

# CONVERSION OF WASTE STONE-FINE SLURRY INTO GEOPOLYMER CEMENT WITH ADDITION OF COAL FLY ASH

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**ABSTRACT:** In the crushed stone production process, waste stone-fine slurry is generated as wastewater, and are landfilled as dehydrated cake after some treatments. Recently, it is becoming difficult to secure landfill sites, and effective utilization of by-products, dehydrated cake, is desired. On the other hand, a large amount of coal fly ash was discharged from a coal-fired power plant, due to the operation suspension of nuclear power plants since the Fukushima nuclear accident occurs. In this study, we attempted to prepare geopolymer cement from waste stone-fine slurry with addition of coal fly ash. Waste stone-fine slurry used in this study was discharged from one of the quarries in Japan. NaOH solution was added into the slurry, and heated at 60 - 180 °C for 0 - 24 h to obtain the high Si solution for preparation of geopolymer cement. After heating, the slurry was cooled to room temperature by quenching with tap water, and various amounts of coal fly ash were added, mixed, and cured at 80 °C for 24 h. The strength and water purification ability of the product was examined. The solution with high Si content to prepare the geopolymer can be obtained at 120 °C for 9 h in 4 - 8 M NaOH solution, and the products obtained from 6 - 8 M NaOH slurry solution with addition of 0.55 - 0.70 weight ratio of coal fly ash have higher strength than other products and Portland cement. The product indicates  $\text{NH}_4^+$  removal ability for wastewater treatment.

*Keywords: Waste stone-fine slurry, Coal fly ash, Geopolymer,  $\text{NH}_4^+$  removal, Alkali reaction*

## 1. INTRODUCTION

In the crushed stone production process, waste stone-fine slurry is generated as wastewater in large quantities from crushing, cutting, polishing, and cleaning processes, and most of them are landfilled as dehydrated cake after some treatments, such as coagulation, sedimentation, and filter press. Currently, it is becoming difficult to secure landfill sites due to the decrease of the landfill space, and the amount of dehydrated cake tends to increase. Therefore, further development of effective utilization of by-products, such as dehydrated cakes, is desired by laws in Japan, and there are some researches to reuse the dehydrated cake for improved soil, roadbed, greening, porous sintered compact, space-filling and so on [1].

Coal as an energy source has an advantage in terms of abundant deposits, compared with the other energy sources. In 2012, the percentage of electric power generation in coal power plants in Japan occupies about 23.4 % to all amounts of electric power [2]. By an increase in coal demand, the discharge amount of coal ash is estimated to be increased. According to the law relating to recycling in Japan, the coal ash derived from a thermal power plant is specially designated as a specified by-product, and the effective usage of this coal ash is strongly required. Recently, the reuse and recycling of coal ash are tried to proceed aggressively, and the percentage and amount of

effective usage in 2014 reach about 98 % and 9.4 million tons/year, respectively. However, more than 0.2 million tons/year of coal ash must be deposited in a landfill. Furthermore, since the Great East Japan Earthquake on March 11, 2011, the focus of energy production in Japan has shifted from nuclear power toward coal-generated power. The fly ash generated at coal-fired power plants was mostly wasted before the earthquake, more fly ash is expected to be generated, and the lack of landfill space is anticipated in Japan. New recycle technologies for the consumption of a large amount of coal ash are desired to develop [3-6].

Geopolymer is a three-dimensional aluminosilicate based construction and building material, which is sustainable and environmentally friendly due to low emission of carbon during their production and processing. Geopolymer cement is generally produced by mixing alkali activator (sodium silicate, sodium hydroxide, water) and various aluminosilicate precursors such as fly ash and bottom ash [7-12], clays [13-15], metakaolin [16, 17], natural soil [18], glass [19], slags [20, 21], volcanic ashes and rice husk ash [22-26]. 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  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and so on, which is similar to the reaction of zeolite synthesis [27, 28], and geopolymer cement has high acid

resistance, high fire resistance and ion exchange ability [29-34]. Therefore, geopolymer cement has attracted attention, and are associated with numerous international patents as well as many commercial engineering projects.

In our previous studies, zeolite can be synthesized from the green tuff stone cake by NaOH reaction, with extracting high content of Si from the cake [35]. Furthermore, geopolymer cement can be prepared by mixing alkali fused stone dust, water, and coal fly ash due to the reaction between the soluble contents of Si and Al from the fused cake and coal fly ash [36]. There is the possibility to produce geopolymer cement from coal fly ash and the slurry by converting the slurry into alkali activator using alkali reaction.

In this study, we attempted to prepare geopolymer cement from the waste fine-stone slurry and coal fly ash. The alkali activator, sodium silicate solution, was prepared from the slurry by treating with NaOH, and the prepared activator was mixed with coal fly ash to form geopolymer cement. The conditions, such as NaOH concentration, heating temperature, heating time, and mixing ratio of coal fly ash, to prepare the geopolymer product with the hard structure were investigated and the water purification ability of the obtained geopolymer cement was evaluated.

## 2. EXPERIMENTAL

### 2.1 Sample

Waste fine-stone slurry generated from one of the domestic crushed stone companies in Japan was used for the experiment. The concentration of fine-stone in the slurry is 928 g/L, and the diameter of the fine stone is under 250  $\mu\text{m}$ . Coal fly ash used in this study was commercially available fly ash type V. The chemical compositions and mineralogical compositions of the fine-stone in the slurry and coal fly ash are shown in Table 1 and Figure 1, respectively. The fine slurry mainly composed of  $\text{SiO}_2$  (61.7 %),  $\text{Al}_2\text{O}_3$  (19.6 %), and some minor elements in the form of quartz ( $\text{SiO}_2$ ), talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), albite ( $\text{NaAlSi}_3\text{O}_8$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), muscovite ( $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ), clinocllore ( $(\text{Mg}, \text{Fe}, \text{Al})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$ ) and so on. Coal fly ash is also mainly composed of  $\text{SiO}_2$  (55.0 %),  $\text{Al}_2\text{O}_3$  (20.8 %), and some minor elements in the form of quartz ( $\text{SiO}_2$ ) and mullite ( $\text{Si}_2\text{Al}_6\text{O}_{13}$ ) with amorphous phases indicating the broad hump of 20 - 30°.

Sodium hydroxide (NaOH) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) were purchased from FUJIFILM Wako Pure Chemical Corporation, Japan, with purities of > 97% and > 99.5 %, respectively.

Table 1 Chemical compositions of fine stone in slurry and coal fly ash.

Contents (%)	Fine stone in slurry	Coal fly ash
$\text{SiO}_2$	61.7	55.0
$\text{Al}_2\text{O}_3$	19.6	20.8
CaO	2.1	5.1
MgO	1.4	0.2
$\text{Fe}_2\text{O}_3$	4.8	10.7
$\text{Na}_2\text{O}$	1.6	1.0
$\text{K}_2\text{O}$	3.3	2.1
$\text{SO}_3$	1.3	1.1

### 2.2 Preparation

#### 2.2.1 Silica solution

Sodium silicate solution for making geopolymer cement was prepared from the slurry with addition of NaOH. NaOH solution (5 mL) was added into the slurry (10 mL) to prepare 15 mL of the slurry with 2 - 8 M NaOH concentration in a 50 mL of pressure vessel, and heated at 60 - 180 °C for 0 - 24 h in an electric furnace. It is noted that rising time to setting temperature is 30 min. After heating, the vessel was quenched with tap water, the solution was filtered, and the concentration of Si in the filtrate was measured using an atomic absorption spectrometer (AAAnalyst 200, Perkin Elmer).

#### 2.2.2 Geopolymer cement

Geopolymer cement was prepared from the slurry treated with NaOH under various conditions. Coal fly ash was mixed with the slurry obtained on various conditions at the mixing weight ratio of ash/slurry = 0.25 - 0.70, poured into a mold ( $\phi 25 \text{ mm} \times 5 \text{ mm}$ ) and set in an oven at 80 °C for 24 h. After heating, the hardness of the product was judged with a bamboo needle to insert into the product. The hardened products were subjected to strength tests using a strength tester (ZT series ZTA-500N, IMADA). The sharp point attachment (S-3) was inserted into the sample at a speed of 30 mm/min to measure the strength when the sample broke. Strength tests for the ordinary Portland cement were carried out to compare strength. Portland cement was prepared at water-cement ratio (W/C) = 50 %, formed in a mold, and cured at room temperature for 7 days.

### 2.3 $\text{NH}_4^+$ Removal

The water purification ability of the product was estimated for the  $\text{NH}_4^+$  removal test. The  $\text{NH}_4^+$  solution with 900 mg/L, which simulated piggery wastewater, was prepared using  $\text{NH}_4\text{Cl}$ . The product block was prepared with a mold of  $\phi 25 \text{ mm}$

× 5 mm to remove the mold and added into 200 mL of  $\text{NH}_4^+$  solution for 168 h. During the immersion of the product block, the concentration of  $\text{NH}_4^+$  in the solution was analyzed using the thymol blue method for monitoring the  $\text{NH}_4^+$  removal.

### 3. RESULTS AND DISCUSSION

#### 3.1 Silicate Solution from The Slurry

Figure 2 shows the Si concentration of the slurry treated with 2 - 8 M NaOH concentration at 60 - 180 °C for 24 h. It is noted that Si concentration for preparing geopolymer cement is set to 20 - 60 g/L [37]. With increasing the NaOH concentration and temperature, Si concentration in the obtained slurry increases. About 60 g/L of Si contains in the slurry treated with 6 - 8 M NaOH at 140 °C and 180 °C, while lower than 20 g/L of Si contains in the slurry treated at 60 °C and 100 °C regardless of NaOH concentration. In the case of 120 °C, with increasing the NaOH concentration, Si content increases from 22 g/L to 49 g/L, which are desired contents for preparing geopolymer cement [37]. Therefore, the temperature of slurry treatment is set to 120 °C in this study.

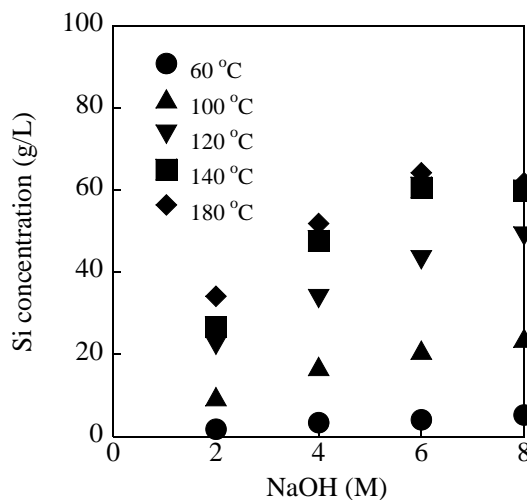


Fig. 2 Concentration of Si in the slurry treated with 2 - 8 M NaOH concentration at 60 - 180 °C for 24 h.

Figure 3 shows the Si concentration of the slurry treated with 2 - 8 M NaOH concentration at 120 °C for 0 - 18 h. With increasing the NaOH concentration and reaction time, Si concentration in the slurry increases, and the slurry treated with 4 - 8 M NaOH for 9 h contains 20 - 35 g/L of Si within 20 - 60 g/L of Si for preparing geopolymer cement [37].

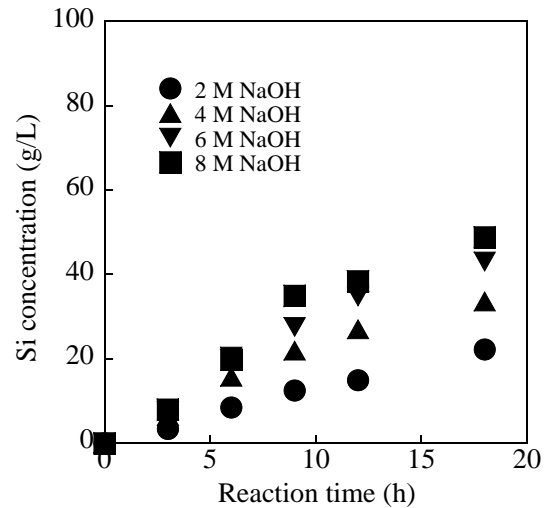


Fig. 3 Concentration of Si in the slurry treated with 2 - 8 M NaOH concentration at 120 °C for 0 - 18 h

Therefore, a silicate solution for preparing geopolymer cement can be prepared from the slurry treated with 4 - 8 M NaOH at 120 °C for 9 h.

#### 3.2 Geopolymer Formation

We attempted to form a geopolymer product from the slurry treated with 4 - 8 M NaOH at 120 °C for 9 h. Figure 4 shows the condition for preparing hardened products with addition of coal fly ash to the slurry with various NaOH concentrations. The horizontal axis indicates NaOH concentration in the slurry, the vertical axis indicates the mixing ratio of coal fly ash, and the plots indicate the condition to obtain the hardened product without sticking a bamboo needle into the product. The hardened product can be obtained when the mixing ratio of coal fly ash are 0.55 and 0.70 regardless of NaOH concentration, and from the slurry with 4 M NaOH concentration regardless of mixing ratio.

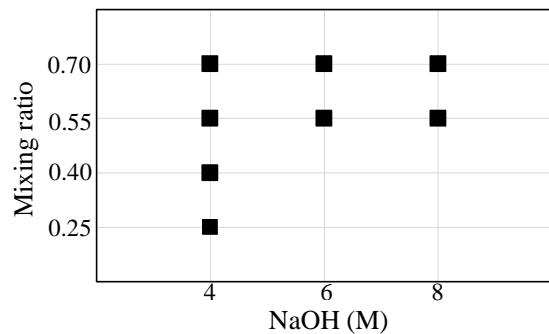


Fig. 4 Conditions for preparing hardened products with addition of coal fly ash to the slurry with various NaOH concentrations.

Figure 5 shows the strength of the product from the slurry with 4 - 8 M NaOH concentration at various mixing ratios of coal fly ash. It is noted that the strength of the Portland cement sample is 167 N using this measurement. The strengths of the product are higher than that of Portland cement and those of the product from the slurry with 6 - 8 M NaOH indicates 345 - 450 N when the mixing ratios are 0.55 and 0.70, while those are low (5 - 25 N) when the ratio are 0.25 and 0.40.

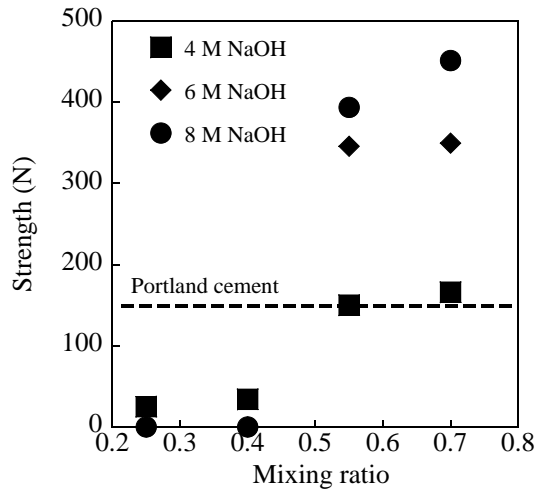


Fig. 5 The strength of the product from the slurry with 4 - 8 M NaOH concentration at a various mixing ratio of coal fly ash

From these results, the geopolymer product with sufficient strength can be prepared from the mixture of the slurry treated with 4 - 8 M NaOH at 120 °C for 9 h and coal fly ash at the mixing weight ratio of coal fly ash to the slurry = 0.55 - 0.70.

### 3.3 Water Purification

Three product blocks were used for this removal test. Product-1 was prepared from the slurry with 6 M NaOH at the weight ratio of coal fly ash = 0.70, Product-2 from the slurry with 8 M NaOH at the weight ratio of ash = 0.70, and Product-3 from the slurry with 8 M NaOH at the ratio of ash = 0.55. Figure 6 shows the XRD patterns of the product. All products indicate almost the same XRD patterns including quartz, mullite, albite, and hydroxysodalite ( $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 8\text{H}_2\text{O}$ ). Hydroxysodalite is formed by alkali treatment of the slurry, while quartz, mullite, and albite are originated from fine-stone and coal fly ash.

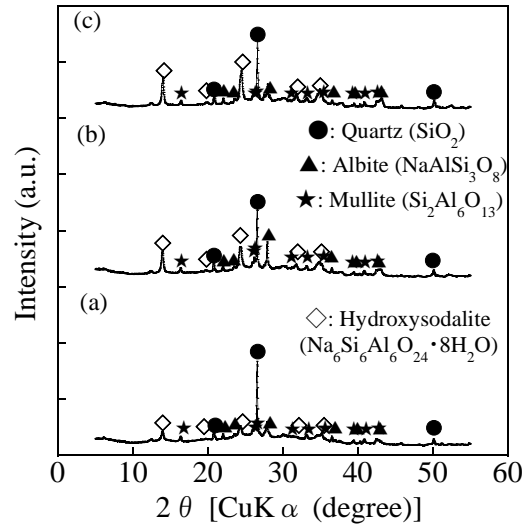


Fig. 6 XRD patterns of the products: (a) Product-1, (b) Product-2, (c) Product-3.

The water purification ability of the obtained geopolymer product was examined using the  $\text{NH}_4^+$  solution. Figure 7 shows the  $\text{NH}_4^+$  concentration in the solution after the immersion of the product block. All products indicate  $\text{NH}_4^+$  removal ability. In comparison with  $\text{NH}_4^+$  removal of the product when the mixing ratios of coal fly ash are the same, Product-2 obtained from the slurry with 8 M NaOH indicates higher  $\text{NH}_4^+$  removal than Product-1 from the slurry with 6 M NaOH. In comparison with  $\text{NH}_4^+$  removal of the product from the slurry with the same concentration of NaOH, Product-3 obtained at the mixing ratio of 0.55 indicates higher  $\text{NH}_4^+$  removal than Product-2 at the mixing ratio of 0.70. Product-3 can decrease  $\text{NH}_4^+$  concentration from 900 mg/L to 540 mg/L for 7 days.

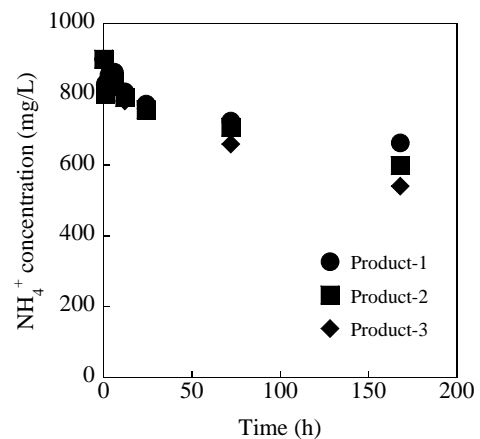


Fig. 7  $\text{NH}_4^+$  concentration in the solution after immersion of the product block.

#### 4. CONCLUSION

We attempted to prepare geopolymer cement from the waste fine slurry and coal fly ash via alkali reaction. The silica solution for preparing geopolymer cement can be prepared from the slurry by treating with 4 - 8M NaOH at 120 °C for 9 h, and the hardened geopolymer product can be formed by mixing with coal fly ash (the mixing weight ratio = 0.55 - 0.70). The product obtained from the slurry treated with 6 - 8 M NaOH by mixing with coal fly ash (the mixing ratio = 0.55 - 0.70) indicates higher strength than ordinary Portland cement and has the  $\text{NH}_4^+$  removal ability. These results suggested that waste slurry can be converted into geopolymer cement with sufficient strength and water purification ability by alkali reaction and mixing with coal fly ash.

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