Development of Cement Solidification Technique for Sodium Borate Waste Produced in PWR Plants – 16061

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ABSTRACT

A cement solidification process for treating sodium borate waste produced in pressurized water reactor (PWR) plants was studied. It is known that the setting and hardening reaction of cement is retarded by the presence of boron compounds. This technique was developed to obtain high uniaxial compressive strength more than 10 MPa which can satisfy various countries disposal regulations. As examples of disposal regulations, France requires 8 MPa for homogeneous solidified products. The sodium/ boron (Na/B) ratio was controlled to about 1 by adding NaOH to simulated liquid waste for the purpose of improving the workablility and mechanical strength. To obtain high volume reduction, simulated liquid waste was dehydrated and powdered by using a wiped film evaporator. Ordinary portland cement (OPC) was used for the solidification. The viscosity of cement mixture was controlled by the water/cement ratio. The resulting viscosity became less than 25 dPa·s, and it was possible to continuously mix the mixture. Solidified cement with containing 73 kg/m^3 of boron had a uniaxial compressive strength of more than 10 MPa.

INTRODUCTION

In PWR plants, boron is added to the primary cooling water for the purpose of control the fission reaction. During operation and maintenance, the liquid waste containing boron and radionuclides are produced. The evaporators are used for condensing liquid waste in most PWR plants from the viewpoint of volume reduction[1)]. The sodium / boron (Na/B) mole ratio of the concentrated liquid waste depends on the plants, and it is usually about 0.2 to 0.5. Concentrated liquid borate waste is stored in interim storage tanks.

Cementation is one of most attractive methods for the treatment and disposal of low- and intermediate- level radioactive waste because of its stability, confinement capability and mechanical strength. However, it is known that the setting and hardening reaction of cement is retarded by the presence of boron compounds[2),3),4),5)]. Obtaining solidified product with high volume reduction is difficult without any pre-treatment[6),7),8)].

We have previously developed a cement solidification technique for treating radioactive liquid waste[9),10)]. The boron content in the solidified products produced by that technique was about 70 kg/m^3, and the final uniaxial compressive strength satisfied the value of 1.47 MPa stipulated in the Japanese disposal regulations. This technique is able to obtain high volume reduction, however it need aftertreatment system for the washing wastewater which contain non- soluble solid. Therefore, we have developed simple cement solidification process for sodium borate[11),12)]. This cement solidification process was based on technique which was practical used in

Japanese nuclear power plant. The purpose of the development was, to obtain high volume reduction with high uniaxial compressive strength more than 10 MPa which can satisfy various countries disposal regulations. As examples of disposal regulations, France requires 8 MPa for homogeneous solidified product[13).The uniaxial compressive strength at about 91 days curing was more than 10MPa and the boron content was about 50kg/m^3 [12)].

In this paper, the allowable range of Na/B mole ratio of simulated concerted liquid waste was studied. Furthermore the improvement in boron content of solidified waste was conducted. Cement solidification experiments were conducted with boron content was about 50 to 70kg/m^3. The simulated sodium borate concentrated liquid was dried and solidified to obtain high volume reduction. The schematic drawing of cement solidification process is shown in Fig. 1.

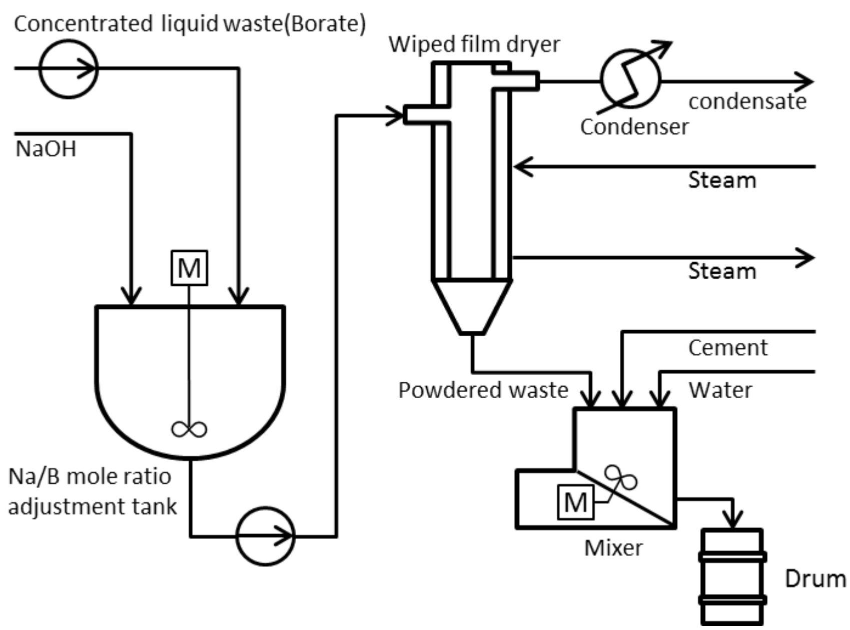

Fig. 1. The schematic drawing of cement solidification process.

EXPERIMENTAL

1) Simulated waste

Simulated liquid waste with concentration about 20000ppm of boron was prepared from $B(OH)_3$ and NaOH. The Na/B mole ratio of simulated liquid waste was controlled 0.85, 0.95, 1.0 and 1.15. The simulated liquid waste was dried to a powder by using a wiped film dryer[9)] for the purpose of obtaining high volume reduction[11),12)]. In order to evaluate the Na/B mole ratio of the powder product, powder was dissolved in water, and its concentrations of Na and B in the solution were measured by neutralizing titration.

Cement solidification was conducted by using powdered waste. Ordinary Portland cement (OPC) manufactured by Taiheiyo Cement Co. was used for the cement solidification.

2) Solidification

The experimental flow is shown in Fig. 2. The powder prepared from simulated liquid waste was used. Simulated sodium borate powder was mixed with water by using a screw agitator for 60 minutes at room temperature. Then the cement was added and mixed for 10 minutes at room temperature. After completing mixing and measuring the viscosity, the mixture was filled into a mold with a diameter 0.05 m and a height of 0.1 m. The uniaxial compressive strength of solidified products were measured after about 91 days curing.

2)-1 Solidification with boron content about 50g/m^3

The water/cement ratio (W/C) was 0.7 which decided from previous study. The amount of the powdered concentrated liquid waste was decided as the boron content will become about 50kg/m^3 [12]. The leaching test was conducted by using solidified waste prepared from simulated liquid waste with the Na/B mole ratio of 1.0.

2)-2 Solidification with boron content about 70kg/m^3

Solidification product was prepared with W/C of 0.7, 0.85 and 1.0. The amount of the powdered concentrated liquid waste was decided as the boron content will become about 70kg/m^3. The solidified product was crush to a powder and analyzed by X-ray diffraction (XRD, RINT Ultima III, Rigaku Co.).

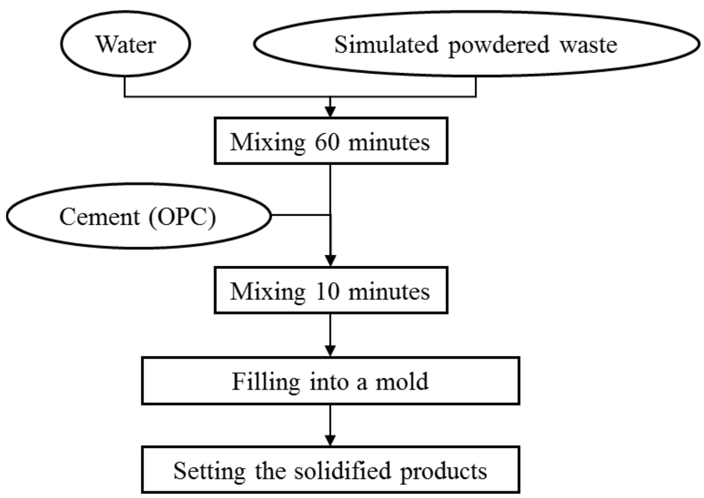

Fig. 2. Experimental flow of cement solidification process.

RESULTS AND DISCUSSION

1) Simulated waste

Sufficiently dried powdered simulated waste was prepared from simulated liquid waste with the Na/B mole ratio of 0.95, 1.0 and 1.15 by using a wiped film dryer. The Na/B mole ratio was 0.92, 0.98 and 1.15. However it was difficult to prepare a powder from simulated liquid with the Na/B mole ratio of 0.85.

2)-1 Solidified product with boron content about 55kg/m^3

The viscosity of the mixture is shown in Fig. 3. The viscosity of cement mixture prepared with Na/B mole ratio of 0.95 and 1.0 was lower than 25 dPa·s. However high Na/B ratio, the maximum viscosity was 47 dPa·s, and it was possible to continuously mix the mixture.

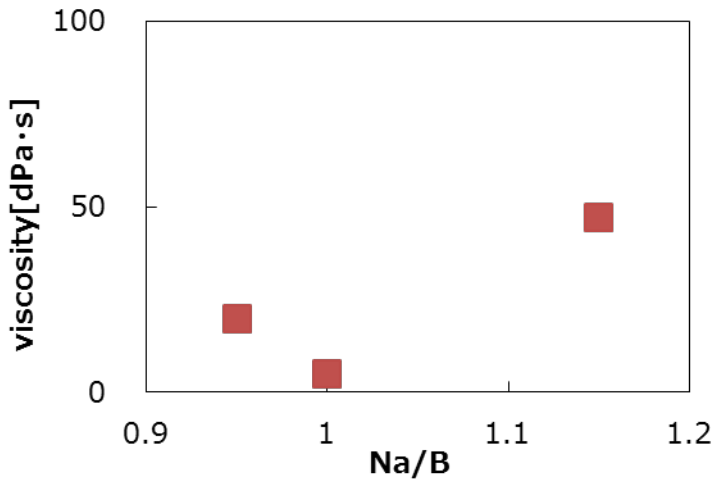

Fig. 3. The viscosity of the mixture prepared with Na/B mole ratio of 0.95, 1.0 and 1.15.

Fig. 4 shows the uniaxial compressive strength of the solidified products. The Na/B mole ratio increased, the strength of the solidified product decreased. However the uniaxial compressive strength was higher than 10MPa in all conditions. The values were higher than 8MPa, which is the stipulated value in the Aube (France) disposal regulations [13)]. The boron content of the solidified product was 56kg/m^3. The swelling at about after 91 days was not observed at any condition.

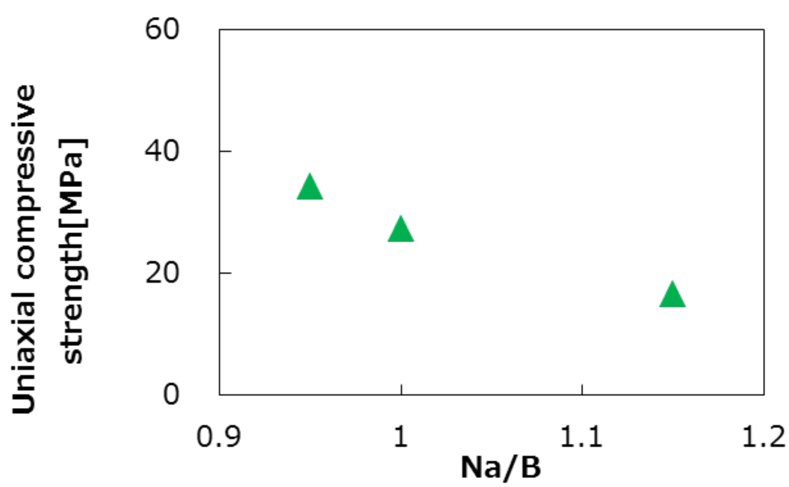

Fig. 4. Uniaxial compressive strength of the solidified products prepared with Na/B mole ratio of 0.95, 1.0 and 1.15.

Fig. 5 shows the effective diffusivity and leached quantity of boron for solidified product prepared with Na/B mole ratio of 1.0. The leaching index of boron was 8.8. About 9.1% of Boron was released into water. Fig. 6 shows the photos of the specimen which was used for leaching test. No specific changes in the specimen geometry of solidified product were observed. The weight loss of the solidified product was less than 5 wt%. Although soluble sodium borate was mixed in the product, the geometry of solidified product was hold.

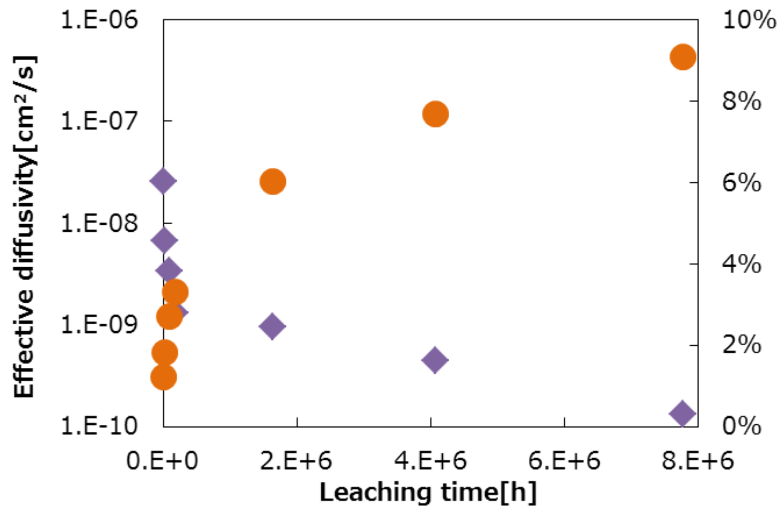

Fig. 5. The effective diffusivity and leached quantity of boron for solidified product prepared with Na/B mole ratio of 1.0.

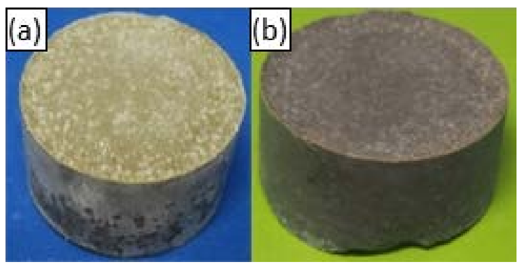

Fig. 6. The photos of the specimen ((a) before leaching test, (b) after leaching test).

2)-2 Solidified product with boron content about 70kg/m³

The viscosity of the mixture is shown in Fig. 7. The viscosity of cement mixture prepared with W/C of 0.85 and 1.0 was lower than 25 dPa·s. However high W/C ratio, the maximum viscosity was 65 dPa·s, and it was possible to continuously mix the mixture. Fig. 7 shows that as the W/C of the mixture increased, the viscosity of the mixture increased.

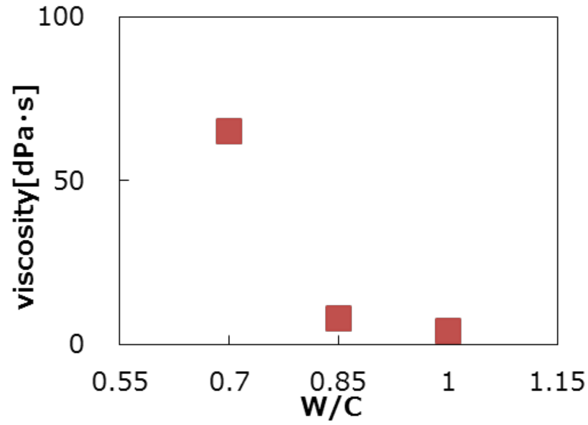

Fig. 7. The viscosity of the mixture prepared with W/C of 0.7, 0.85 and 1.0.

Fig. 8 shows the uniaxial compressive strength of the solidified products prepared with W/C of 0.7, 0.85 and 1.0. The W/C decreased, the strength of the solidified product increased. The uniaxial compressive strength was higher than 10MPa in all conditions. The values were higher than 8MPa, which is the stipulated value in the Aube (France) disposal regulations[13)]. The boron content of the solidified product was 73kg/m^3. The material separation was observed at condition of W/C 1.0. However the swelling at about after 91 days was not observed at any condition.

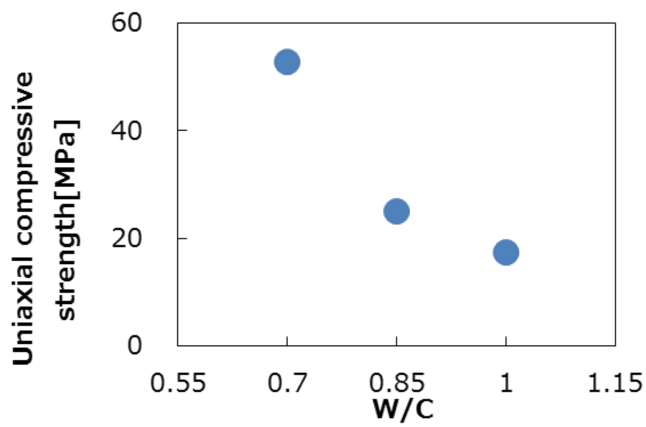

Fig. 8. Uniaxial compressive strength of the solidified products prepared with W/C of 0.7, 0.85 and 1.0.

An XRD profiles of the solidified product prepared with W/C=0.85 are shown in Fig. 9. The crystal peaks corresponding to sodium borate hydrate ($NaB(OH)_4 \cdot 2H_2O$), portlandite ($Ca(OH)_2$), calcium silicate ($Ca(SiO_4)O$) and calcium aluminate borate hydrate ($Ca_6Al_2B_4(OH)_{18} \cdot 30H_2O$) were observed. The crystal peaks corresponding to Ulexite ($NaCaB_5O_6(OH) \cdot 6H_2O$) were not observed. It was thought that high Na/B mole ratio prevent the generation of Ulexite which produce the swelling of the solidified product[12),14)].

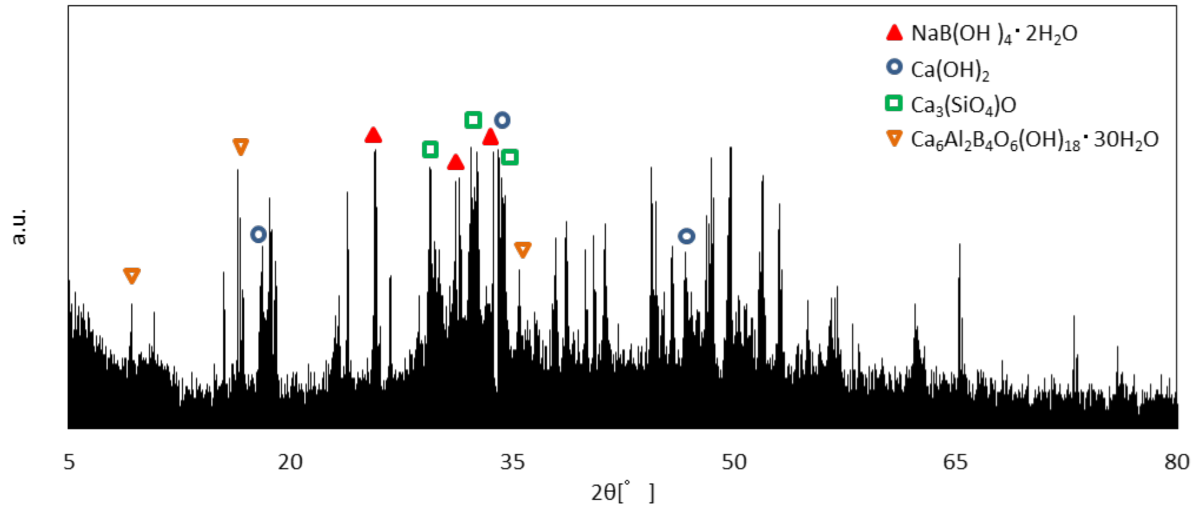

Fig. 9. XRD profile of the solidified product prepared with W/C=0.85.

CONCLUSIONS

Solidified product with different Na/B mole ratio was prepared from simulated PWR concentrated liquid waste by using a wiped film dryer. Simulated Powdered waste was obtained at condition of Na/B mole ratio 0.95 to 1.15. The uniaxial compressive strength of solidified product prepared by the powder with Na/B mole ratio of 0.95, 1.0 and 1.15 were higher than 10 MPa. The solidified product could hold the geometry after the leaching test.

The improvement in boron content of solidified waste was expected. Solidified waste with containing 73 kg/m^3 of boron had a uniaxial compressive strength of 25 MPa, with a water/cement ratio of 0.85. The solidified product has high volume reduction than previous work.

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