# Recycling of Fly Ash Resource in Ceramic Processing: Reaction Mechanism and Structure Controlling

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Fly ash, an industrial waste, is utilized as a valuable ceramic resource owing to its components, spherical morphology, and porous structure. Utilizing its characteristic physical properties, fly ash has been widely reused as an admixture for concrete to improve workability and increase bulk, as a raw material for construction materials, and as a precursor for geopolymer and zeolite syntheses. In addition, we developed a surface activation technique for fly ash, which opens up a new strategy for the fabrication of cementless concrete. By mechanochemical treatment, via a planetary ball milling process of fly ash, the reactivity of fly ash was significantly improved, resulting in enhanced silicon and aluminum ion elution in a low-concentration alkali solution (3 M), whereas raw fly ash particles can only elute these ions in a highly concentrated alkali solution (8~20 M). Along with the developed technique, we fabricated solidified bodies that exhibited a compressive strength equivalent to that of Ordinary Portland Cement with only fly ash. It can be suggested that the reaction mechanisms and structural control play important roles in determining the multiple functions of fly ash in practical applications. We demonstrated typical examples of fly ash recycling in ceramic processing with respect to the synthesis methods, reaction mechanisms, and physical/chemical structure control in corresponding applications.

Keywords: fly ash, ceramic processing, ceramic material, reaction mechanism, structure controlling

#### 1. Introduction

Fly ash, which is a sub-product discarded from thermal power plants, mainly comprises quartz (SiO<sub>2</sub>) and mullite  $(3Al_2O_3 \cdot 2SiO_2)$ . Fly ash is produced when coal is burned in a boiler and molten ash particles are cooled at the boiler outlet<sup>[1-4]</sup>. In addition, since 2011, the proportion of electricity generated by thermal power plants in Japan has increased significantly, and as the domestic demand for coal increases, the amount of fly ash discarded is expected to increase. Conventionally, fly ash is disposed by landfilling, particularly in China, India, and other developing countries where large amounts of carbon dioxide (CO<sub>2</sub>) are emitted. This has become a serious environmental problem, such as a decrease in landfill sites and leaching of heavy metal ions containing fly ash particles<sup>[5-8]</sup>. Additionally, the disposal of ceramic resources has become a problem, and attempts have been made to reuse fly ash as a valuable inorganic material. However, fly ash shows high chemical stability; therefore, ions are hardly eluted unless it is a highly concentrated alkaline solution of 8-14 M. Therefore, generally, it is used by utilizing its

physical properties, such as an admixture for increasing bulk and improving workability, and as an adsorbent for purifying wastewater. To chemically reuse fly ash, we solved this problem using mechanochemical (MC) treatment via a planetary ball mill and activating the fly ash particle surface. With this technique, reactivity with a low-concentration of alkaline solution (3 M) improves and increases the elution of Si and Al ions by two effects: increasing the specific surface area owing to the grinding effect and activating the fly ash surface owing to the MC effect<sup>[9-11]</sup>. Moreover, using a solidification reaction in which aluminosilicate is generated through a condensation reaction between the eluted ions, we fabricated a solidified body utilizing only fly ash, which has a high compressive strength equivalent to that of conventional Ordinary Portland Cement (OPC). As aforementioned, fly ash is conventionally disposed of in landfills, however, its value has recently been reconsidered, and it has been reused and applied via various methods and technologies. In this paper, we investigated the synthesis method, reaction mechanism, and applications of ceramic materials utilizing fly ash.

# 2. Construction material

# 2-1. Admixture mixing in concrete

During the fabrication process, the fly ash particles are spherical because the melted coal is collected in air using an electrostatic precipitator during the cooling process. Thus, it could improve the workability and reduce the amount of water in the cement paste based on the particle morphology, therefore, decreasing the contraction rate. Regarding the correlation between the additional amount of fly ash and rheological properties, as shown in Fig. 1, Dengwu et al. have reported that the apparent viscosity decreases due to the ball-bearing effect by fly ash particle morphology<sup>[12]</sup>; however, in thixotropy where the network structure formed by colloidal aggregation and nucleation of calcium silicate hydrate is severed with shear stress, the addition of fly ash particles increases the distance between cement particles and suppresses hydration reaction<sup>[13]</sup>, and therefore, increasing the addition amount of fly ash particles has a negative effect on rheological properties. In addition, the particle size of fly ash is approximately 10-100 µm, and larger than the size of voids in concrete. Therefore, the particle distance between cements is increased by mixing fly ash in concrete<sup>[14, 15]</sup>, and this is attributed to two effects: suppression of the hydration reaction and a decrease in cracks due to chemical contraction<sup>[16-18]</sup>. Although there is a concern that the compressive strength decreases owing to the delay in the hydration reaction, the generated calcium hydroxide reacts with SiO<sub>2</sub> derived from fly ash particles, reducing the porosity and improving the microstructure; thus, it is expected to improve long-term stability<sup>[19, 20]</sup>. Stefanovic et al. explained that the addition of fly ash promoted the pozzolanic reaction, in which Si and Al ions eluted from

the fly ash particles reacted at the particle interface between the POC and fly ash<sup>[59]</sup>. Moreover, they bind via a hydration reaction to form calcium compounds. This improved the initial strength of the solidified bodies. The hydration mechanisms of POC and fly ash are shown in Fig. 2.

### 2-2. Precursors for geopolymer

The emission of CO<sub>2</sub> is a serious global environmental problem in the cement industry. Approximately 0.8 tons of CO<sub>2</sub> is produced per ton when the raw material calcium carbonate is thermally decomposed at 1400  $^{\circ}C^{[21-24]}$ . Thus, attempts have been made to develop construction materials without cement, such as geopolymers. Geopolymers are fabricated by mixing fly ash, an industrial waste, with highly concentrated water glass (8-14 M) to elute Si and Al ions from fly ash particles, and the solidification reaction progresses through a condensation reaction during the curing and drying process<sup>[25-29]</sup>. In general, OPC utilizes unused resources, such as calcium carbonate and clay, and the solidification reaction proceeds with a hydration reaction<sup>[30]</sup>, whereas geopolymers are fabricated from low-cost industrial waste. Moreover, aluminosilicate, which is a binder, undergoes a solidification reaction due to the condensation reaction with the eluted Si and Al ions<sup>[31]</sup>. The reaction mechanism and the internal geopolymer structures formed are shown in Fig. 3 and 4, respectively<sup>[26]</sup>. Geopolymers exhibit high acid and thermal resistance and reduce the emission of CO<sub>2</sub> by approximately 30% compared to conventional OPC. In this section, we describe the synthesis method and structural control of the geopolymers.



**Fig. 1** Shear stress versus shear rate hysteresis cycle of cement paste (Reprinted from Constr. Build. Mater. 2018, 188, 170-177. Copyright: © 2018 Elsevier Ltd. All rights reserved.)



**Fig. 2** The mechanism of hydration reaction of OPC and fly ash mixture (Reprinted from J. Serb. Chem. Soc. 2007, 72, 6, 591-604. Copyright: © The property of National Library of Serbia.)



**Fig. 3** Descriptive model of the alkali activation of fly ash (Reprinted from Cement. Concrete. Res. 2005, 35, 6, 1204-1209. Copyright: © 2004 Elsevier Ltd. All rights reserved.)

#### 2-2-1. Synthesis method

In the fabrication process of geopolymers, the ratio of Si ions, which serve as the framework, to Al ions, which contribute to the condensation reaction (Si/Al ratio), plays an important role, and changes in the Si/Al ratio affect the formed chemical structure, compressive strength, and long-term stability. Yaguand fabricated geopolymers with Si/Al from 1 to 3 and reported that as the Si/Al ratio increased to 1.5, the geopolymer properties improved and the efflorescence decreased significantly<sup>[32]</sup>. Efflorescence is generated on the bulk surface by eluting alkali metal ions with water, suggesting that the structure is saturated with alkali metal ions. Therefore, the reduction in efflorescence indicates that a large amount of Al is substituted in the silicate structure, and aluminosilicate is precipitated over a wide range. Conversely, Loweistein's principle of aluminium insolubility explains that Al ions do not bond with each other, and only Si-O-T(T: Si, Al) forms in the geopolymer's structure<sup>[33, 34]</sup>; therefore, during the fabrication process of geopolymer, even if Si/Al ratio is





significantly lowered, the amount of Al that does not contribute to the geopolymer's structure increases, and different characteristics are expressed. In addition, the alkali concentration and ionic species of the alkali metal ions used in the raw material affect the chemical and physical properties of geopolymers. Duxson fabricated geopolymers utilizing alkali activators derived from sodium, potassium, and mixed alkali activators and reported the coordination state of Al in the structure and the bonding superiority of alkali metal ions <sup>[35]</sup>. The proportion of octahedral Al in the geopolymer structure is the highest when a sodium alkali activator is used, suggesting that potassium alkali activators exhibit higher basicity<sup>[36]</sup>. Nevertheless, the dissolution rate is faster for sodium because the respective ionic radii are  $Na^+ < K^+$ , and thus it is argued that this promotes the elution of Si and Al ions because the smaller size of sodium stabilizes the silicate monomer<sup>[38, 39]</sup>.

### 2-2-2. Microstructure controlling

Microstructure is a key factor when discussing mechanical properties of construction material, and it is simultaneously a difficult issue to completely control. For example, reducing the viscosity of the paste and improving its workability and filling rate are expected to decrease the porosity of solidified bodies and internal water. However, micropores can sometimes lead to the dispersion of residual stress and an improvement in compressive strength. In this section, the microstructural control of geopolymers is discussed. Assi et al. classified fly ash particles by particle size and investigated the influence of particle size on the microstructure. The compressive strength reduces as the particle size and porosity increase, and from 0.25 mm and more, the compressive strength increases because the porosity improves<sup>[60]</sup>. Furthermore, the amount of generated calcium silicate (CSH) gel decreased as the particle size increased, suggesting that larger particles have higher crystallinity and show lower activation with alkali solution. Conversely, it is considered that when the particle size is 0.25 mm or more, the proportion of amorphous SiO<sub>2</sub> increases, which improves the reactivity during the solidification process and increases the amount of generated CSH gel filling the gaps between particles <sup>[40]</sup>.

# 2-3. Novel cement-less concrete material

As aforementioned, geopolymers are valuable materials because they exhibit high acid and thermal resistance and can utilize industrial waste. However, considering its use as a construction material, safety during the moldering process and control of the solidification process are problematic because of the presence of water glass, which is a high-concentration alkaline solution (8-14 M). A highly concentrated water glass is used because fly ash particles exhibit high chemical stability, thus, almost no ions are eluted. Therefore, we improved the reactivity between fly ash particles and a low-concentrated alkali solution and increased the elution of ions through the MC treatment utilizing a planetary ball mill. Moreover, using this technique, we developed cementless concrete that utilizes only fly ash through a condensation reaction with eluted ions. In this section, we discuss the investigation of the MC treatment and its applications using particles.

#### 2-3-1. Mechanochemical (MC) activation

Mechanochemistry is the field of chemistry that promotes chemical reactions using mechanical forces and energy. In general, chemical reactions proceed through heat treatment and solvents, whereas in mechanochemistry, diffusion and phase transitions proceed by applying mechanical energy, such as friction and pressure to particles and crystals. Kato et al. performed MC treatment of fly ash particles using a planetary ball mill. Contrary to rotational motion, a planetary ball mill contributes to the kinetic energy of rotation and revolution to constantly overlap the centrifugal force, providing a large amount of energy to the material in the pot. Fig. 5 shows that the scheme of changes in particle morphology and surface state during the MC treatment process. Kato et al. reported that in the early stages of MC treatment, the particle size decreases,



**Fig. 5** The schematic illustration of changing particle during MC treatment (Reprinted from Ceram. Int. 2018, 45, 849-853. Copyright: © Elsevier Ltd and Techna Group S.r.l. All rights reserved.)

and the specific surface area increases due to the grinding effect; in the middle stage of MC treatment, the fly ash particle surface is activated due to the MC effect; in the final stage, energy is applied for grinding the coarse aggregates and agglomerates, formed by the strong impact of mechanical energy, and increases Si and Al ion elution in a low concentrated alkali solution  $(3 \text{ M})^{[9]}$ . Fig. 6 shows the particle morphology of fly ash particles before and after MC treatment, and it is confirmed that the spherical particles are deformed and smaller in size and aggregate with increasing treatment time<sup>[9]</sup>. The elution behavior of Si and Al ions in alkali solution are shown in Fig. 7, surface activation by energy contribution accelerates ion elution with increasing treatment time<sup>[9]</sup>. In addition, Sangu et al. investigated the effect of the ball material used in MC treatment on particle surface activation and reported that the energy contributed by balls to particles increases,



**Fig. 6** NThe particle morphology of raw and MC treated powders (a) raw, (b) 1 hour, (c) 6 hours, (d) 24 hours (Reprinted from Ceram. Int. 2018, 45, 849-853. Copyright: © Elsevier Ltd and Techna Group S.r.l. All rights reserved.)



**Fig. 7** The dissolution amounts of ions into 3 M NaOH solution (a) The dissolution amount of Si and Al ions, (b) The dissolution amount of Si and Al ions per unit surface area. (Reprinted from Ceram. Int. 2018, 45, 849-853. Copyright: © Elsevier Ltd and Techna Group S.r.l. All rights reserved.)

and the grinding effect is promoted as the material density increases, whereas the MC effect can be obtained efficiently as the friction coefficient between fly ash particles and balls, even if the contribution energy is small. Because a large number of Si ions derived from quartz are eluted, it is argued that surface activation by friction forces contributes to the quartz. The changes in the crystalline phase in the fly ash particles and the Si and Al ions elution behavior in alkaline solution through MC treatment utilizing different ball material is shown in Fig. 8 and the sample names Z, F and A represent the materials of balls utilized in MC treatment (Z:  $ZrO_2$ , F: Fe, A: Al<sub>2</sub>O<sub>3</sub>).

#### 2-3-2. Solidification process

This material is an alternative to the MC-treated fly ash particles. Regarding the solidification mechanism, in



**Fig. 8** (a)-(d) <sup>29</sup>Si NMR spectra of fly ash particle treated MC process utilizing balls with different materials. (a) Raw fly ash, (b) Z6h, (c) F6h, (d) A6h, (e) The composition ratio of fly ash particles. (f)-(g) the elution behavior of Si and Al ions from fly ash particles in 3 M KOH solution. (Reprinted from Ceram. Int. 2023, 49, 34327-34332. Copyright: © 2023 Published by Elsevier Ltd.)

OPC, hydrates are generated by the hydration reaction of calcium compounds, which are the main components of OPC, connect particles, and proceed to the solidification reaction. However, it is argued that surface activation by friction force contributes to solidification process through a condensation reaction with Si and Al and generates an aluminosilicate gel. The structure of this material is controlled by the MC treatment time and changes in the particle morphology. In addition, Kato et al. reported that as the MC treatment time increase, the crystalline phase in the fly ash particles changes amorphous, and crystal strain also increases accordingly, the strain of mullite phase is particularly noticeable, and it is confirmed that this affects the Si/Al ratio of cementless concrete <sup>[10]</sup>. The crystalline/amorphous ratio of fly ash particles before and after MC treatment calculated from the <sup>29</sup>Si NMR spectrum, and the influence of MC treatment time on crystal strain of fly ash particles and the mechanical strength of fly ash solidified bodies are shown in Fig. 9.

# 3. Zeolite synthesis utilizing fly ash

Zeolites are aluminosilicates and classified as natural and artificial zeolites. Natural zeolites have a porous structure and include abundant minerals that are highly safe for human health; however, their functionality varies owing to their uneven composition. Conversely, artificial zeolite is low-cost and high-performance



**Fig. 9** (a) <sup>29</sup>Si NMR spectra of fly ash particles treated MC treatment. (b) The ratio of crystalline and amorphous in MC treated fly ash particles. (c)-(d) The quantity of strain in mullite and quartz phase in raw and MC treated fly ash particles. (e) Compressive strength of fly ash solidified bodies utilized raw or MC treated fly ash particles. (Reprinted from J. Ceram. Soc. Jpn. 2023, 128, 4, 224-228. Copyright: © 2020 The Ceramic Society of Japan. All rights reserved.)

material fabricated by crystallizing industrial waste, such as fly ash by alkali treatment<sup>[41-43]</sup>. Moreover, the high functionality of artificial zeolites has attracted significant attention, and various synthesis methods and applications have been investigated, as discussed below.

## 3-1. Synthesis method

Zeolite synthesis from fly ash particles was first proposed by Holler and Wirsching, and since then, numerous researchers have proposed various liquid/bulk ratios, solvents, and synthesis temperatures and times depending on the application <sup>[44]</sup>. Generally, it is synthesized by mixing fly ash particles into an alkaline solution and stirring the mixture at high temperature and pressure for a long time. The mechanism of zeolite crystallization can be classified into two stages: nucleation and crystal growth. First, through hydrothermal synthesis, an amorphous silicate gel of the zeolite precursor is formed through a condensation reaction between Si and Al ions, generating crystal nuclei. Subsequently, crystal growth is promoted by nucleus saturation through typical S-shaped crystallization centered around the generated nucleus. Owing to the metastable nature of zeolites, the rate of crystal growth is determined by the treatment time. Crystal growth is also proposed; however, the detailed reaction mechanism has not been explained. Mintova et al. reported the zeolite formation mechanism as follows <sup>[45, 46]</sup>: (i) Zeolite precursor is brought to a critical state via hydrothermal treatment. (ii) At the initial stage of crystallization (10-15%), crystal growth propagation through the silicate gel becomes dominant. (iii) Crystallization then proceeds due to agglomeration and Ostwald growth of particles. Furthermore, crystal growth proceeds at the interface between the silicate gel and liquid phase, and as the crystal grows, amorphous particles are rearranged into highly crystalline zeolites.

# 3-2. Structure control

One of the excellent characteristics of zeolites is their morphology selectivity; during the synthesis process, the pore diameter can be controlled by changing the pH, temperature, pressure, reaction time, and composition<sup>[47-50]</sup>. Controlling the pore diameter directly affects the functionality of zeolites when they are used as catalysts or adsorbents. Examples of zeolite frameworks are shown in Fig. 10. The middle of the line segments forming the frameworks represents the T atoms (T: Si, Al), and each vertex represents an oxygen atom. A



**Fig.10** Scheme of zeolite structure, zeolite-A, zeolite-X, Y and sodalite (Reprinted from Chem. Rev. 1993, 93, 321-339. Copyright: © 1993 American Chemical Society.)

spherical unit cell is called a "sodalite cage"; it is classified as sodalite, A-type, or Y-type depending on the bonding state of each lattice. A structure surrounded by n T atoms is called an n-ring, and an A-type is an 8-ring and a Y-type is a 12-ring, with pore diameters of 0.41 nm and 0.74 nm, respectively. In addition, similarly to geopolymers, the Si/Al ratio plays an important role in the synthesis process, and changing the Si/Al ratio affects crystallinity, crystal size, and functionality. Moreover, the Si/Al and Si/alkali ratios play important roles in controlling the zeolite structure; Miguel et al. reported that the proportion of sodalite structure increases as the concentration of alkali solution increases, whereas the X-type structure shifts to X-type as the Si/Al ratio decreases<sup>[51]</sup>. In addition, Alechine et al. adjusted the Al ion concentration in solvents utilizing sodium aluminate and aluminum hydroxide, and synthesized zeolite from fly ash in the range of Si/Al = 0.27 to  $0.80^{[52]}$ . Consequently, they controlled the crystal size in the range of 0.67 to 3.18 µm and reported that the crystal size and Si NMR peak area observed proportional relationships with decreasing Si/Al ratio. Conversely, the crystallinity is inversely proportional to the precipitation of the amorphous phase near the crystal grain. The precipitated amorphous phase is considered to be soda lime generated through Ostwald growth between crystal grains due to the supersaturation of Al ions during the zeolite formation process; when the Si/ Al ratio is high, crystallization occurs without interference from impurities, and a cubic structure is formed<sup>[53]</sup>. Moreover, in a synthesis process with a similar Si/Al ratio, Purnomo and Zhang reported that they obtained pure zeolite when Si/Al  $\leq 0.80$ , and amorphous zeolite when Si/Al  $\geq 1.07^{[54-56]}$ .

#### 3-3. Selective ions adsorption

As a forementioned, zeolites have micropores of various shapes in the voids of the three-dimensional network structure formed by the bonding of tetrahedral (Si, Al)O<sub>4</sub>, and crystal water and cations are incorporated into the micropores. Zeolite-containing crystal water has a stable structure; however, it exhibits strong adsorption properties during dehydration and can be utilized as an adsorbent. Although silicate structures comprising only Si are electrically neutral, a negative charge is generated when Si are substituted with Al, and alkali metal ions are attracted to the vicinity of the Al ions owing to positive charge compensation. Furthermore, because the cations in the zeolite structure move freely within the voids, ion exchange is possible in the liquid phase. He et al. attempted to remove heavy metal ions from wastewater using a zeolite made from fly ash and clarified the selectivity of the modified cation. The tendency of modified cations to remove heavy metal ions was observed in the order  $Al^{3+}$  >  $NH_4^+ > Ca^{2+} > Mg^{2+} > Na^+$ , suggesting that the competitive ability among cations depends on the ionic charge and radius<sup>[57]</sup>. Moreover, NH<sup>+</sup>, which shows high adsorption capacity despite being a monovalent cation, is considered to have complex interactions with heavy metal ions. Also, Mokzycki et al. focused on ion exchange functionality of fly ash zeolite utilizing copper, and investigated the morphology change and functionality by changing the concentration of precursor copper nitrate. The adsorption-desorption isotherms of X-type zeolite with different amounts of precursor metal added to evaluate the ion exchange function are shown in Fig. 11(a), and Fig. 11 (b) gives the maximum adsorption amount of the material calculated from the Langmuir model and Freundlich model based on the isotherms. Mokzycki et al. reported that the optimal concentration for the modification of X-type zeolite towards phosphate ions adsorption is 0.05 M of  $Cu(NO_3)_2 \cdot H_2O$ , moreover, pores are partially blocked and the adsorption functionality decreases if the amount added is further increased<sup>[58]</sup>.

## 4. In summary

In this study, we focused on fly ash, an industrial waste, and introduced its application, reaction mechanism, and structural control of a synthesized material. Utilizing the properties of industrial waste as a valuable ceramic resource can contribute to solving environmental problems related to construction materials that exhibit a compressive strength equivalent to that of conventionally used OPC. However, because the solidification reaction progresses through a condensation reaction, which is different from the solidification



Fig. 11 (a)  $N_2$  adsorption-desorption isotherms of X-type zeolite utilizing Na or Cu doped. (b) Adsorption isotherms of X-type zeolite synthesized with Na or doped Cu.

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mechanism of OPC, controlling the solidification process on a practical scale is an additional attempt. Fly ash has also been used to synthesize zeolites and remove heavy metal ions and dyes. However, the properties of synthesized materials depend on their composition, pH, and temperature. Thus, functionality and synthesis methods must be adapted depending on the country of application, and it is necessary to understand the reaction mechanism and structural control in more detail.

## Reference

 Dwivedi, A., Jaon, K. M., Fly ash-waste management and overwise: A review. *Res. Is. Sci. Techno.* 2014, 6(1), 30-35.

- [2] Shemi, A., Mpana, R. N., Ndlove, S., Van Dyk, L. D., Sibanda, V., Speepe, L., Alternative techniques for extracting alumina from coal fry ash. *Miner. Eng.* 2012, 34, 30-34.
- [3] Ahmaruzzaman, M., A review on the utilization of fly ash. Prog. Energy. Combust. Sci. 2010, 36, 327-363.
- [4] Ding, J., Ma, S., Zhang, Y., Research and industrialization progress of recovering alumina from fly ash: A concise review. *Waste Manage*. 2017, 60, 357-387.
- [5] Malhotra, V. M., Making concrete greener with fly ash, *Concr. Int.* 1999, 21, 61-66.
- [6] Carlson, C. L., Andriano, D. C., Environmental impacts of coal combustion residues, *J. Environ. Qual.* 1993, 22, 227-247.
- [7] Ferraiolo, G., Zilli, M., Converti, A., Fly ash disposal and utilization, J. Chem. Techno. Biotechnol. 1999, 47, 281-305.
- [8] Gao, S., Zhang, Y., Sun, S., Wang, M., Study on the extracted process of mullite from coal fly ash by-product sodium silicate, *J. Ceram. Soc. Japan.* 2019, 127(2), 90-97.
- [9] Kunihiko, K., Yunzi, X., Takashi, H., Takashi, S., Surface modification of fly ash by mechano-chemical treatment. *Ceram. Int.* 2019, 45(1), 849-853.
- [10] Kunihiko, K., Yunzi, X., Takashi, H., Takashi, S., Fabrication of solidified bodies by utilizing mechanochemically modified fly ash powder. J. Ceram. Soc. Japan. 2020, 128(4), 224-228.
- [11] Takumi, S., Yunzi, X., Kunihiko, K., Takashi, H., Takashi, S., Influence of ball materials on the surface activation behavior of coal ash particles during a mechanochemical process. *Ceram Int.* 2023, 2023, 49(21), 34327-34332.
- [12] Dengwu, J., Caijun, S., Qiang, Y., Influence of shearmixing rate and fly ash on rheological behavior of cement pastes under continuous mixing, *Constr. Build. Mater.*, 2018, 188, 170-177.
- [13] Roussel, N., Ovarlez, S., Garrault, S., The origins of thixotropy of fresh cement pastes, *Cem. Concr. Res.* 42(1). 2012. 148-157.
- [14] Jiao, D., Shi, C., Yuan, Q., Effect of constituents on rheological properties of fresh concrete-a review, *Cem. Concr. Compos.* 2017. 83. 146-159.
- [15] Vance, K., Kumar, A., Sant, G., The rheological properties of ternary binders containing Portland cement, limestone, and metakaolin or fly ash, *Cem. Concr. Res.* 2013. 52. 196-207.
- [16] Sarker, P., MacKenzie, L., Strength and hydration heat of concrete using fly ash as a partial replacement of cement, Proceedings of the 24<sup>th</sup> Biennial Conference of the Concrete Institute of Australia, 2009.
- [17] Hu, X., Shi, Z., Shi, C., Drying shrinkage and cracking

resistance of concrete made with ternary cementitious components, *Constr. Build. Mater.* 2017, 149, 406-415.

- [18] Hu, X., Shi, C., Shi, Z., Early age shrinkage and heat of hydration of cement-fly ash-slag ternary blends, *Constr. Build. Mater.* 2017, 153, 857-865.
- [19] Shi, C., Jiao, D., Zhang, J., Design of high performance concrete with multiple performance requirements for #2 Dongting Lake Bridge. *Constr. Build. Mater.* 2018, 165, 825-832.
- [20] Joshaghania, A., Moeinib, M. A., Balapourb., M., Effects of supplementary cementitious materials on mechanical and durability properties of highperformance nonshrinking grout, J. Sustainable. Cem.-Based. Mater. 2018, 7(1), 38-56.
- [21] Jacott, M., Comenes, F., Energy use in the cement industry in North America: emissions, waste generation and pollution control, 1990-2001; 2003
- [22] Damineli, B. L., Kemeid, F. M., Aguiar, P. S., John, V. M., Measuring the eco-efficiency of cement use. *Cem. Concr. Compos.* 2010, 32(8), 555-562.
- [23] Bakari, A. M. M. Al., Abdulkareem, O. A., Rafiza, A. R., Zarina, Y., Norazian, M. N., Kamarudin, H., Review on processing of low calcium fly ash geopolymer concrete, *Aust. J. Basic. Appl. Sci.*, 2013, 7, 342-349
- [24] Islam, A., Alemgraram, U. J., Jumaat, M. Z., Bashar, I. I., Kabir, S. M. A., Engineering properties and carbon footprint of ground granulated blast-furnace slag-palm oil fuel ash-based structural geopolymer concrete. *Conctr. Build. Mater.*, 2015, 101, 503-521.
- [25] Davidovits, J., Geopolymers inorganic polymerie new materials, J. Therm. Anal. 1991, 37, 1633-1656.
- [26] Fernandez-Jimenez, A., Palomo, A., Criado, M., Microstructure development of alkali-activated fly ash cement: a descriptive model, *Cem. Concr. Res.* 2005, 35, 1204-1209.
- [27] Palomo, A., Grutzeck, M. W., Blanco, M. T., Alkaliactivated fly ashes: A cement for the future. *Cem. Concr. Res.*, 1999, 29, 1323-1329.
- [28] Fernandez-Jimenez, A., Palomo, A., Mid-infared spectroscopic studies of alkali-activated fly ash structure, *Microporous. Mesoporous. Mater.* 2005, 86, 207-221.
- [29] Davidovits, J., Geopolymer chemistry & applications, Institut. GEOPOYMERE, 2008, 500.
- [30] Mehta, P. K., High-performance, high-volue fly ash concrete for sustainable development, *Int. Work. Sustain. Dev. Concr. Technol.*, 2004. 3-14.
- [31] Yi-miao, N., Hong-wen, M., Jing, Y., Yu-zhu, S., Ru-chen, L., Fei, G., Mechanism of polymerization during the solidification of flyash-based geopolymers. *Geoscience*.

2006, 20(2), 340-346.

- [32] Yaguang, W., Xiaoming, L., Wei, Z., Zepeng, L., Yuliang, Z., Yong, L., Yongyu, R., Effects of Si/Al ratio on the efflorescence and properties of fly ash based geopolymer, *J. Clean. Prod.*, 2020, 244(20), 118852.
- [33] Loewenstein, W., The distribution of aluminum in the tetrahedra of silicates and aluminates. *Ame. Mine.*, 1954, 39(1), 92-97.
- [34] Davis, M. E., Lobo, R. F., Zeolite and molecular sieve synthesis. *Chem. Mater.*, 1992, 4(3), 756.
- [35] Duxson, P., Lucky, G. C., Separovic, F., Devanter, van, J. S. J., Effect of alkali cation on aluminum incorporation in geopolymeric gels, *Ind. Eng. Che. Res.* 2005, 44(4), 832-839.
- [36] Kirkpatrick, R. J., Philips, B. L., <sup>27</sup>Al NMR spectroscopy of minerals and related materials, *Appl. Magn.*, 1993, 4, 213-236.
- [37] Hua, X., Van Deventer, J. S. J., The geopolymerisation of alumino-silicate minerals, *Int. J. Mine. Pros.*, 2000, 59, 247-266.
- [38] Konstantinos, S., Panias, P., Nomikos, P., Sofianos, A., Comparison of fire resistant geopolymers for passive fire protection of concrete tunnel linings., 2017, 4(1), 3327
- [39] Hua, X., Van Deventer, J. S. J., Lucky G. C., Effect of alkali metals on the preferential geopolymerization of stilbite/kaolinite mixture., *Ind. Eng. Chem. Res.*, 2001, 40, 3749-3756.
- [40] Luchang, X., Zhijun, W., Yuan, Z., Fangtian, W., Junhui, W., Yanlei, K., Fly ash particle size effect on pore structure and strength of fly ash foamed geopolymer, *Adv. Polym Tech.*, 2019, 3, 1-10.
- [41] Nevin Koshy, D. N. S., Fly ash zeolites for water treatment application, *J. Environ. Chem. Eng.*, 2016, 4(2), 1460-1472.
- [42] Li, L., Wang, S. B., Zhu, Z. H., Geopolymeric adsorbents from fly ash for dye removal from aqueous solution. J. Colloid. Interface. Sci. 2006, 300, 52-59.
- [43] Alvarez-Ayuso, E., Querol, X., Plana, F., Alastuey, A., Moreno, N., Izquierdo, M., Font, O., Monero, T., Diez, S., Vazquez, E., Barra, M., Environmental, physical and structural characterization of geopolymer matrixes synthesized from combustion fly ashes., *J. Hazard. Mater.*, 2008, 154, 175-183.
- [44] Holler, H., Wirsching, U., Zeolite formation from fly ash., Fortschritte der Mineral., 1985, 63, 21-43.
- [45] Mintova, S., Olson, N. H., Bein, T., Electron microscopy reveals the nucleation mechanism of zeolite Y from precursor colloids. *Angew. Chem. Int. Ed. Engl.* 1999, 38(21), 3201-3204.
- [46] Mintova, S., Olson, N. H., Bein, T., Mechanism of zeolite

A nanocrystal growth from colloids at room temperature. *Science*. 1999, 283(5404), 958-960.

- [47] Bandura, L., Franus, M., Jozefaciuk, G., Franus, W., Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup. *Fuel.*, 2015, 100-107.
- [48]Zhan, Y. H., Lin, J. W., Li, J., Preparation and characterization of surfactant-modified hydroxyapatite/ zeolite composite and its adsorption behavior toward humic acid and copper (II). *Environ. Sci. Pollut. Res.*, 2013. 20. 2512-2526.
- [49] Franus, W., Wdowin, M., Franus, M., Synthesis and characterization of zeolites prepared from industrial fly ash. *Environ Monit Assess.*, 2014, 186, 5721-5729.
- [50] Izidro, J. D. C., Fungaro, D. A., Abbot, J. E., Wang, S. B., Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems. *Fuel.*, 2013, 103, 827-834.
- [51] Miguel, M., Matthew, D. O., Sivadinarayana, C., Jeffrey, D. R., Controlling crystal polymorphism in organic-free synthesis of Na-zeolites, *J. Am. Chem. Soc.* 2013, 135, 2641-2652.
- [52] Alechine, E. A., Ojo, O. F., Nicholas, M. M., Leslie, F. P., Influence of aluminum source on the crystal structure and framework coordination of Al and Si in fly ash-based zeolite NaA. *Powder. Techno.*, 2017, 306, 17-25.
- [53] Cundy, C. S., Cox, P. A., The hydrothermal synthesis of zeolites: precursors, inter-mediates and reaction mechanism, *Microporous. Mesoporous. Mater.*, 2005, 82. 1-78.
- [54] Purnomo, C. W., Salim, C., Hinode, H., Synthesis of pure Na-X and Na-A zeolite from bagasse fly ash, *Microporous. Mesoporous. Mater.*, 2012, 162, 6-13.
- [55] Wdowin, M., Franus, M., Panek, R., Badura, L., Franus, W., The conversion technology of fly ash into zeolites., *Clean. Techno. Environ. Policy*, 2014. 16. 1217-1223.
- [56] Zhang, X., Tang, D., Zhang, M., Yang, R., Synthesis of NaX zeolite: influence of crystallization time, temperature and batch molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> on the particulate properties of zeolite crystals, *Powder. Techno.* 2013, 235, 322-328.
- [57] Kuang, H., Yuancai, C., Zhenghua, T., Yongyou, H., Removal of heavy metal ions from aqueous solution by zeolite synthesized from fly ash, *Environ. Sci. Pollut. Res.*, 2016, 23, 2778-2788.
- [58] Mokrzycki, J., Fedyna, M., Marzec, M., Szerement, J., Panek, R., Klimek, A., Bajda, T., Mierzwa-Hersztek, M., Copper ion-exchanged zeolite X from fly ash as an efficient adsorbent of phosphate ions from aqueous

solutions, J. Environ. Chem. Eng. 2022, 10, 108567.

- [59] Stefanovic, G., Cojbasic, L., Sekulic, Z., Matijasevic, S., Hydration study of mechanically activated mixtures of Portland cement and fly ash. J. Serb. Chem. Soc. 2007, 72(6), 591-604.
- [60] Assi, N. L., Deaver, E. E., Ziehl, P., Effect of source and particle size distribution on the mechanical and microstructural properties of fly Ash-Based geopolymer concrete. *Const. Build. Mater.* 2018, 167, 372-380.