this method is specified as 10 (mL/g). However, in case of alkaline solid sample, the solution with a liquid-solid ratio of 10 becomes alkaline easily. Therefore, in this study, the liquid-solid ratio was set to be 20 (mL/g). The

Table 4 Detection limits of 8 toxic metal elements (mg/L).

Element	As	Cd	Cr	Cu	Mn	Pb	Se	Zn
Detection limits	0.020	0.003	0.004	0.013	0.004	0.021	0.053	0.011

standard acidic and neutral buffers mentioned above were used as leachates to reduce the pH fluctuation, but the alkaline leachate (caustic soda solution) was not a buffer.

9 kinds of elements were traced, including chromium (Cr), manganese (Mn), copper (Cu), lead (Pb), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd) and chlorine (Cl). The actual leaching concentration (C_i) of each metal element in the extraction liquid was determined by the ICP-AES analysis, while the chlorine leaching concentration was measured by an ion chromatography. **Table 4** shows the detection limits for 8 metal elements.

In this study, the authors have tried to calculate the immobilization efficiency (IE) of arsenic and heavy metal element (here called toxic element). The mass of raw GF included in the foamed geopolymer sample, which was used to prepare the extraction liquid, was calculated based on the mix proportions of the foamed geopolymer (see **Table 3**). The content (C_m) of each toxic element in the foamed geopolymer sample was then calculated according to the contents of toxic elements in the dried raw GF shown in **Table 2**. The IE of toxic element was defined as $(C_m - C_i)/C_m \times 100\%$. When calculating the C_m , toxic elements in the AA were ignored due to extremely small quantities, but toxic elements in the BFS and the CFA were taken into account based on the XRF results shown in **Tables 1** and **2**. In case of Mixtures 3 to 5, since the foamed geopolymer samples before the leaching test were dried, the GF content in per unit dry geopolymer was slightly larger than the value given by the mix proportions shown in **Table 3** because of moisture evaporation. Thus, when calculating the GF content in the dried geopolymer sample, the water content in the mix proportions of Mixtures 3 to 5 was ignored. However, in case of Mixture 1, the used geopolymer samples were not dried before the leaching test so that moisture content was unknown. Therefore, two GF contents had to be used to calculate the C_m . One of GF contents was equal to the mix proportions of Mixture 1 and the other was determined by using the same method as the Mixtures 3 to 5. For this reason, the IEs of Mixture 1 with and without complete evaporation of moisture were calculated, respectively. The actual IE is considered to lie between these two values. However, the IE difference between with and without moisture evaporation was less than 0.5% for all the metal elements. Therefore, the median of the upper and lower IE values was used to evaluate the immobilization ability of Mixture 1.

In addition, in order to judge if the leaching concentrations of traced toxic metals meet with the environmental criteria specified by the National Land Development Technology Research Center, Japan, for recycled construction materials, extraction liquids of Mixtures 3

and 5 were prepared according to the recycled construction material evaluation method (JSCE 2003). This method specifies that leachate should have about a pH of 4.0, the solution containing solid sample with a size of 20 to 50 mm, the leachate with a liquid-solid ratio of 10 (mL/g) should be stirred for 24 hours, and that the extraction liquid obtained by filtering the solution using filter with the opening size of 0.45 μm . Hereafter, this method is briefly called stirring method. Mixtures 3 to 5 are practical because they have the suitable size and distribution of voids and thermal conductivity and Mixture 3 and 4 have almost the same compositions except the aluminum content. Therefore, only Mixture 3 and 5 were analyzed by the stirring method.

In the stirring method, the used leachate was a phthalate buffer solution with a pH of 4.01. First, dried foamed geopolymer was cut into cubes with a side of about 20 mm and two cube samples were randomly selected and placed in a 250 ml plastic bottle. Then, the leachate was added until the liquid-solid ratio reached 10 and a rotor was put into the bottle for magnetic stirring. The magnetic stirring was conducted for 24 hours at a speed of about 200 rpm. After the stirring, the solution was filtered firstly through a qualitative filter paper with a maximum opening size of 10 to 15 μm and then through a membrane filter with a maximum opening size of 0.45 μm to collect extraction liquid. The extraction liquids were also analyzed by the ICP-AES. The analysis result was an average of three extraction liquids for each foamed geopolymer.

3. Results and Discussion

3.1 Appearance of foamed geopolymer

The 28-day-old foamed geopolymers of Mixture 1 and 2 and the 7-day-old foamed geopolymers of Mixtures 3 to 5 are shown in **Fig. 3**. The five geopolymers had a similar gray color. The void size of Mixture 1 without adding the foaming stabilizer was less than 8 mm, while Mixture 2 adding the foaming stabilizer had the void size of less than 4 mm. Though the addition of the foaming stabilizer can decrease the void size, the size distribution of voids in the foamed geopolymers of Mixture 1 and 2 was non-uniform and the maximum size of the voids was large. However, Mixtures 3 to 5 are relatively uniform and the void size was small, which was less than 3 mm. One of the reasons for this was the high molar concentration of the NaOH solution used in Mixture 1 and 2, because the higher the alkalinity of AA, the faster the foaming rate (Hayashi *et al.* 2020). Therefore, it is important to reduce the alkalinity of AA in order to produce foamed geopolymer with uniform and small voids. In the Mixtures 3 to 5, the voids were smaller and more uniform in the order of Mixture 4, Mixture 3 and Mixture 5. Since BFS reacts faster than CFA, more BFS content leads to rapid formation of GP matrix and rapid increase in viscosity of GP matrix, which makes the formation of big bubbles difficult. In addition, small dosage of forming

agent also decreased the forming rate and forming amount, so that the voids of Mixture 4 were the smallest and the most uniform among the five mixtures.

3.2 Physical properties of foamed geopolymer

Figures 4 and 5 show the bulk density and thermal conductivity of the five foamed geopolymers at the age of 7 days (Mixtures 3 to 5) or 28 days (Mixtures 1 and 2), respectively. The bulk density of Mixture 1 was 0.498 g/cm³. In terms of only bulk density, Mixture 1 is suitable as an alternative of usual aerated lightweight concrete (ALC) using Portland cement, because the bulk density of ALC is generally 0.45 to 0.55 g/cm³ according to JIS A 5416: 2016. Mixture 2 had a slightly higher bulk den-

sity, but a lower thermal conductivity than Mixture 1. Mixtures 3 and 5 had the same bulk density and Mixtures 3 to 5 almost had the same thermal conductivity of only 0.099 W/mK, which was much lower than the range 0.15 to 0.19 W/mK for general ALC (as reported by the manufacturer, Asahi Kasei Construction Materials Corp.), even though Mixture 4 had a slightly higher bulk density than Mixture 3 because of smaller Al addition. Due to small density and low thermal conductivity, Mixtures 3 to 5 would be practical as insulation and finishing materials.

3.3 Mechanical properties

Figure 6 shows the flexural and compressive strengths of

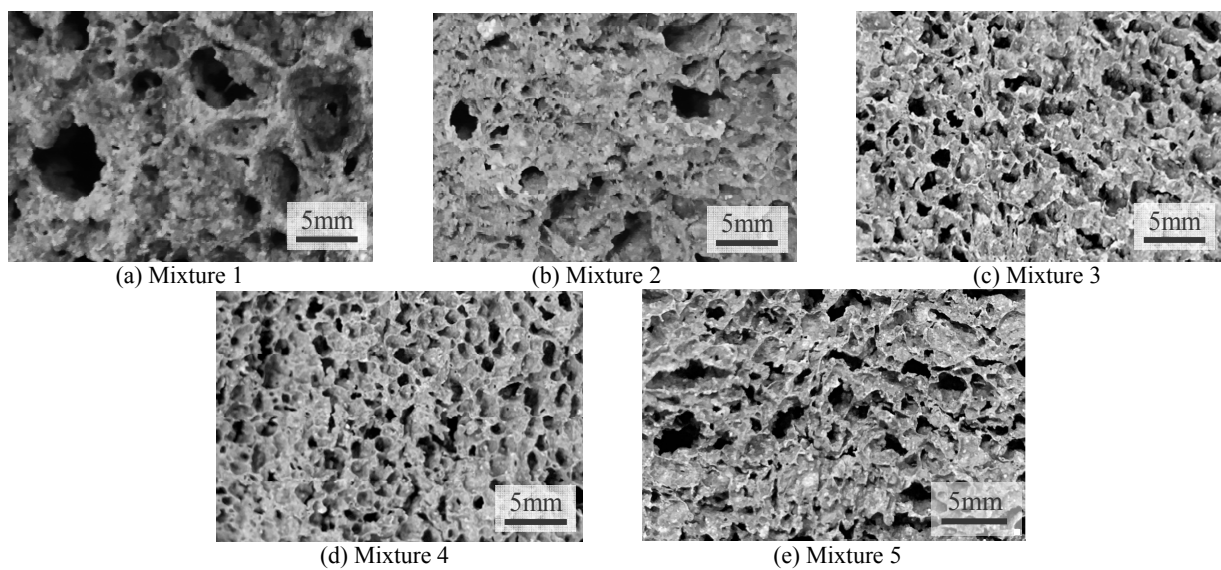


Fig. 3 Foamed geopolymers.

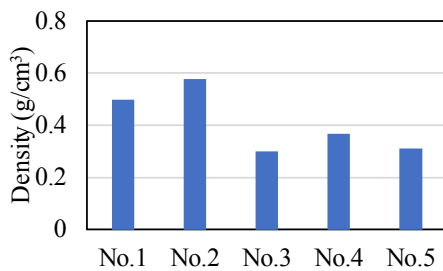


Fig. 4 Bulk density of foamed geopolymer.

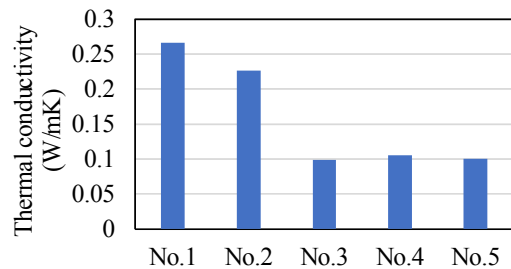
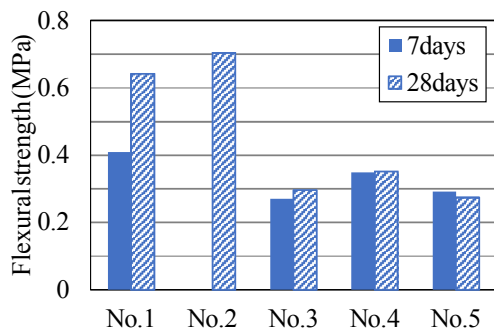
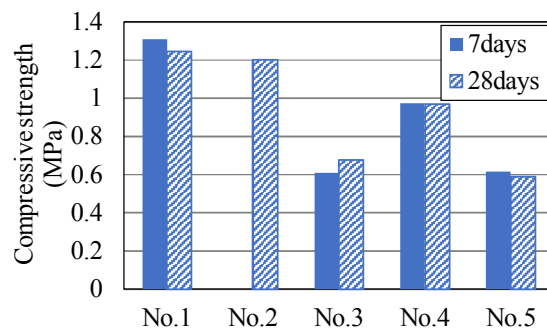


Fig. 5 Thermal conductivity of foamed geopolymer.



(a) Flexural strength



(b) Compressive strength

Fig. 6 Strengths of foamed geopolymers at the ages of 7 and 28 days.

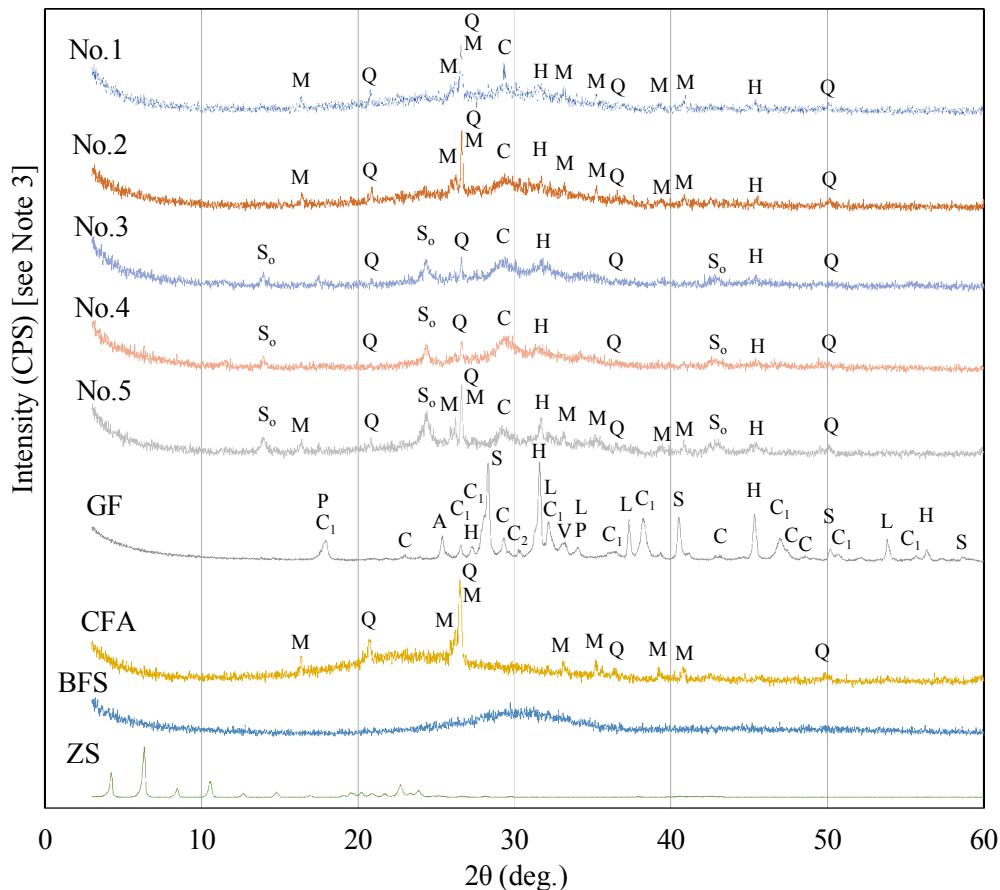
the five foamed geopolymers at different ages. Due to breakage of the 7-day-old specimens, Mixture 2 had no strength test results. In general, larger liquid-solid ratio yields smaller strength. Despite Mixture 2 had a larger liquid-solid ratio than Mixture 1, two series of GP had about the same flexural and compressive strengths at 28 days. This is because Mixture 2 had smaller voids and higher density. In addition, the flexural and compressive strengths of Mixtures 3 to 5 were smaller than Mixtures 1 and 2. This is because their bulk densities were smaller. The strengths of Mixture 4 were slightly greater than the Mixture 3 and 5, of which bulk densities were slightly smaller than Mixture 4. Therefore, it can be said that the bulk density of foamed geopolymer greatly affects its strength.

Regardless of the formulation, the strengths of the foamed geopolymers were low and there was little change between 7 and 28 days of curing age. Therefore, the physical properties and the XRD analysis results at 7 days can be compared with those at 28 days. The SEM images, given later, show that many BFS and CFA particles were incompletely reacted. Since the foamed

geopolymer is porous, water evaporates quickly during the heat curing. The drying during the 80°C curing may interfere the dissolution of Si^{4+} , Al^{3+} and Ca^{2+} from the active fillers to depress the polymerization reaction of GP in long-term. Steam curing would be a solution besides the fiber addition method.

3.4 XRD results

Figure 7 shows the XRD patterns for raw materials and the foamed geopolymers. Mixture 1 and 2 were analyzed at 28 days age, but Mixtures 3 to 5 at 7 days age. Broad hump, centered at around $2\theta=29$ degrees, was observed from all the geopolymers, which corresponds to the amorphous geopolymer gels. The crystalline phases in CFA were quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Two crystalline compounds were found from the Mixtures 1, 2 and 5, in which 60% of the filler materials was CFA. However, in the Mixtures 3 and 4, there was no mullite, which used only 20% of the CFA. In addition, sodalite ($Na_4Al_3(SiO_4)_3Cl$) peaks were observed in Mixtures 3 to 5 adding more GF (20%) than Mixtures 1 and 2. It is considered that the sodalite was produced due to large



[Note 1]: M: Mullite, $3Al_2O_3 \cdot 2SiO_2$; Q: Quartz, SiO_2 ; C: Calcite, $CaCO_3$; V: Vaterite, $CaCO_3$; H: Halite, NaCl; S: Sylvite, KCl; S₀: Sodalite, $Na_4Al_3(SiO_4)_3Cl$; P: Portlandite, $Ca(OH)_2$; L: Lime, CaO; A: Anhydrite, $CaSO_4$; C₁: Calcium Chloride Hydroxide, $CaCl(OH)$; C₂: Wollastonite, $CaSiO_3$.

[Note 2]: Crystalline compounds with underlines have distinct peak differences between the GF and the geopolymers.

[Note 3]: The XRD patterns in this figure are offset in the vertical direction to make the comparison easy, and the vertical axis does not show directly the actual intensity value of the refracted X-rays.

Fig. 7 XRD patterns of raw materials and foamed geopolymers.

amount of chlorine from the GF. However, the peaks found from the zinc stearate powder were not observed in the five geopolymers. This may be because the dosage of zinc stearate was too small, or the zinc (Zn) element was fixed into GP matrix like other heavy metal elements.

As shown in **Fig. 7**, the Ca(OH)_2 , CaO and CaSO_4 were not found in the foamed geopolymers, which reacted off with sodium silicate. The peaks of CaCl(OH) also disappeared in the XRD patterns of the geopolymers. It is considered that the CaCl(OH) was consumed due to the reaction of $\text{CaCl(OH)} + \text{NaOH} \rightarrow \text{Ca(OH)}_2 + \text{NaCl}$ and the formed Ca(OH)_2 further reacted off with sodium silicate. The peaks of CaCO_3 were observed in the geopolymers. This result indicates that the CaCO_3 contained in the GF was not involved in the alkali-activated reaction. Low NaCl peaks were found in the geopolymers, the presence of NaCl may be due to original component of the GF and the chemical bond of Cl^- and Na^+ ions. Cl^- and Na^+ ions came from the GF, the decomposition of CaClOH and the AA solution, respectively. However, sylvite (KCl) peak was not found, suggesting the KCl was incorporated into the GPs. The peak intensity of

CaCO_3 of Mixture 1 was greater than that of Mixture 2. This is due to the large voids of Mixture 1, which makes Mixture 1 prone to carbonation. It is noted that the peak of Friedel's salt $[\text{Ca}^{2+} + \text{Al(OH)}_4^- + \text{Cl}^- + \text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}]$ was not found in the five geopolymers, which was identified in the non-foamed geopolymers with 0% and 40% lead smelting slag (Liu *et al.* 2019). The peak of MgCO_3 was not found from the GF's XRD chart and the GPs due to small content below the XRD detection limit.

3.5 SEM results

The surface morphologies of GF sample determined by SEM are shown in **Fig. 8**. It can be seen that the GF mainly consists of porous particles and irregular particles with rough surface. The tiny particles were agglomerated together to form the clusters with porous, rough and loose structure. This is due to low incineration temperature of 800 to 1000°C, which is below the melting temperatures of most minerals. Therefore, the GF had a larger specific surface area than the coal fly ash particle that has smooth spherical surface. **Figure 9** shows the results of EDS analysis. The GF mainly contained Ca, Cl,

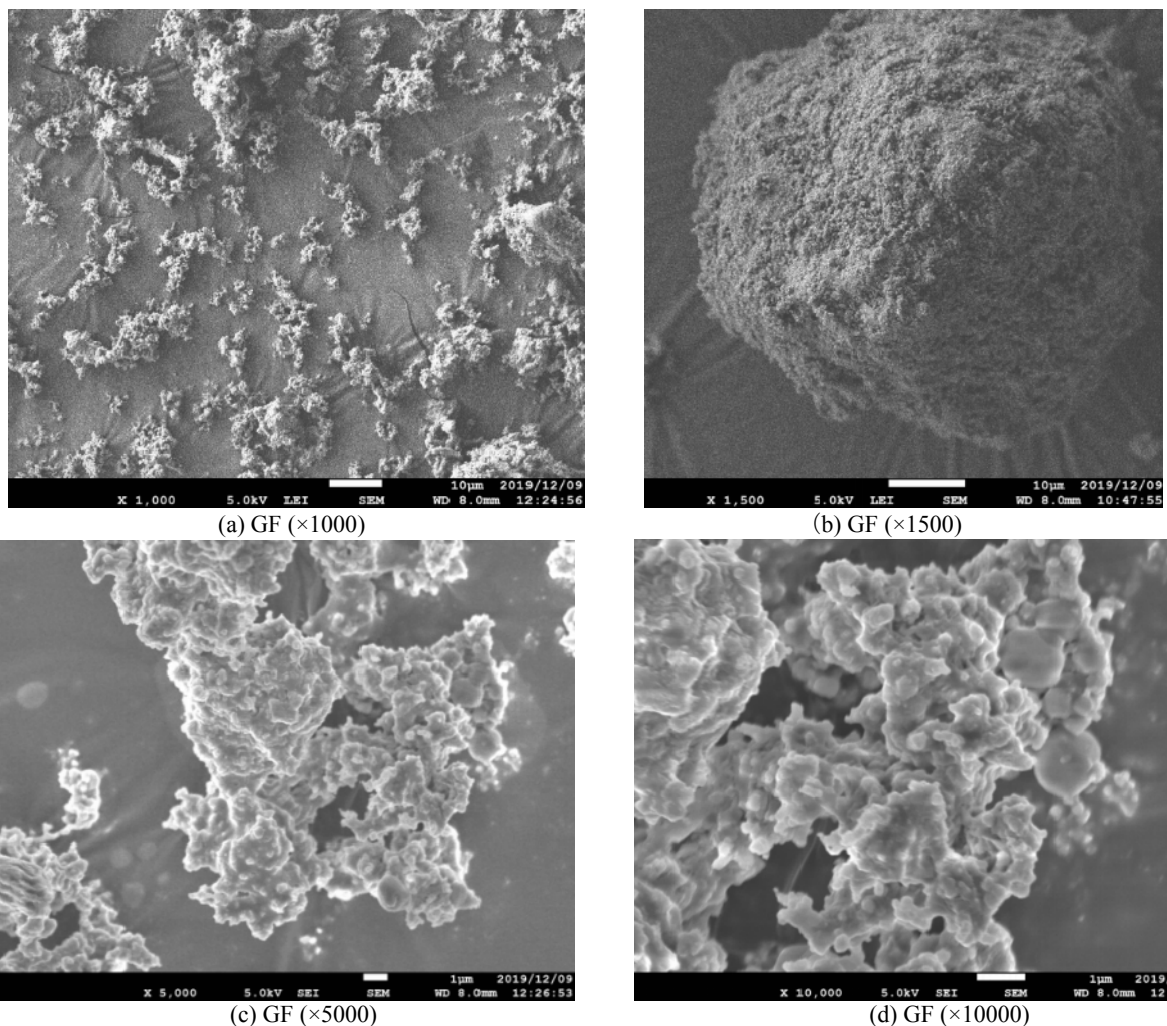


Fig. 8 SEM images of GP sample.

Na and K, small amounts of S and Si were also detected, which are consistent with the XRF analysis.

Figure 10 shows the selected micrographs of GP matrices. Based on the results of EDS analysis omitted here, the substances in some local areas were noted. The analyzed geopolymer matrices located between the large voids and contained small pores. The GP matrices were not dense and had cracks. It is thought that the cracks were caused by the dry shrinkage during the 80°C curing. Incompletely reacted CFA and BFS particles were found. Although many CFA particles are not completely reacted, their white outlines suggest that their surfaces had been dissolved by the AA solution [see **Fig. 10(a)**]. Black particles were observed in **Figs. 10(a)** and **10(b)**. The round black particles in **Fig. 10(a)** were incompletely reacted CFA particles, whereas the irregular black particles were quartz particles. From **Fig. 10(a)**, the hybrid compound of $\text{CaCO}_3/\text{MgCO}_3$ was also observed, of which the outer CaCO_3 covered the central MgCO_3 . In addition, as shown in **Figs. 10(c)** and **10(d)**, KCl and NaCl crystal particles were found, though KCl and MgCO_3 peaks were not found in the XRD patterns of geopolymers. The three areas that appeared to be loose were actually part of the inner walls of voids. The obliquely dense band from top to bottom shown in **Fig. 10(d)** was enriched in Si^{4+} and Al^{3+} , but almost did not contain Ca^{2+} . Its composition is presumed to be N-A-S-H gel, where C, N, A and H denote CaO , Na_2O , Al_2O_3 , SiO_2 and H_2O , respectively, since there were many CFA particles nearby.

As shown in **Fig. 10(e)**, the geopolymer matrix of Mixture 3 using 60% of BFS was dense, which was C-A-S-H gels according to the EDS analysis results, though there were many fine cracks probably caused by drying shrinkage. In addition, almost no unreacted CFA particles were observed, but there were incompletely

reacted BFS particles and GF particles. Moreover, many sodalite crystals were observed from **Fig. 10(f)**. This is consistent with the results of XRD analysis. On the other hand, from **Figs. 10(g)** and **10(h)**, CFA and BFS particles that remained undissolved were confirmed in Mixture 5. Though the mixing ratio of BFS was only 20%, C-A-S-H gel was found in the geopolymer matrix of Mixture 5 other than N-A-S-H gel. The areas marked by the dotted lines were rich in Ca, Mg and Cl according to the EDS analysis and were porous as can be seen in **Figs. 10(g)** and **10(h)**. In these areas, there might be calcium/magnesium chloride hydroxide [$\text{Ca, MgCl}(\text{OH})$] from GF.

Moreover, the geopolymer matrices of Mixture 2 were further analyzed by SEM-EDS at the 22 spots shown in **Fig. 11**. The atom percentages of the analyzed elements were converted respectively to the molar percentages of their oxides. The molar percentages of the oxides are shown in **Table 5**. In the area A*, the big black particle was a pore filled with Epofix resin during the sample preparation, containing mostly carbon. The crystals in the spots 1 and 2 were calcite (CaCO_3), the spot 8 was quartz crystal, the spot 13 and 10 were incompletely reacted CFA particle and spots 3 and 4 were residues of incompletely reacted BFS and GF on the basis of the CaO content. The matrix gels of geopolymer are generally called N-A-S-H and C-A-S-H, though strictly speaking, they should be called Na-rich N-C-A-S-H and Ca-rich N-C-A-S-H gels, respectively. The presence of C-A-S-H gel and N-A-S-H gel was identified from the SEM images, the former shows sponge-like texture with $\text{CaO}/\text{Na}_2\text{O} > 1.0$ in molar, but the latter has a flat plate structure with $\text{CaO}/\text{Na}_2\text{O} < 1.0$ (Li *et al.* 2018). In this study, two gels were distinguished using the molar ratio of $(\text{C}+\text{M})/(\text{N}+\text{K})=1.0$, where C, M, N and K represent CaO , MgO , Na_2O and K_2O , respectively, because MgO

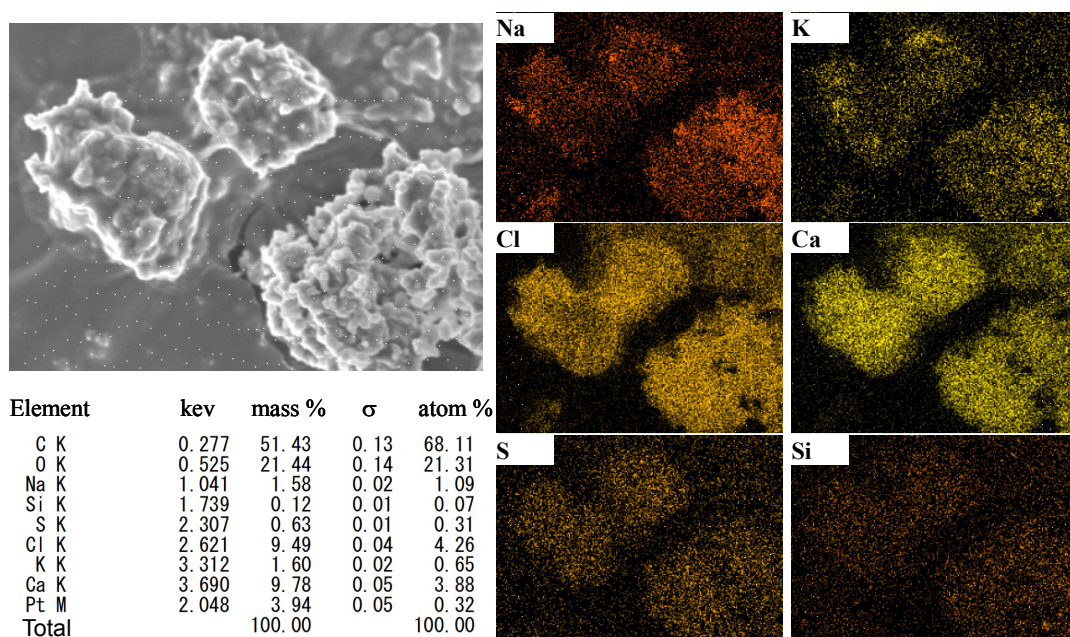
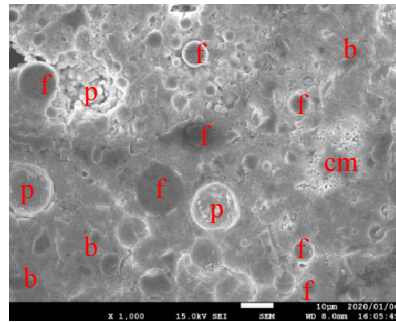


Fig. 9 SEM-EDS analysis of GF.

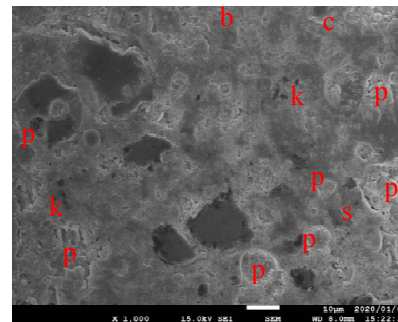
and K_2O components were found in the foamed geopolymer and CaO and MgO , Na_2O and K_2O are the same type of oxides, respectively. According to these criteria, the authors assumed that there were C-A-S-H gels in the spot 7, 9, 11, 12, 14, 15 and 16. In these spots, the mole ratios of $(C+M)/(N+K)$ were larger than 1.0, indicating that there was much Ca or Mg. However, in the spot 5 and 6, the mole ratios of $(C+M)/(N+K)$ were less than 1.0, which suggests that in the two spots N-A-S-H gels might be formed.

On the other hand, in the area B*, the $(C+M)/(N+K)$ of the spots 17 to 20 were less than 1.0, but the spots 21 and 22 had the mole ratios beyond 1.0. Hence, it is considered that there were N-A-S-H gels in the spots 17 to 20, but the spots 21 and 22 had C-A-S-H gels. The spots 17 to 20 were nearby the voids. Foaming reaction of Al powder may provide many Al^{4+} , which contributed to the formation of N-A-S-H gels in the spots 17 to 20.

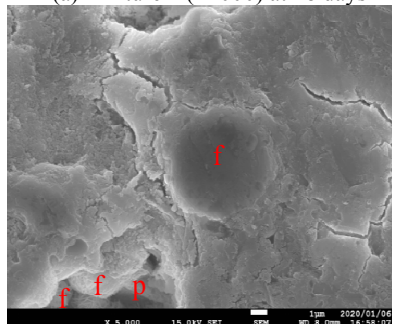
The point analyses were also performed on the geopolymer matrices of Mixtures 3 and 5 and most of the



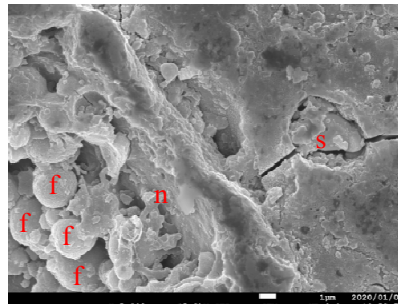
(a) Mixture 1 ($\times 1000$) at 28 days



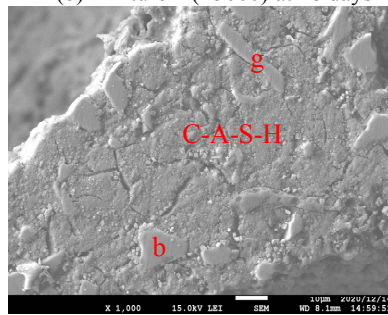
(c) Mixture 2 ($\times 1000$) at 28 days



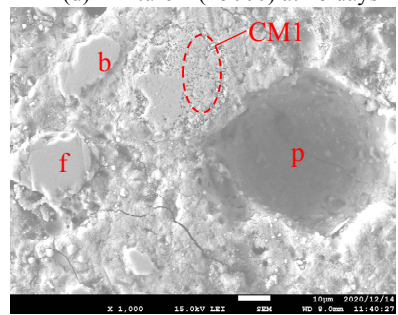
(b) Mixture 1 ($\times 5000$) at 28 days



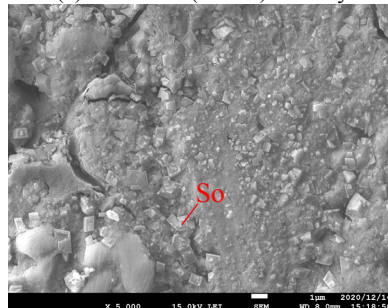
(d) Mixture 2 ($\times 5000$) at 28 days



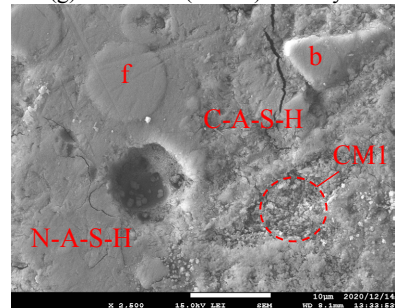
(e) Mixture 3 ($\times 1000$) at 7 days



(g) Mixture 5 ($\times 1000$) at 7 days



(f) Mixture 3 ($\times 5000$) at 7 days



(h) Mixture 5 ($\times 2500$) at 7 days

[Note]: p: Pore; f: Incompletely reacted CFA; b: Incompletely reacted BFS; g: GF particle; n: NaCl particle; k: KCl particle; cm: Coexistence of $CaCO_3$ and $MgCO_3$; c: Calcite particle, So: Sodalite; CM1: Ca, $MgCl(OH)$.

Fig. 10 SEM images of foamed geopolymers.

Table 5 Results of SEM-EDS point-analysis for Mixture 2.

Spot	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Cl	(C+M)/(N+K)	Composition
1	3.51	0.00	1.43	0.00	92.92	0.00	0.00	0.00	1.59	0.54	*	Calcite
2	3.67	0.00	1.59	0.00	92.32	2.42	0.00	0.00	0.00	0.00	*	Calcite
3	35.30	0.00	2.81	0.00	56.96	1.00	0.76	0.00	1.54	1.63	76.16	Residues of BFS and GF
4	10.93	0.00	8.60	0.00	63.83	16.65	0.00	0.00	0.00	0.00	*	
5	69.46	0.00	29.13	0.00	0.63	0.00	0.33	0.45	0.00	0.00	0.81	N-A-S-H gel
6	47.36	0.00	29.24	0.00	6.34	0.00	10.34	0.83	3.11	2.78	0.57	N-A-S-H gel
7	51.57	0.00	11.99	1.04	22.47	1.50	4.77	1.20	1.81	3.66	4.02	C-A-S-H gel
8	99.03	0.00	0.54	0.00	0.00	0.00	0.43	0.00	0.00	0.00	*	Quartz
9	54.98	0.00	8.09	1.23	20.60	1.13	5.72	1.85	2.26	4.13	2.87	C-A-S-H gel
10	90.74	0.00	2.78	0.00	3.14	0.50	1.59	0.27	0.00	1.00	1.96	CFA particle
11	16.04	0.00	6.28	0.00	68.48	7.25	0.00	0.00	0.00	1.95	*	C-A-S-H gel
12	18.31	0.00	7.63	0.00	62.60	8.89	0.00	0.00	0.00	2.57	*	C-A-S-H gel
13	80.60	2.47	10.03	1.44	1.30	1.11	1.45	1.59	0.00	0.00	0.79	CFA particle
14	66.66	0.00	8.80	0.00	10.69	1.01	6.00	1.15	2.12	3.57	1.64	C-A-S-H gel
15	56.51	0.00	19.41	1.89	12.65	1.05	3.25	1.29	1.64	2.31	3.02	C-A-S-H gel
16	52.78	0.00	9.42	1.99	19.41	1.15	3.35	2.43	2.69	6.79	3.56	C-A-S-H gel
17	65.80	0.00	12.42	0.74	4.79	1.31	7.15	0.74	3.22	3.83	0.77	N-A-S-H gel
18	49.29	0.00	18.02	0.00	7.59	1.54	14.54	0.90	4.25	3.86	0.59	N-A-S-H gel
19	55.37	0.00	19.25	1.65	6.05	0.00	10.98	1.13	0.00	5.57	0.50	N-A-S-H gel
20	54.41	0.00	20.00	0.00	9.26	1.02	10.04	0.93	0.00	4.34	0.94	N-A-S-H gel
21	50.89	0.00	18.92	1.03	11.69	0.00	9.64	1.05	3.13	3.65	1.09	C-A-S-H gel
22	56.75	10.86	13.22	3.05	5.16	2.48	4.19	1.46	1.64	1.19	1.35	C-A-S-H gel

[Note] The asterisks (*) indicate values that could not be calculated because the denominator is zero.

products were C-A-S-H gels. In summary, the main product of foamed geopolymer using BFS, CFA and GF was C-A-S-H gel, though few N-A-S-H gels were also found.

3.6 Leaching of toxic metal elements

Figure 12 shows the immobilization efficiency (IE) of heavy metal elements, measured by the ultrasonic oscillation method. As explained above, in case of Mixture 1, the IE was an average of the lower and upper IE values,

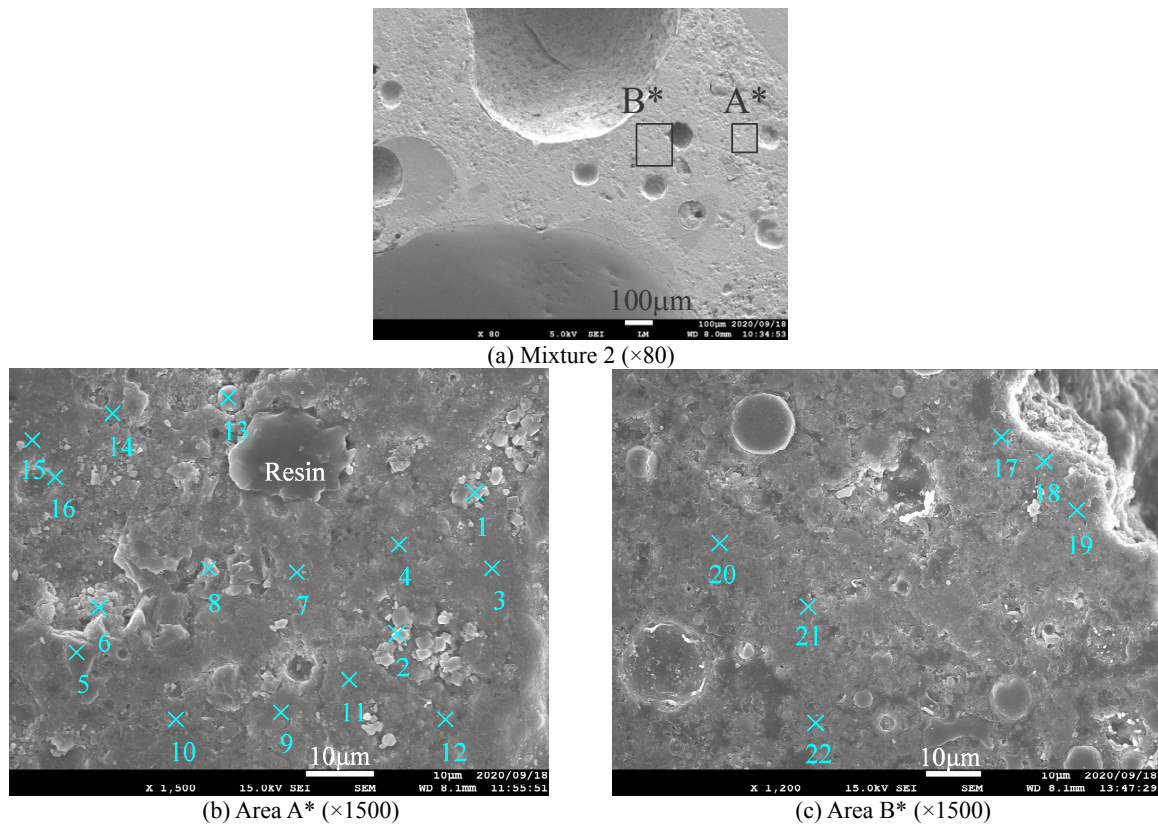


Fig. 11 The spots of EDS analysis of foamed geopolymer (Mixture 2).

while in case of Mixtures 3 to 5, the IE was gotten by using the dried foamed geopolymer sample. In addition, the calculation of IE assumed that the toxic elements of GF are soluble. This time it cannot be said that the IE is completely proper, but the IE values obtained under the same conditions can be used to compare the immobilization efficiencies of the same geopolymer in different leaching environments. It can be seen from Fig. 12 that in any of the three leachates, the toxic elements almost did not leach from any of the foamed geopolymers except As and the IE of each toxic element was above 98%. That is to say, the pH of leachate does not affect the GP's immobilization capacity of heavy metal elements. This is attributed to the chemical immobilization of heavy metals assimilated as charge-balancing elements and physical encapsulation of heavy metals fixed into the 3-dimensional GP gel structure (Izquierdo 2009). In neutral and alkaline environments, Zn and Mn were excellently immobilized in the geopolymers, but in neutral environment, the immobilization of Cr was somewhat weak, which met with the MSWI bottom ash-based geopolymer (Chen 2016). It has been reported that Cr (VI) is much more leachable than Cr (III) and cannot be effectively immobilized in geopolymer (Zhang *et al.* 2008). It is considered that the valence of Cr may change from Cr (III) in GF to Cr (VI) in the foamed geopolymers.

However, the immobilization efficiency of As depended on the pH of leachate and the mixing ratio of BFS. When the mixing ratio of BFS was 10% or 20%, the IE of As was 80 to 92% and did not greatly change with the pH of leachate. When the mixing ratio of BFS was 60% (Mixture 3 and 4), the IE of As was more than 95% and increased with increasing the pH of leachate. The high pH of geopolymer enhances the oxyanionic element mobility, increasing the leaching of As and Se that are not assimilated within the geopolymer structure but remain presumably encapsulated (Izquierdo 2009). However, Friedel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) has a

strong fixing capacity for As through anion exchange (Zhang *et al.* 2011; Min *et al.* 2019). If considering the composition of Friedel's salt, the formation of Friedel's salt needs more dissolution of Ca^{3+} and Al^{3+} . Compared to CFA, the dissolution of Ca^{2+} and Al^{3+} from BFS is easy. Hence, The IEs of As of Mixture 3 and 4 using 60% BFS were high, as shown in Fig. 12. The immobilization capacity of As increases with the mixing ratio of BFS and when the mixing ratio of BFS is 40% it becomes obviously low (Liu 2013). Hence, the Mixture 4 adding 60% of BFS is suitable for the immobilization of As. In the foamed geopolymers, the IEs of heavy metals did not change with the material age except As, since the IEs were high even in the early age. However, the IE of As increased with the age of GP, as shown in Fig. 12.

Table 6 shows the leaching concentrations of traced toxic metals in the GF and the four foamed geopolymers in different pH leachates and at different ages, measured by the ultrasonic oscillation method. The leaching concentrations of toxic metals from the geopolymers were reduced by one to three orders, as compared to those from the raw GF. Except As, the leaching concentrations were lower than the leaching limits established by Japanese government for the recycled construction materials of general waste incineration residues used in water environment (JSCE 2003). From the results given in Table 6, it was found that if the mixing ratio of BFS was 60% and the foamed GPs were not in acid environment, the As leaching concentration satisfied the environmental limit too. The leaching concentrations of Cd and Se were not detected in almost all the foamed geopolymers, which were below the instrumental detection limits, as shown in Table 4. The content of Se in the raw GF was so few that it also could not be detected in the XRF. Moreover, at spectral wavelengths of 196.026 nm and 203.985 nm, the peaks of Se are very close to or even overlap with those of Mn (196.025 nm) and Cr (203.991 nm), which is one of the reasons why the Se leaching concentration could not be measured accurately

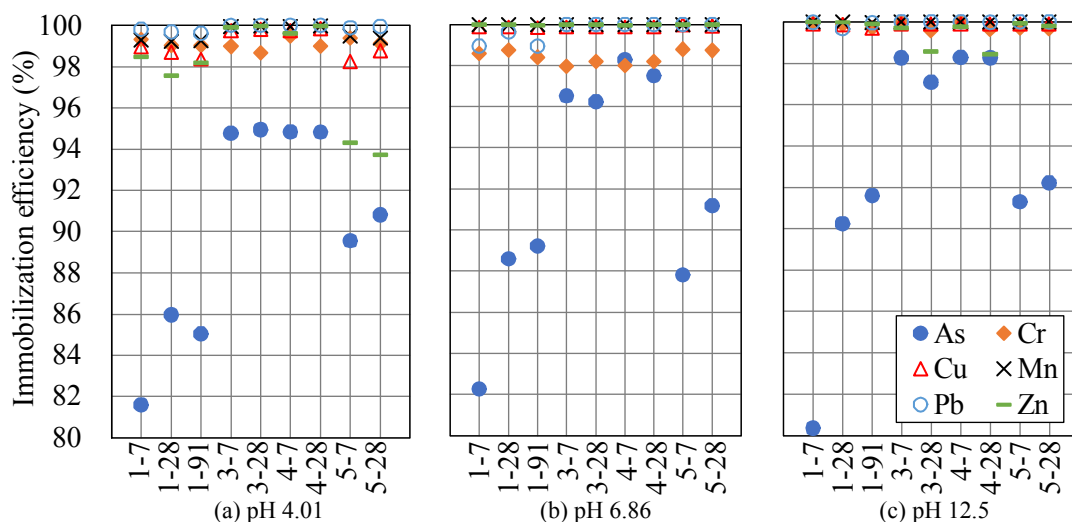


Fig. 12 Immobilization efficiency of toxic elements in different pH leachates for different geopolymer samples [lateral axis: Series No. of mixture+age (days)].

Table 6 Leaching concentration (mg/L) of traced toxic elements.

Element	pH of leachate	Raw GF	CFA	BFS	Mixture 1			Mixture 3		Mixture 4		Mixture 5		Leaching limit ^a
					7 days	28 days	91 days	7 days	28 days	7 days	28 days	7 days	28 days	
Cr	4.01	0.15	0.15	0.03	0.02	0.02	0.02	0.02	0.03	0.01	0.02	0.02	0.03	0.05 ^b
	6.86	0.24	0.1	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
	12.5	0.11	0.03	nd	nd	nd	0.01	nd	0.01	nd	0.01	0.01	0.01	
Cu	4.01	nd	0.14	nd	0.06	0.08	0.10	0.02	0.02	0.02	0.01	0.18	0.12	None
	6.86	nd	0.01	nd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	nd	0.01	
	12.5	nd	nd	nd	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	
Mn	4.01	nd	0.66	2.44	0.22	0.27	0.26	0.02	nd	0.02	nd	0.18	0.21	None
	6.86	nd	0.07	0.09	0.01	nd	0.01	nd	nd	nd	nd	nd	nd	
	12.5	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd	
Pb	4.01	0.07	nd	nd	0.02	0.03	0.04	nd	nd	nd	nd	0.02	0.01	0.01
	6.86	0.01	nd	nd	0.04	0.04	0.11	nd	nd	nd	nd	nd	nd	
	12.5	0.29	nd	nd	nd	0.04	0.01	nd	nd	nd	nd	nd	nd	
Zn	4.01	0.15	0.13	0.02	0.45	0.81	0.60	0.05	nd	0.24	nd	3.84	4.23	None
	6.86	0.04	0.01	nd	nd	nd	0.01	0.01	nd	0.03	nd	nd	nd	
	12.5	0.90	nd	nd	nd	0.01	0.04	0.19	0.93	0.15	1.02	0.05	0.14	
As	4.01	0.02	0.23	0.03	0.05	0.04	0.04	0.03	0.03	0.03	0.03	0.06	0.05	0.01
	6.86	0.02	0.12	0.01	0.04	0.03	0.03	0.02	0.02	0.01	0.01	0.07	0.05	
	12.5	0.01	nd	0.01	0.04	0.03	0.02	0.01	0.02	0.01	0.01	0.05	0.04	
Cd	4.01	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	0.02	0.02	0.01
	6.86	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
	12.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
Se	4.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01
	6.86	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
	12.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	

[Notes] *nd*: Concentrations that were too small to be detected; *a*: Japanese environmental criteria values (Environment Agency Notification No. 46) for recycled construction materials contacting directly with water; *b*: Environmental criteria value of Cr (VI).

Table 7 Results of standard dissolution test (mg/L).

Mixture	Cr	Cu	Mn	Pb	Zn	As	Cd	Se
3	0.05	0.01	nd	nd	0.02	0.04	nd	nd
5	0.11	0.01	nd	nd	nd	0.09	nd	nd
Leaching limit ^a	0.05 ^c	None	None	0.01	None	0.01	0.01	0.01
Leaching limit ^b	0.15 ^c	None	None	0.03	None	0.03	0.03	0.03

[Notes] *nd*: Concentrations that were small to be detected; *a*: Japanese environmental criteria values for recycled construction materials contacting directly with water; *b*: Japanese environmental criteria values for recycled construction materials used without water contact; *c*: Environmental criteria value of Cr (VI).

in the ICP-AES analysis.

Table 7 shows the leaching concentrations of toxic metals from Mixture 3 and 5, which were measured by the stirring method. The leaching concentrations of Mn, Pb, Cd and Se were too small to be detected. Except As, other toxic metals' leaching concentrations were not beyond the leaching limits for recycled construction materials used without water contact (JSCE 2003).

The As leaching concentration of Mixture 3 was 0.04 mg/L, which was slightly larger than the leaching limit (0.03 mg/L) for recycled construction materials used without water contact. However, during the solution consisting of leachate and foamed geopolymer sample with an initial size of about 20 mm was stirred for 24 hours in order to prepare the extraction liquid used for the ICP-AES analysis, the GP sample was gradually broken up to small sizes beyond the range (20 to 50 mm) specified by the stirring method due to their low strength. The small size and porous nature of the GP samples resulted

in more contact with the leachate, so that the toxic metals' leaching concentrations might be overestimated. The preparation of extraction liquid of porous and weak material is an issue. Therefore, the leaching concentration of As in foamed geopolymer using more than 60% of BFS is likely to satisfy the leaching limit (0.03 mg/L).

3.7 Chlorine leaching

The preparation method of the extraction liquid for the leaching concentration analysis of chloride ion (Cl) was the same as that for the toxic metals. However, the leaching concentration of Cl in the neutral leachate (pH=6.86) was determined by an ion chromatography with a precise of 0.1 mg/L, according to JIS K 0102:2019. The chlorine content in the foamed GP sample was calculated based on the mix proportions of GP and assuming that the chlorine in the raw GF was in a free state because the chlorine ions of GF were present in KCl, NaCl and CaClOH, and that the CaClOH had reacted to release its

Table 8 Leaching concentration and immobilization efficiency of chlorine measured for Mixture 1 at different ages.

Age	Leaching concentration (mg/L)	IE (%)
28 days	480	58.0
91 days	360	68.5

chlorine ion, as shown in **Fig. 7**. The geopolymer samples were 28-day and 91-day old Mixture 1. Since the water content of geopolymer sample was unknown prior to the leaching experiment, two immobilization efficiencies (IE) of chlorine were calculated for the dry and wet conditions, respectively. The average of the two IEs is shown in **Table 8**.

As shown in **Table 8**, the IE of chlorine of Mixture 1 was 58.0% at 28 days and rose to 68.5% at 91 days. In case of Portland cement, it is considered that Friedel's salt immobilizes chlorine. Concrete using OPC as binder has a chlorine fixation capacity of 50 to 60%, but when above 50% of OPC is replaced by fly ash, the chlorine fixation capacity decreases greatly to about 25% (Miura *et al.* 2011). For geopolymer, it is believed that geopolymer gels (N-A-S-H and C-A-S-H) can accommodate chlorine into them as chlorine has a preference to incorporate into N-A-S-H gels in particular (Li *et al.* 2018). If there are sufficient amounts of $\text{Ca}(\text{OH})_2$, Cl^- and Al_2O_3 , Friedel's salt may be formed to stabilize more chlorine in geopolymer. This time the Friedel's salt was not found in the foamed geopolymers from the XRD results. This may be due to the rapid drying of the foamed geopolymers during the 80°C curing, which prevented the CFA from dissolving significantly to release more Al_2O_3 . The SEM-EDS analysis described above confirmed the presence of incompletely reacted CFA particles and the formation of C-A-S-H gels, which suggests the insufficiency of Al_2O_3 . Thus, it was judged that the chlorine ions were present in the geopolymer gels and in KCl, NaCl crystals. Since the IEs of heavy metals of other mixtures were not lower than those of Mixture 1, the chlorine immobilization capacities of Mixtures 2 to 5 are estimated to be above 70% in a long-term age though the measurement has not been done.

Because of the small mixing ratio of GF, the total amount of free chlorine ions in the foamed geopolymer is so small that they may not promote the corrosion of steel reinforcement. Moreover, the reinforcement built into ALC, such as rebar mat and steel wire mesh, are usually pre-treated to prevent corrosion. Therefore, high chloride content of GF will not affect the practical use of foamed geopolymer.

4. Conclusions

In this study, in order to develop a technology to recycle the municipal solid waste incineration fly ash (MSWI-FA) safely, the authors first discussed the mixture method of foamed geopolymer with addition of MSWI-FA and then investigated the various properties of

the foamed geopolymers, including bulk density, strength, thermal conductivity, leaching concentration and immobilization efficiency of heavy metals and chlorine. The polymerization reaction products, crystalline compounds and microstructure for the foamed geopolymers were also examined through XRD and SEM-EDS analyses. The conclusions obtained are as follows.

Since MSWI-FA contains metallic aluminum, it is difficult to achieve high strength due to the foaming reaction when making ordinary geopolymer. However, this feature makes it possible to produce foamed geopolymer by adding additional aluminum powder.

- 1) MSWI-FA contains CaO , $\text{Ca}(\text{OH})_2$ and CaSO_4 , which make the geopolymer using MSWI-FA to set very quickly. Therefore, when producing foamed geopolymer, the addition of MSWI-FA should not be too much, less than 20% is appropriate and the foaming agent with fast foaming reaction is preferred.
- 2) Strong alkali leads to the foaming reaction being too rapid, resulting in large bubbles, uneven void distribution and rapid setting of geopolymer. The molar concentration of NaOH used in alkali activator should not exceed 10 M/L.
- 3) In addition to CaO , $\text{Ca}(\text{OH})_2$ and CaSO_4 , KCl, NaCl, $\text{CaCl}(\text{OH})$ and CaCO_3 etc. were found in the MSWI-FA. CaO , $\text{Ca}(\text{OH})_2$, CaSO_4 , KCl and $\text{CaCl}(\text{OH})$ disappeared in the foamed geopolymers, but sodalite was detected in the foamed geopolymers with 60% of BFS. The geopolymers, using BFS, CFA and MSWI-FA as precursors, consisted of C-A-S-H gels, incompletely reacted precursors and a small amount of N-A-S-H gels.
- 4) The foamed geopolymer had very high immobilization capacity of heavy metals (Cd, Cr, Cu, Mn, Pb, Zn) except As. The immobilization efficiency of As changed with the pH of leachate and BFS content. Compared to the acid leaching environment, the immobilization efficiency of As in the neutral and alkaline environments was higher. When the mixing ratio of BFS was not less than 60%, the immobilization efficiency of As became high, all the leaching concentrations of traced heavy metals including As satisfied the Japanese leaching criteria for recycled construction materials that do not directly contact with water. That is to say, from the point of view of heavy metal hazards it is safe to use the foamed geopolymer without direct contact with water, which uses less than 20% of MSWI-FA and more than 60% of BFS.
- 5) The chlorine immobilization capacity of the foamed geopolymer is expected to exceed 70% in a long-term age. Geopolymer gels (N-A-S-H and C-A-S-H) can accommodate chlorine. In particular, chlorine has a preference to incorporate into N-A-S-H gels.

Acknowledgments

We would like to thank Sanko Holdings Co., Ltd. for the financial support of this research project and Mr. K.

Shooji and Mr. H. Satou, employees in Sanko Holdings, for their experimental collaboration.

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