

# PREPARATION OF GEOPOLYMER CEMENT FROM CRUSHED STONE BY-PRODUCT USING ALKALI FUSION

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**ABSTRACT:** In the crushed stone production process, crushed stone fines, such as dust and slurry cake, are generated as by-products, and most of them are landfilled. Recently, it is becoming difficult to secure landfill sites, and effective utilization of by-products is desired. On the other hand, geopolymer cement has attracted attention due to the higher acid resistance than that of ordinary Portland cement. In this study, we attempted to prepare geopolymer cement from crushed stone by-products using alkali fusion. In the experiment, crushed stone dust, discharged from one of the quarries in Japan, the fused dust, which prepared from the dust by heating at 500 °f with NaOH addition (weight ratio of addition is 1:1.6) for 0.5 h using rotary kiln, tap water and coal fly ash were used as raw materials. Crushed stone dust, fused dust, and tap water are mixed on various mixed ratio, with or without the addition of coal fly ash, heat at 30 °f or 80 °C for 24 h, and then stand at room temperature, in the air or distilled water to prepare geopolymer cement. Acid resistances for the obtained product and ordinary Portland cement was also investigated. As a result, 7 g of mixture of crushed stone dust, water and fused dust (mix ratio is 1: 1: 2) with 3 g of coal fly ash, heated at 80 °C, and cured in water to obtain the geopolymer cement with hard structure, and the obtained geopolymer cement indicates higher acid resistance than ordinary Portland cement.

*Keywords: Crushed stone, Slurry cake, Coal fly ash, Alkali fusion, Geopolymer cement*

## 1. INTRODUCTION

In the crushed stone industry, crushed stone dust and cake is generated as a by-product in large quantities from crushing, cutting, polishing and cleaning processes in the stone production process. Currently, most of them are landfilled, but in recent years it is becoming difficult to secure landfill sites, and further development of effective utilization of by-products, such as crushed stone dust and cakes, is desired by laws in Japan [1].

Crushed stone dust is mainly composed of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and the particle is fine and uniform. It is also characterized as sparingly soluble. In previous studies, we succeeded to convert sparingly soluble crushed dust into highly soluble dust by alkali fusion treatment to synthesize zeolitic materials [2 - 9].

Geopolymer cement is cement produced from mixing sodium silicate, sodium hydroxide, water and some industrial by-products, such as coal fly ash, blast furnace slag and so on [10 - 12]. Geopolymer cement has attracted attention because it has less CO<sub>2</sub> emissions in the manufacturing process than ordinary Portland cement and has high acid resistance [10] [13 - 17].

Ordinary Portland cement is mainly solidified by the formation of needle-like calcium silicate hydrate (C-S-H), while geopolymer cement is mainly solidified by the polymerization of silicate ions sparked by metal ions, such as Al<sup>3+</sup>, Fe<sup>2+</sup> and

so on, which is similar to the reaction of zeolite synthesis [18, 19]. Therefore, there is a possibility to make geopolymer cement using fused dust.

In this study, we attempted to prepare geopolymer cement from crushed stone by-product using the dust fused with alkali. The conditions, such as mixing ratio and curing methods, to prepare the geopolymer product with the hard structure were investigated and the acid resistance of the prepared geopolymer cement was evaluated.

## 2. EXPERIMENT

### 2.1 Sample

Crushed stone dust generated from one of the domestic crushed stone companies in Japan was used for the experiment. Coal fly ash used in this study was commercially available fly ash type IV. The fused dust was prepared by mixing crushed stone dust with sodium hydroxide at a weight ratio of 1: 1.6 and heating at 500 °C for 0.5 h using a rotary kiln [2].

### 2.2 Preparation of Geopolymer Cement from Dust

Crushed stone dust, tap water and the fused dust were mixed so that total weight of the mixture is 7 g. In addition, the mixture with or without coal fly

ash was prepared to clarify the effect of coal fly ash addition. The mixing ratio of the mixture is shown in Table 1. The mixture was cured at room temperature for 1 day and 7 days, and 7 days passed and heated at 50 °C for 24 hours. The hardness of the product was judged with a bamboo needle to insert into the product.

Table 1 The mixing ratio of the mixture.

	The mixing ratio
Dsut : Water	1 : 1
	1 : 2
	2 : 1
Fused dust : Water	1 : 1
	1 : 2
	2 : 1
Dsut : Water : Fused dust	1 : 1 : 1
	2 : 1 : 1
	1 : 1 : 2
	1 : 2 : 1
	1 : 2 : 2
	2 : 2 : 1
	2 : 1 : 2
	3 : 1 : 1
	1 : 1 : 3
	1 : 3 : 1
	3 : 1 : 2
2 : 1 : 3	

Next, 1 - 7 g of coal fly ash was added to 7 g of the mixture (the mixed ratio of dust : water : fused dust is 1 : 1 : 2). The mixture was kneaded, and the condition of the mixture was observed to obtain the product precursor with high workability.

The raw materials and the products were observed with a scanning electron microscope (SEM, JSM-6510A, manufactured by JEOL).

### 2.3 Curing Experiment

The curing experiment was conducted to increase the strength of the product.

The mixture (7 g) of dust, water and fused dust (the ratio is 1 : 1 : 2) with 3 g of coal fly ash was used for curing experiment. The mixture was filled and formed in a ring with a formwork of  $\phi$  25 mm  $\times$  5 mm. The ring stands for 24 h in a drying oven at 30 °C and 80 °C, and the product after 24 h was removed from the ring to observe the condition. In addition, the ring with the mixture was heated at 80 °C for 24 h, removed from the ring and then stand at room temperature in air or in 200 mL of distilled water for 96 h. After 96 h, the product was picked up from the beaker and the state was observed. For

curing in water, the elution amounts of Si, Al, Na and Ca to water were examined using atomic absorption spectrometer (AAAnalyst 200, Perkin Elmer).

### 2.4 Acid Resistance Test

Acid resistance test was conducted for the product in comparison with Portland cement. The sample was prepared with a mold of  $\phi$  25 mm  $\times$  5 mm. The product was formed by heating at 80 °C and standing in water for 24 hours. The Portland cement (Ordinary Portland Cement, N.C.C. Ltd.) was mixed at 50 % of water to cement ratio, poured into a mold, and stand at room temperature for 24 h. Each sample was immersed in a 5 % sulfuric acid solution (200 mL) for 10 days, and the pH of the sulfuric acid solution and the mass of the samples were measured every 24 h.

## 3. RESULTS AND DISCUSSION

### 3.1 Formation of Geopolymer

The ternary diagrams of mixing condition for the formation of the hardened body (a) without coal fly ash and (b) with coal fly ash are shown in Fig. 1. The plots indicate the condition when hardened body was confirmed.

For the product without coal ash (Fig. 1(a)), hardening could not be confirmed when the amount of water was large (above 40 %) and those of crushed stone dust and fused dust were small. With decreasing the amount of water and increasing the amounts of crushed stone dust and fused dust, the number of days used for hardening the product became shorter.

For the product with coal fly ash (Fig. 1), hardening could not be also confirmed when the amount of water was large and those of crushed stone dust and fused dust were small. In comparison with the product without coal fly ash, the conditions for no hardening decrease, and the product becomes a powder when the amount of water is small and that of the crushed stone dust is large. In addition, under the same mixing condition, the time for hardening becomes shorter. It is considered that the addition of coal fly ash accelerates the formation of geopolymer. It is noted that the product added with coal fly ash was harder than the product without coal fly ash added.

Figure 2 shows the condition after kneading the mixture with varying amount of coal ash added. The ratio of crushed stone dust, water, and fused dust is 1 : 1 : 2. The mixture after kneading was in liquid form when the amount of coal ash added was 1 - 3 g, while the mixtures with 5 g and 7 g of coal fly ash added were semisolid and powder, respectively.

The viscosity increases as the amount of coal ash added increases. Therefore, it is considered that the mixture with 3 g of coal fly ash addition has good workability to obtain the geopolymer cement product.

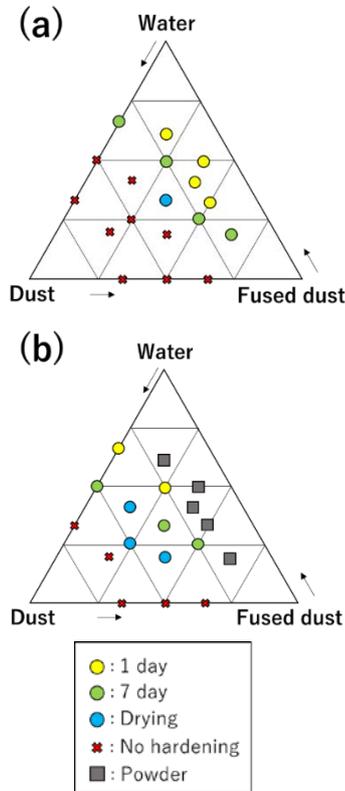


Fig.1 Ternary diagrams of mixing condition for the formation of the hardened body (a) without coal fly ash and (b) with coal fly ash.

The XRD patterns of the raw materials and the product are shown in Fig. 3. The product was obtained by adding 3 g of coal fly ash to the mixture (the mixed ratio is 1: 1: 2 of crushed stone dust, water and fused dust). Crushed stone dust contains  $\text{SiO}_2$  and  $\text{CaCO}_3$  (Fig. 3(a)), and the fused dust consists of alkali salts, such as  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_4\text{SiO}_4$  (Fig. 3(b)). On the other hand, coal fly ash consists of  $\text{SiO}_2$ ,  $\text{Si}_2\text{Al}_6\text{O}_{13}$  and amorphous glass (Fig. 3(c)). Peaks of  $\text{SiO}_2$ ,  $\text{CaCO}_3$  and  $\text{Si}_2\text{Al}_6\text{O}_{13}$  remained, and  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_4\text{SiO}_4$  disappeared in the product formed by mixing these raw materials (Fig. 3(d)). In addition, hydrated sodalite ( $\text{Na}_6\text{Al}_6\text{Si}_6 \cdot 8\text{H}_2\text{O}$ ) was produced in the product.

Raw materials were observed with SEM, as shown in Fig. 4. Crushed stone dust has aggregates particle of thin flake-like sticks with about 20  $\mu\text{m}$  diameter (Fig. 4(a)). The fused dust is the particles with some small particles, alkaline salts, on the surface (Fig. 4(b)). Coal fly ash was a spherical particle with a smooth surface having a particle diameter of 5 to 10  $\mu\text{m}$ .

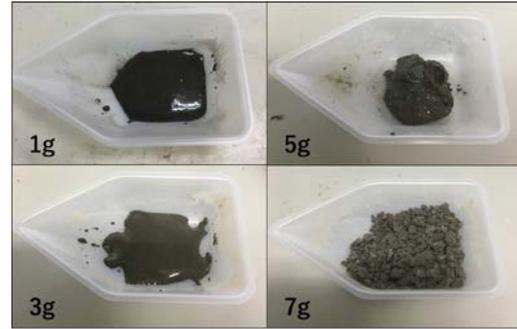


Fig.2 Observation of the mixture with various amount of coal fly ash.

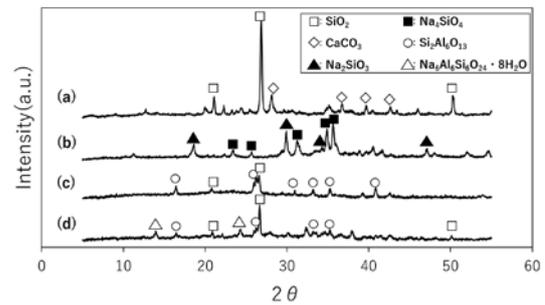


Fig.3 XRD patterns of (a) crushed stone dust, (b) alkali fused dust, (c) coal fly ash and (d) product.

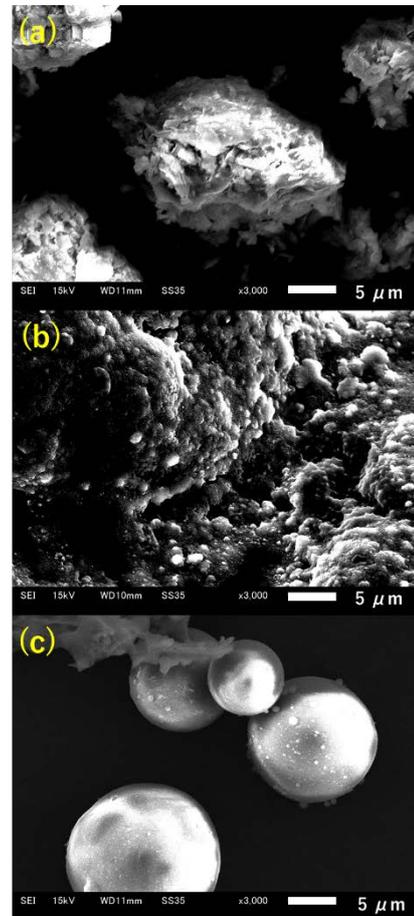


Fig.4 SEM image, (a) dust, (b) fused dust and (c) coal fly ash.

The product prepared with or without coal fly ash was observed with SEM, as shown in Fig. 5. The product was prepared from the mixture with a ratio of crushed dust, water and fused dust of 1: 1 : 2 with or without the addition of coal fly ash. For the product without coal fly ash, particles of crushed stone dust were covered and solidified by gel-like materials. For the product with coal fly ash, the product composed of many ball-like shapes, which would be coal fly ash covered with some gel-like materials and sodalite-like crystals and crushed stone dust like particles covered with gel-like materials. For the XRD pattern of the product with coal fly ash, there was no change in the crystal structure of the crushed stone dust and coal fly ash. It is considered that crushed stone dusts and coal fly ash were covered with the gels formed from fused dust and water, and coal fly ash was more impregnated in the product to be hardened.

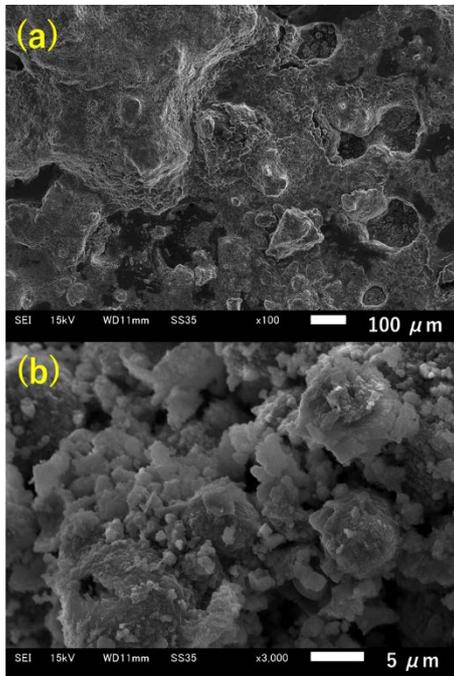


Fig.5 SEM image, (a) the product without coal fly ash and (b) the product with coal fly ash.

### 3.2 Curing

Figure 6 shows the state of the sample after 24 h standing at 30 °C and 80 °C. Although the sample at 30 °C is wet and brittle because chipping occurred at demolding, the sample at 80 °C is hardened and no chipping occurred at demolding.

Figure 7 shows the state of the product after 72 h in air and water. For the product prepared in air, some precipitates were observed on the surface. It is noted that the product became fragile and cracked by washing the precipitates on the surface with distilled water. For the product prepared in water, no component was precipitated on the surface, and

the hard structure of the product was kept.

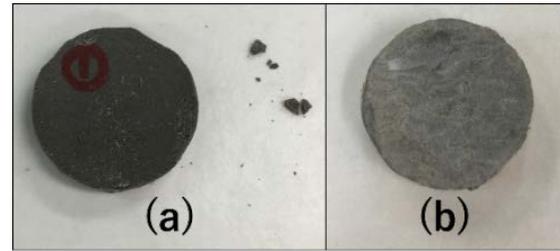


Fig.6 Sample state after standing at (a) 30 °C and (b) 80 °C for 24 h.

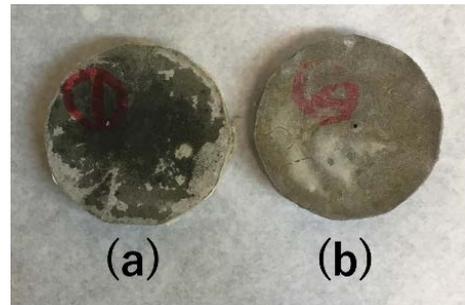


Fig.7 Observation of the product after 72 h in (a) air and (b) water.

Figure 8 shows the elution amounts of Si, Al, Ca and Na into water. While Al and Ca were hardly eluted, elution of Si and Na was confirmed. Elution of Si and Na into water increased to 46 mg/g and 85 mg/g, and be constant after 48 h. The percentages of Na and Si eluted from the product into water are about 60% and 25%, respectively. Therefore, the precipitate on the surface of the product prepared in the air is caused from excess amounts of Na and Si in the product, and the product prepared in water has no precipitate on the surface and hardened due to the removal of excess Si and Na during the curing in water.

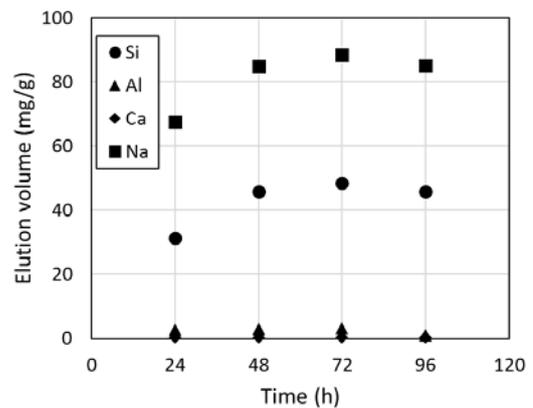


Fig.7 Elution amounts of Si, Al, Ca and Na into water.

### 3.3 Acid Resistance

Figure 9 shows the state of the sample before and after an acid resistance test. The shape and color of Portland cement change to be small and the color becomes white after the test, while the shape of the product did not change after the test.

Figure 10 shows the mass changes of the product and Portland cement in sulfuric solution. It is noted that the pH of the sulfuric acid solution was stable at below pH 1 during the immersion period. The mass of portland cement decreases for 10 days, while that of the product decreases in 2 days and be almost constant after 2 days. After 10 days, the mass of the product is 90 % of the product before the test, while that of Portland cement is 20 % of the Portland cement before the test. It was found that the obtained product has acid resistance of geopolymer cement.

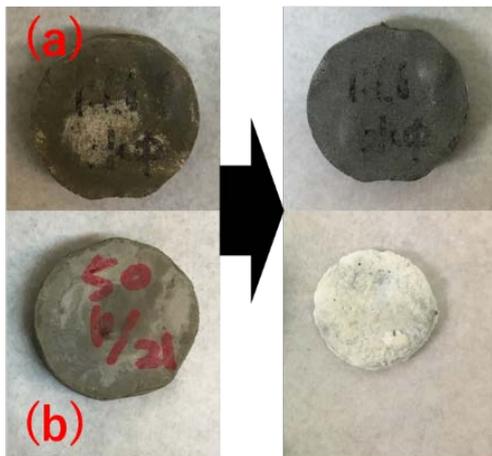


Fig.7 Observation of (a) product and (b) Portland cement before and after immersion in sulfuric solution.

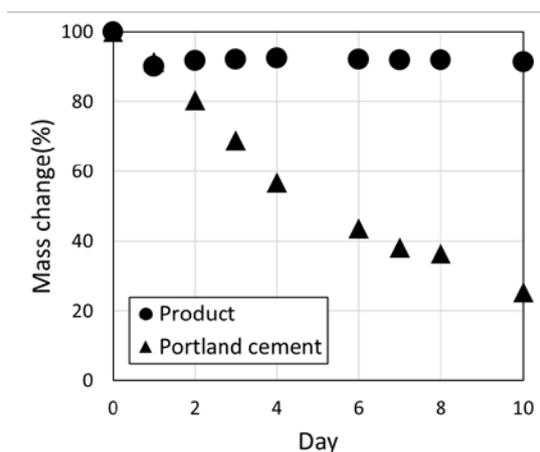


Fig.7 Mass change of the product and Portland cement in sulfuric acid solution.

### 4. CONCLUSIONS

The aim of the research was to prepare geopolymer cement from crushed dust, water, fused dust and coal fly ash. A hardened geopolymer product was obtained by adding 3 g of coal ash to 7 g of the mixture with the ratio of crushed stone dust: water: fused dust = 1: 1: 2. It was found that curing in water after heating at 80 °C was effective for producing stable geopolymer. From the acid resistance test, it was found that the prepared geopolymer cement has higher acid resistance than Portland cement.

### 5. ACKNOWLEDGMENTS

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