Effect of Sodium / Boron Mole Ratio on the Cement Solidification for Sodium Borate Waste Produced in PWR Plants – 15261

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ABSTRACT

A cement solidification process for treating sodium borate waste produced in pressurized water reactor (PWR) plants was studied. The process was developed to obtain a high mechanical strength of more than 10 MPa which can satisfy various countries disposal regulations. To obtain high volume reduction and high mechanical strength of the solidified product, simulated concentrated borate liquid waste was dehydrated and powdered by using a wiped film evaporator. To investigate the effect of the sodium / boron (Na/B) mole ratio on the strength of cement solidified waste, simulated concentrated borate liquid waste with Na/B mole ratio between 0.21 and 0.85 were used. Solidified cement containing powdered waste with a Na/B mole ratio 0.85 showed to excellent operability and uniaxial compressive strength.

INTRODUCTION

During operation and maintenance, the liquid borate waste containing radionuclides are produced in pressurized water reactor (PWR) plants. Borate and radionuclides in the reactor water are removed by ion-exchange resin. In order to elute the borate and radionuclides from ion-exchange resin, sodium hydroxide (NaOH) solution is used as an eluting solution. The evaporators are used for condensing liquid waste in most PWR plants from the viewpoint of volume reduction. Liquid sodium borate is produced by adding NaOH to liquid borate waste for the purpose of improving the solubility in the condensing process. 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 with containing about 10000 ppm to 50000 ppm as boron is stored in 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[1),2),3),4)]. Obtaining solidified product with high volume reduction is difficult without any pre-treatment. T.Chauveau et al. [5)] solidify the sludge including boron by adding calcium hydroxide ($Ca(OH)_2$) to the sludge and using mixed cement with silica sand and crystal. Some researchers has proposed or reported the cement solidification methods for concentrated borate liquid waste. Céline Cau Dit Coumes et al. [6)] is proposing the method adding NaOH to the concentrated borate liquid waste and using solidify material with calcium sulfate, alumina cement and silica sand. E. Benavides[7)] has reported high boron content in a solidified waste by adding $Ca(OH)_2$. In the paper, E. Benavides solidified 140L of concentrated boron liquid waste containing 45000ppm of boron into the 200L standard drum. The calculated boron content was about 31.5kg/m^3. These methods use concentrated borate liquid as kneading water, therefor it is difficult to improve the volume reduction.

We have previously developed a cement solidification technique for treating radioactive liquid waste [8),9)]. The technique was developed to satisfy the Japanese disposal regulations. 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. The technique consists of three processes: (i) a pre-treatment process to convert soluble borate into a non- soluble form by adding a calcium agent, (ii) a drying process to reduce the volume of the liquid waste and to produce powder, and (iii) a cementation process to solidify the dried powder in cement materials. 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[10)]. This cement solidification was based on technique which was practical used in Japan. Soluble sodium borate powder was used in this process, thus it is expect to be simple system. The non-soluble converting system and the calcium borate precipitate system are not necessary. Powder with Na/B mole ratio of 0.24 and silica sand was used to obtain high uniaxial compressive strength. The uniaxial compressive strength at 28 days curing was more than 10MPa and the boron content was about $70kg/m^3$. Although this process can cause polymerization of sodium borate and increase viscosity of the mixture. Also there was possibility of swelling of the solidified product by the long period curing.

Based on our previous technique, we developed cement solidification process controlling Na/B mole ratio of the sodium borate powder to improve the stability of the solidified product. This process 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 product[11)].

I. Tsuyumoto[12)] reported polymerization of sodium borate occurs by the high concentration sodium borate solution with Na/B mole ratio of 0.22 and 0.27. On the other hand M. Maeda[13)] calculated and reported that the sodium borate ions takes several forms by pH. In high pH area the alkaline hydrolysis occurred and sodium borate ion change into $B(OH)_4^-$ form[14)]. For the purpose of preventing polymerization sodium borate with high Na/B mole ratio by adding NaOH was used. In this paper, the effects of Na/B mole ratio in the properties of the solidified cement products were studied. Cement solidification experiments were conducted with sodium borates having different Na/B mole ratio. 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.

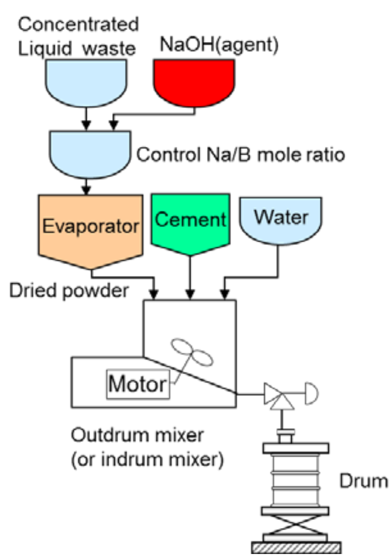

Fig. 1. Schematic drawing of cement solidification process.

EXPERIMENTAL

Simulated liquid waste with concentration about 20000ppm of boron was prepared from $B(OH)_3$ and NaOH. The simulated liquid waste was dried to a powder by using a wiped film evaporator[8)] for the purpose of obtaining high volume reduction. The powder was analyzed by X-ray diffraction (XRD, RINT Ultima III, Rigaku Co.). In order to evaluate the Na/B mole ratio of the powder product, powdere was dissolved in aqua regia, and its concentrations of Na and B in the solution were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Advantage, Thermo Fisher Scientific).

Cement solidification was conducted by using powdered concentrated liquid waste. Ordinary Portland cement (OPC) manufactured by Taiheiyo Cement Co. was used for the cement solidification. The water/cement ratio (W/C) was 0.7. In case of Na/B mole ratio of 0.85, solidification was also conducted with W/C of 0.45, 0.54, 1. The amount of the powdered concentrated liquid waste was decided as the boron content will become about 70kg/m^3 when Na/B is 0.24[12)]. The experimental flow is shown in Fig. 2. Simulated sodium borate powder was mixed with water by using a screw agitator for 60 minutes at room temperature. The viscosity and pH of the solution were measured. 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 (about 7, 28 and 91 days after) of solidified products were measured.

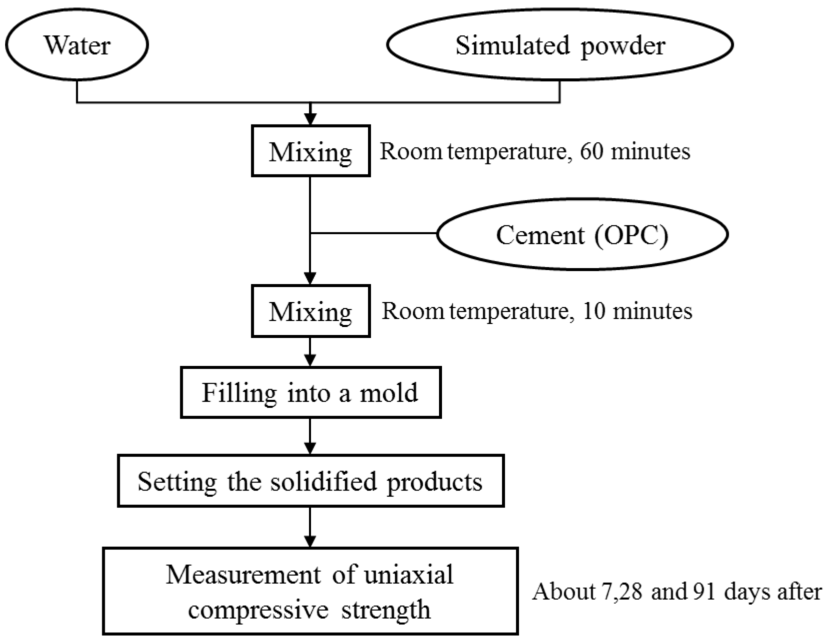

Fig. 2. Experimental flow of cement solidification process.

RESULTS AND DISCUSSION

In all conditions, sufficiently dried powdered simulated liquid waste was obtained by using a wiped film evaporator. After each operation, the evaporation the wiped film evaporator was cleaned by hot water. It was cleanable and the pictures are shown in Fig. 3. Sodium borate dissolve into water, therefore the process can be more simple and aftertreatment system is not necessary. The results of elemental analysis of powder prepared from simulated liquid waste, Na/B mole ratio of the powder and decontamination factor (DF) are shown in Table 1. DF was defined by eq. (1):

$$DF= C_{in} / C_{out} \qquad (1)$$

where C_{in}(ppm) is concentration of element in simulated liquid and C_{out}(ppm) is concentration of element in condensed water. The higher the Na/B mole ratio was, the higher DF was. The DF of Na was 183 and DF of

B was 167 when the powder with Na/B mole ratio of 0.85 was prepared.

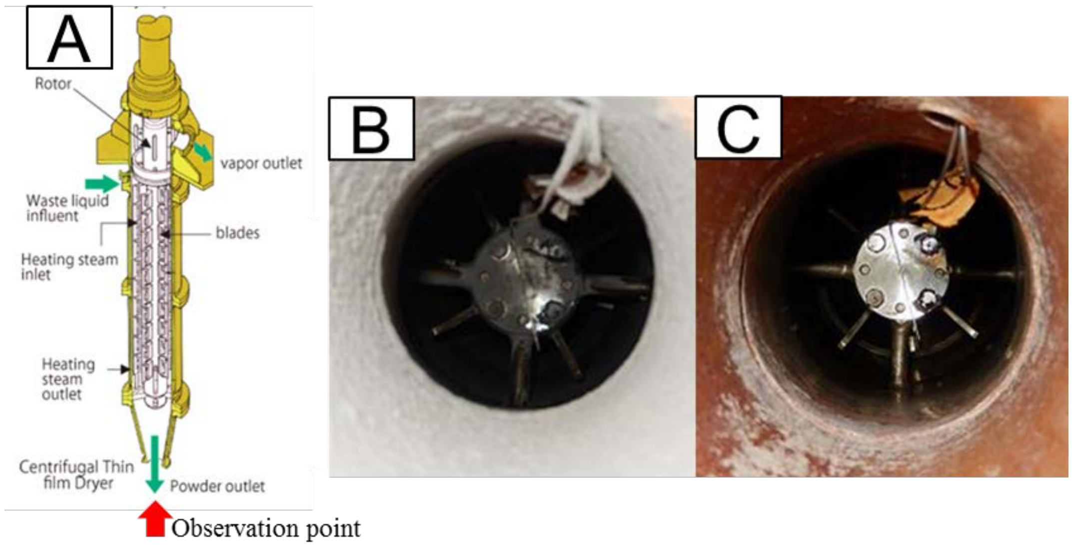

Fig. 3. Schematic diagram and views of evaporator
(A: Observation point B: Before cleaning C: After cleaning by hot water).

Table 1. Results of elemental analysis of powder prepared from simulated liquid waste, Na/B mole ratio of the powder and DF.

No.	Na	B	Na/B	DF of Na	DF of B
	wt%	wt%	mol/mol		
1	10	22	0.21	27	25
2	12	21	0.27	42	40
3	13	21	0.29	25	25
4	15	18	0.39	129	111
5	27	15	0.85	183	167

XRD profiles of the powder prepared by using the wiped film evaporator are shown in Fig. 4. The higher the Na/B mole ratio was, the higher crystallinity was. It is considered that, high DF was obtained by the high crystallinity powder having large particle diameter. The powder with Na/B mole ratio of 0.39 and 0.85 was corresponded to boron and sodium compounds and the crystal form was $Na_2BO_4 \cdot 5H_2O$ and $Na_3B_3O_5[OH]_2$ respectively.

The pH value of the solution with Na/B mole ratio of 0.21, 0.27, 0.29, 0.39 and 0.85 after mixing 60 minutes was 7.8, 8.3, 8.0, 9.0 and 13 respectively. The higher the Na/B mole ratio was, the higher pH was. The viscosity of the solution and the mixture is shown in Fig. 5. It was difficult to mix cement mixture prepared by the powder with Na/B mole ratio of 0.39 because of the increase of viscosity. Therefore the amount of the cement was decreased and the W/C was about 0.84. Fig. 5 shows that as the solution viscosity increased, the viscosity of the mixture increased. The solution and the mixture which used the powder with N/B mole ratio of 0.39 had high viscosity. The sodium borate ion takes several ion forms by pH[10]. The borate ion takes $B(OH)_4^-$ form when the pH value of the sodium borate solution is higher than 11. It is thought that in the alkaline solution the alkaline hydrolysis occurred and the sodium borate polymer change into $B(OH)_4^-$ form. Thus, the viscosity of the sodium borate solution with high pH decreased.

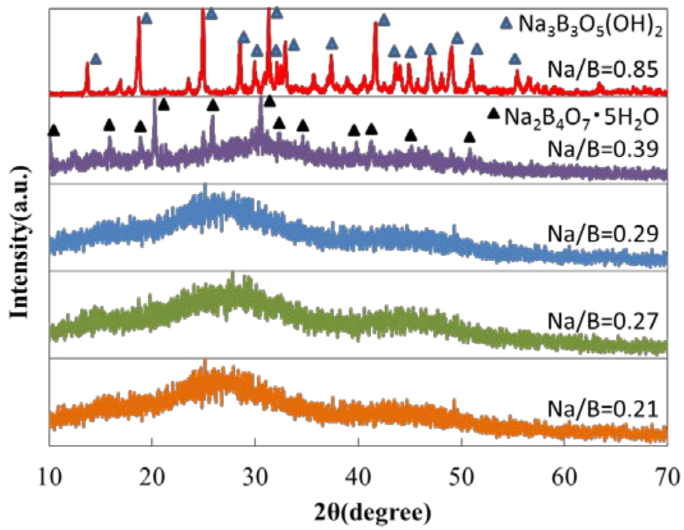

Fig. 4. XRD profile of the powder prepared by using the wiped film evaporator.

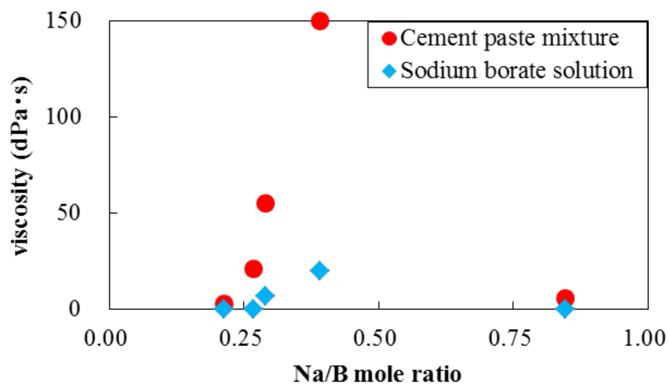

Fig. 5. The viscosity of the solution and the mixture.

Fig. 6 shows the uniaxial compressive strength of the solidified products prepared with W/C 0.7. The strength of solidified product prepared from the powder with Na/B mole ratio of 0.85 increased with the curing time. Although the strength of solidified products prepared from the powder with Na/B mole ratio of 0.21, 0.27, 0.29 and 0.39 decreased at about 91 days, because of the swelling. It was thought that the Ulexite ($NaCaB_5O_6(OH)\cdot6H_2O$) was produced in the solidified product and the swelling was occurred by the growth of Ulexite[15)]. The Ulexite is a mineral with needle crystal form made from Na, B, Ca, and water. Therefore the growths of Ulexite cause damage to the solidified product.

Fig. 7 shows the uniaxial compressive strength of the solidified products prepared by the powder with Na/B mole ratio of 0.85. The strength of solidified product increased with the curing time. These values were higher than 8MPa, which is stipulated in the Aube (France) disposal regulations[11)].The boron content was about 50kg/m^3 and it was higher than 31.5kg/m^3 [7)]. The W/C decreased, the strength of solidified product increased. The swelling at about after 91 days was not observed at any condition. It was suggested that using powder with high Na/B mole ratio prevent produce of Ulexite.

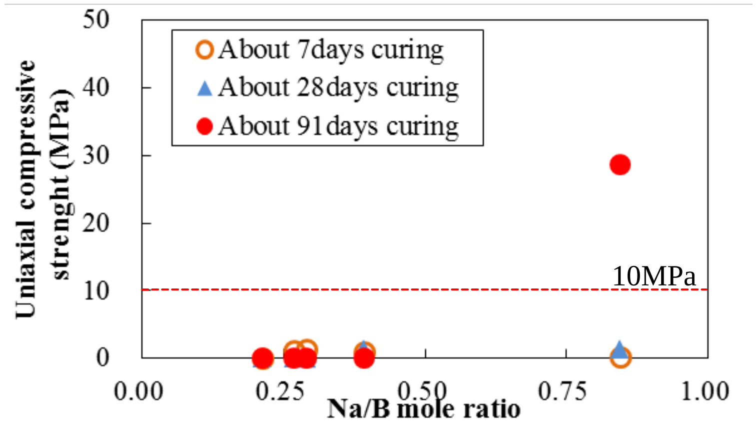

Fig. 6. Uniaxial compressive strength of the solidified products prepared with W/C 0.7.

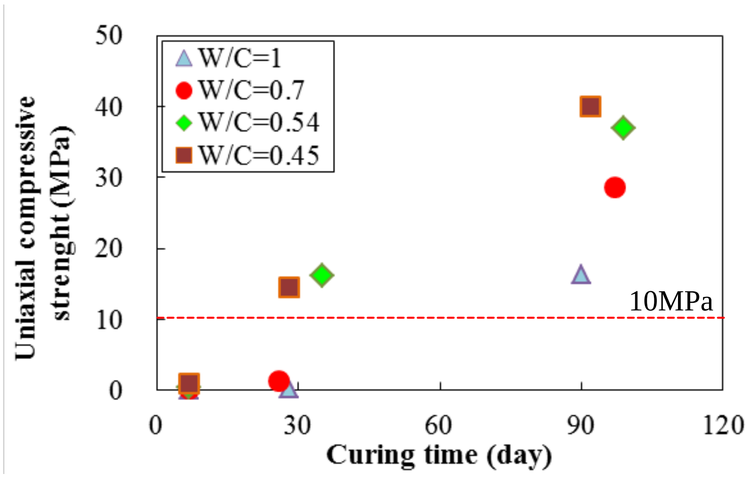

Fig. 7. Uniaxial compressive strength of the solidified products prepared by the powder with Na/B mole ratio of 0.85.

CONCLUSIONS

A powdered waste with different Na/B mole ratio was prepared from simulated PWR concentrated liquid waste by using a wiped film evaporator. The evaporator was cleanable by hot water. The sodium borate with Na/B mole ratio of 0.85 which had high pH prevented increase of viscosity. It was thought that the alkaline hydrolysis convert the sodium borate polymer into $B(OH)_4^-$ form. The uniaxial compressive strength of solidified product prepared by the powder with Na/B mole ratio of 0.85 was higher than 10 MPa in all conditions. The uniaxial compressive strength was significantly improved. The content of boron in the solidified product was about 50kg/m^3. The developed cement solidification technique is more simple than previous technique.

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