

## **Geopolymer Solidification of Intermediate Level Waste – 17078**

Kanae Matsuyama \*, Hirofumi Okabe \*, Chiaki Shimoda \*,  
Shinya Miyamoto \*, Masaaki Kaneko \*, Michitaka Saso \*, Masumitsu Toyohara \*  
\* Toshiba Co.

(kanae.matsuyama@toshiba.co.jp)

### **ABSTRACT**

To reduce the amount of hydrogen generated due to water radiolysis in stored intermediate-level waste, geopolymer solidification, followed by drying, was studied. From the viewpoints of high thermal stability and low processing cost, geopolymer solidification is an excellent method for conditioning intermediate level waste. In this study, in order to determine if radioactive waste could be treated using geopolymer solidification, tests were conducted by using a simulated slurry generated from contaminated water treatment. The uniaxial compressive strength of the geopolymer solidified waste containing 50 wt.% of the slurry was more than 10 MPa. To reduce the amount of hydrogen generated, the geopolymer-solidified waste was dehydrated, and the water content of the remaining solid was less than 1 wt.%. Moreover, the value of the uniaxial compressive strength of dehydrated geopolymer-solidified waste was similar to that of the untreated one. The volume reduction rate of the slurry solidification was obtained at the applicability limit.

### **INTRODUCTION**

In general, when concentrated radionuclides and water are present together in solidified wastes, hydrogen is generated by water radiolysis. Although long-term safekeeping of solidified wastes, which have concentrated radionuclides in a sealed container without vents, is necessary, the hydrogen concentration in the container increases with time. If the hydrogen concentration increases to about 4 vol% in air, there is a danger of explosion [1]. Therefore, it is necessary to reduce the amount of water in solidified wastes to reduce the amount of hydrogen generated.

According to the International Atomic Energy Agency (IAEA) specifications, intermediate-level waste is defined as waste that contains long-lived radionuclides in quantities that need a greater degree of containment and isolation from the biosphere than is provided by near surface disposal. Thus, disposal in a facility at a depth between tens and hundreds of meters is necessary for intermediate level waste [2]. In Japan, disposal of intermediate level waste at a sufficient depth for at least a hundred thousand years, because of long half-life nuclides, is required. Therefore, disposal of intermediate-level waste in a sealed container without vents is considered to be a desirable storage container [3].

Cement solidification is a widely-used method for stabilizing low level and intermediate-level waste generated from nuclear facilities because of its stability,

confinement capabilities and low processing cost. However, if crystallization water in the cement can be decomposed by the heat generated from hydration of cement and decay of radioactive nuclides, cement solidification has a problem in terms of long-term stability [4]. Vitrification is a possible method for stabilizing high-level radioactive wastes from nuclear facilities because of its long-term stability, confinement capability and thermal stability. On the other hand, since vitrification needs high temperature processing, vitrification of low- and intermediate-level radioactive wastes has several problems due to radionuclides volatilization during processing, processing cost and so on.

From the viewpoints of high thermal stability and low processing cost, geopolymer solidification is an excellent method for conditioning intermediate-level waste. Geopolymers form an amorphous three dimensional framework structure via an inorganic poly condensation reaction [5]. The geopolymer frame structure does not contain water because it is composed of silicon, aluminum and oxygen and so on. Moreover, when geopolymer-solidified wastes are dehydrated, the geopolymer maintains its structure and mechanical strength. Therefore, geopolymer solidification is the most appropriate method for stabilizing intermediate-level waste.

In this study, in order to determine if radioactive waste could be treated by using geopolymer solidification, tests were conducted by using a simulated slurry generated from contaminated water treatment. A carbonate slurry and spent adsorbents generated from the contaminated water treatment facility in the Fukushima Daiichi Nuclear Power Station contain high concentrations of radionuclides [6]. Thus, they are currently stored in high integrity containers (HICs) at the Fukushima Daiichi Nuclear Power Station. Since the quantity of the generated waste continues to increase, a simple, low cost, high volume-reducing treatment method is needed.

A scheme for the geopolymer solidification process is shown in Fig. 1. The carbonate slurry in the tank is extracted and transferred to dewatering equipment. In dewatering equipment, the slurry is concentrated to reduce the volume. The concentrated slurry and the geopolymer materials are mixed in the mixing tank. The mixture is transferred to a molding machine, and the solidified wastes are molded. After heat drying, the dried solidified wastes are stored in a container.

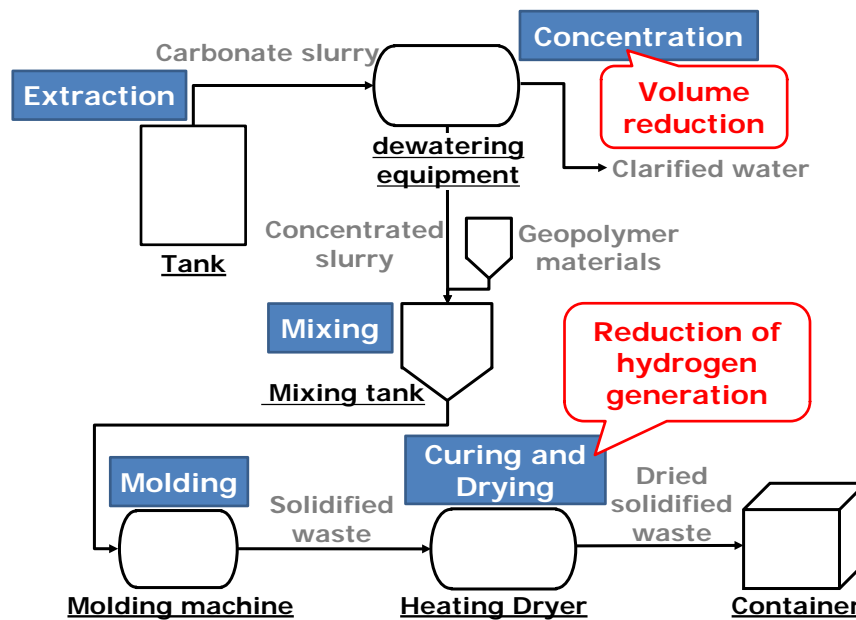


Fig. 1. Schematic drawing of the geopolymer solidification process for carbonate slurry.

## EXPERIMENTAL

### Simulated Waste and Geopolymer Materials

The simulated slurry was prepared with the reagents by reference to the analytical data of the carbonate slurry from the contaminated water treatment facility at the Fukushima Daiichi Nuclear Power Station [7]. The water content of the simulated slurry was estimated to be 50 wt.% after concentration in a dewatering equipment. Metakaolin (MK), blast furnace slag (BFS) and fly ash (FA) were used for the geopolymer base materials. The chemical compositions (weight percentage) of the geopolymer base materials, determined by using X-ray fluorescence (XRF) spectrometer (Rigaku Corp., ZSX Primus II) and a fundamental parameter method, are shown in Fig. 2. In addition to the geopolymer base materials, a sodium silicate solution, a potassium silicate solution, sodium hydroxide and potassium hydroxide were used as geopolymer materials.

The Si/Al mole ratio of the geopolymer materials were adjusted to 1.3 (MK) and 2.2 (MK+BFS, MK+BFS+FA). In order to adjust the Si/Al mole ratio, silicon dioxide was added to the geopolymer base materials.

### Solidification

The experimental flow is shown in Fig. 3. Simulated carbonate slurry was mixed using a screw agitator for 5 min. Then the geopolymer materials were added, and the reaction was mixed for 5 min at room temperature. The mixture was poured into a mold with a diameter 0.05 m and a height of 0.1 m. The uniaxial compressive strengths of solidified wastes were measured by using a compressive strength test machine after curing for about 14 d. After curing, the solidified wastes

were removed from the mold and dried. After drying, the uniaxial compressive strength of the dried solidified wastes, which is used to indicate its soundness, was measured.

### **Optimal Combination of Geopolymer Materials**

In order to determine the optimal combination of the geopolymer materials, the uniaxial compressive strengths of the solidified wastes prepared with four combinations of starting materials were measured. MK, sodium silicate solution, potassium silicate solution, sodium hydroxide and potassium hydroxide were used for the geopolymer materials. The solidified wastes were prepared with 50 wt.% carbonate slurry and the equivalent amount of alkali.

### **Allowable Amount of the Carbonate Slurry**

In order to determine the allowable amount of the carbonate slurry in the solidified waste, the uniaxial compressive strengths were measured. Weight percentages of the carbonate slurry in the solidified wastes of 0, 40, 50, 60, 70 and 90 were tested. The geopolymer base material was MK, and the weight percentage of water in the geopolymer materials was about 40 wt.%.

### **Apparent Viscosity of the Geopolymer Mixture**

The apparent viscosity was measured continuously by using a rotational viscometer because the carbonate slurry is a non-Newtonian fluid. The geopolymer mixtures were prepared with MK, MK+BFS and MK+BFS+FA as the geopolymer base materials.

### **Changes in the Water Content Ratio and Compressive Strength after Drying Process**

The demolded solidified wastes were dried at 330 °C for about 2 d in a furnace. After drying, the uniaxial compressive strength of the solidified wastes was measured. The water content ratio of the solidified waste was measured by using Karl Fischer's method as the index for the hydrogen generated from solidified waste.

### **Volume Reduction Rate**

The volume reduction ratio was determined assuming that the carbonate slurry volume (the water content ratio = 85 wt.%) in the HIC was 1. In addition, the water content of the carbonate slurry was 50 wt.%, and the amount of the carbonate slurry in the solidified waste was 50 wt.%.

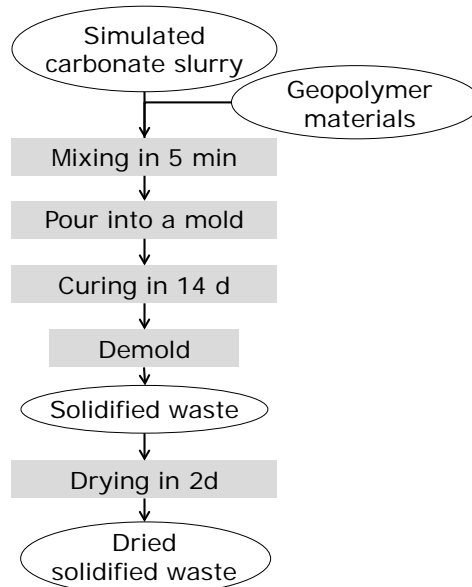
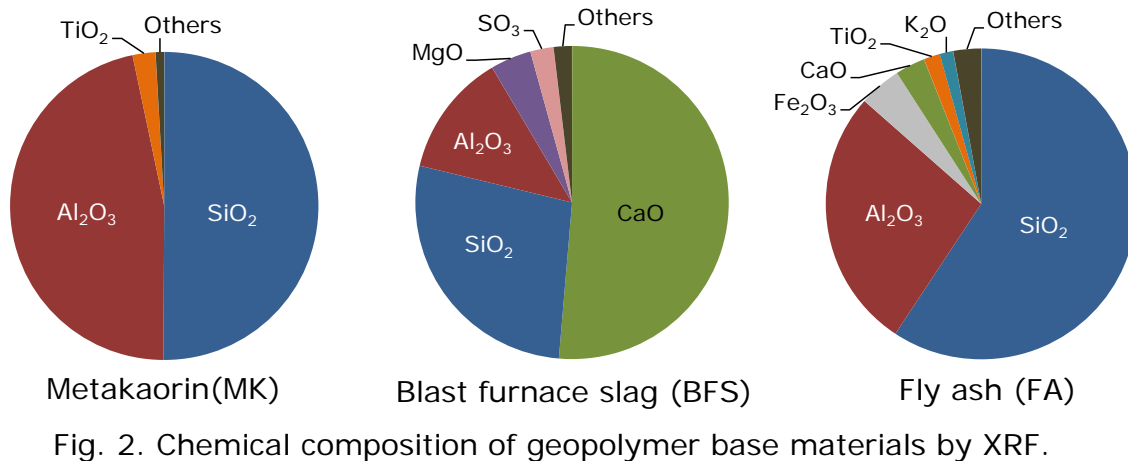


Fig. 3. Experimental flow of geopolymer solidification process.

## RESULTS AND DISCUSSION

### Optimal Combination of Geopolymer Materials

Fig. 4 shows the uniaxial compressive strength of the solidified wastes prepared with the combination of geopolymer materials indicated and 50 wt.% carbonate slurry. MK, a sodium silicate solution, a potassium silicate solution, sodium hydroxide and potassium hydroxide were used as geopolymer materials. The compressive strength of the solidified wastes with the sodium silicate solution and potassium hydroxide was the highest of the four combinations used. The compressive strength of all the solidified waste prepared with 50 wt.% carbonate slurry was more than 5 MPa. Therefore, the application possibility of the geopolymer solidification to carbonate slurry was confirmed.

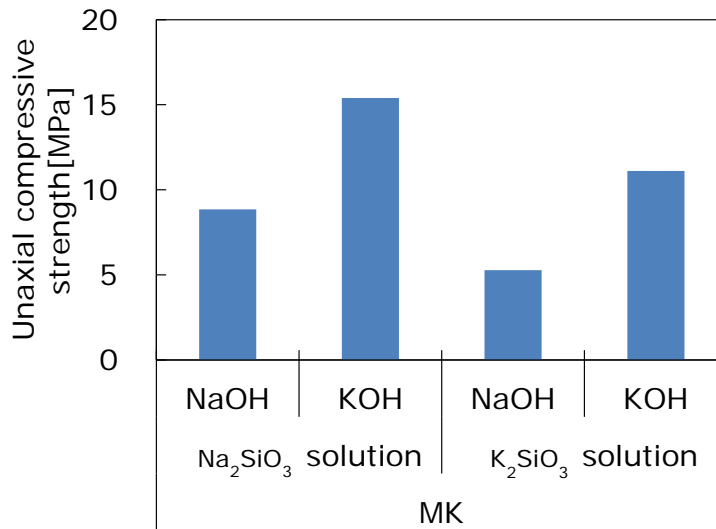


Fig. 4. Uniaxial compressive strength of the solidified wastes prepared with the combination of geopolymer materials indicated and 50 wt.% carbonate slurry.

#### Allowable Amount of the Carbonate Slurry

Fig. 5 shows the uniaxial compressive strength of the solidified wastes prepared with weight percentages of the carbonate slurry of 0, 40, 50, 60, 70 and 90. Although the compressive strength of the solidified waste decreased with an increase in the weight percentage of the carbonate slurry, the uniaxial compressive strength of the solidified waste with less than 50 wt.% slurry was more than 10 MPa. The values were higher than the value for cement wastes in Japan (1.47 MPa), which is used as a guide for soundness [8]. Although the compressive strength of the solidified waste was more than 10 MPa for the solidified waste with less than 50 wt.% slurry, the apparent viscosity of the geopolymer mixture prepared with MK was more than 100 dPa·s after adding the geopolymer materials.

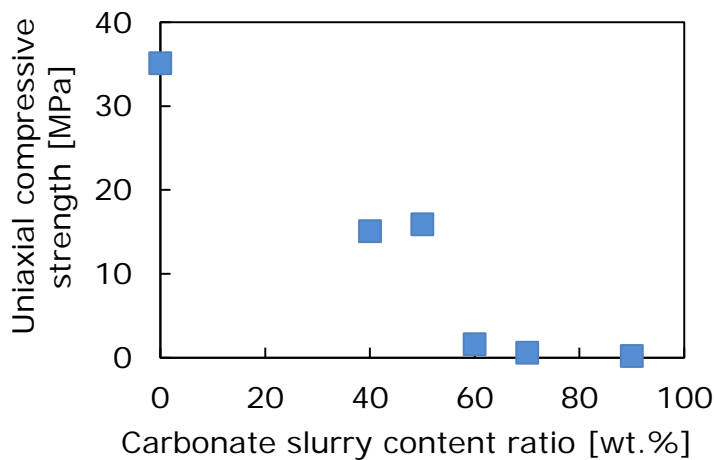


Fig. 5. Uniaxial compressive strength of the solidified wastes prepared with weight percentages of the carbonate slurry of 0, 40, 50, 60, 70 and 90.

### Apparent Viscosity of Geopolymer Mixture

The apparent viscosity of the mixture is shown in Fig. 6. The apparent viscosity of geopolymer mixture prepared with MK increased more than 100 dPa·s immediately after adding the geopolymer materials. Therefore, in order to reduce the viscosity of the geopolymer mixture, the mix ratio of geopolymer base materials was adjusted. By replacing MK with BFS and BFS+FA in the mixture, a comparatively low viscosity (lower than 25 dPa·s) was maintained for a longer period. In this case, “comparatively low viscosity” means a viscosity lower than that of a cement mixture with a water/cement ratio of 0.45 which was used as the viscosity reference value of a continuously mixable standard.

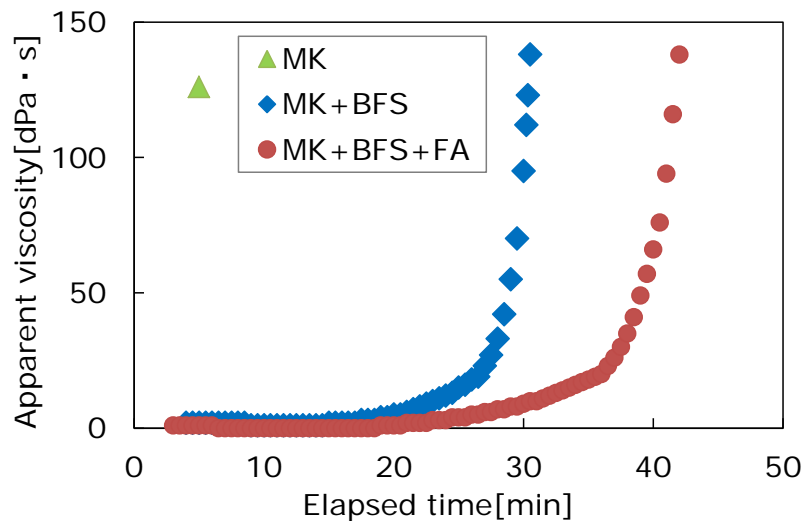


Fig. 6. The apparent viscosity of MK, MK+BFS, MK+BFS+FA.

### Changes in the Water Content Ratio and Compressive Strength after Drying Process

TABLE I shows the water content ratio and the uniaxial compressive strength of the solidified wastes before and after drying. The water content ratio was decreased from 36.2 wt.% (25 °C) to less than 1 wt.% (300 °C) after drying. Decreasing the water content of the solidified waste is effective for reducing the amount of hydrogen generated during storage period. The uniaxial compressive strength of the dehydrated geopolymer solidified waste after drying is similar to that for the untreated solidified waste before drying. Therefore, because of the high thermal stability and the reduction of the amount of generated hydrogen, geopolymer solidification is an excellent method for processing intermediate level waste.

TABLE I. Water content ratio and uniaxial compressive strength of solidified wastes before and after drying.

State of the solidified waste	Water content ratio [wt.%]	Uniaxial compressive strength [MPa]
Before drying	36.2	15.8
After drying	0.96	15.2

### Volume Reduction Rate

Fig. 7 shows the volume reduction rate of the carbonate slurry and the solidified waste. Assuming that the carbonate slurry volume (the water content ratio = 85 wt.%) in the HIC was 1, the volume reduction ratio of solidified waste was determined to be 0.34.

By the geopolymer solidification, the volume of the carbonate slurry is reduced to 1/3 and slurry is stabilized by the dried solidified waste which generates a small amount of hydrogen in a storage period.

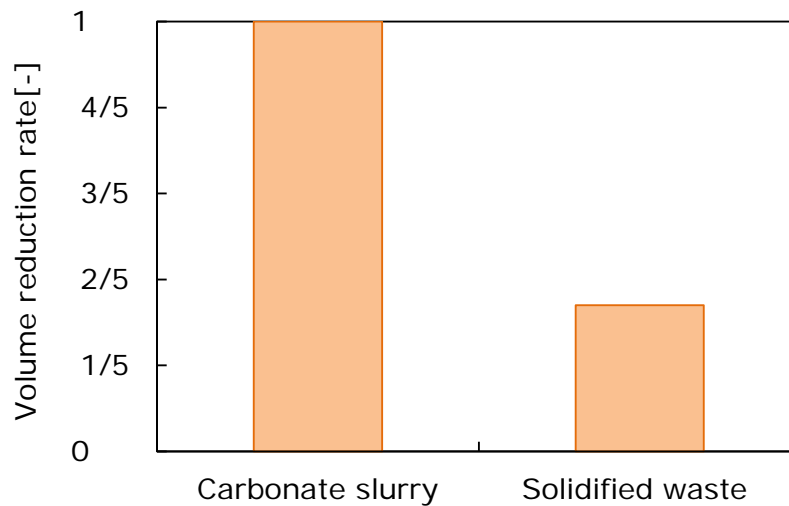


Fig. 7. Volume reduction rate of the carbonate slurry and the solidified waste.

### CONCLUSIONS

To reduce the amount of hydrogen generated from water radiolysis, geopolymer solidification, followed by a drying process, of intermediate-level waste was studied. To assess the applicability of this process towards radioactive waste, tests were conducted using a simulated slurry generated from contaminated water treatment. The uniaxial compressive strength of the geopolymer-solidified waste containing wt.% of the slurry was more than 10 MPa with a volume reduction rate of geopolymer solidified waste of 1/3 of the slurry in a HIC. In addition, by varying the



mixture of geopolymer base materials, the apparent viscosity of geopolymer mixture was reduced. After the drying process, the compressive strength did not change, whereas the water content ratio of dried solidified waste was lower than 1 wt.%. Thus, because of the high thermal stability, low processing cost and the reduction of the amount of generated hydrogen and volume, geopolymer solidification is an excellent method for processing intermediate level waste. In addition, geopolymer solidification could be applicable not only to a slurry but also various radioactive wastes such as spent adsorbents or ion-exchange resins and so on.

## REFERENCES

1. H.F.Coward and G .W.Jones, *Limit of inflammability of gases and vapors*, pp.15-19, No.503, U.S. Bureau of Mines Bulletin, Washington, U.S.A (1952).
2. International Atomic Energy Agency, *Classification of Radioactive Waste*, pp.4-8, IAEA Safety Standards Series No.GSG-1, International Atomic Energy Agency, Vienna, Austria (2009).
3. Atomic Energy Society of Japan, *Technical-requirements and inspection-method for manufacturing sub-surface disposal waste package*, pp2-14 (in Japanese), AESJ-SC-F014:2015, Atomic Energy Society of Japan, Tokyo, Japan (2015).
4. M. D. Andersen et al, "A new aluminium-hydrate species in hydrated Portland cements characterized by  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectroscopy," *Cement and Concrete Research*, 36, 3–17 (2006).
5. J. Davidovits, *Geopolymer chemistry applications*, pp. 39-60, 3<sup>rd</sup> Ed., Institut Geopolymere, Saint-Quentin, France (2011).
6. Tokyo Electric Power Company, Incorporated, website, "Contaminated Water Treatment" (2011).  
URL; <http://www.tepco.co.jp/en/decommision/planaction/alps/index-e.html>.
7. International Research Institute for Nuclear Decommissioning, website, "Selection requirements organize and applicability of test results of slurry stabilization technology" (in Japanese)  
URL;<http://irid.or.jp/topics/pressinfo/3949.html/>
8. Japan Nuclear Energy Safety organization, *About the confirmation method for abandonment of homogeneous and uniform solidification and a filling solidification*, pp.28-31 (in Japanese), JNES-SS-0801, Japan Nuclear Energy Safety organization Safety Standard Division, Tokyo, Japan (2008).