DEVELOPMENT OF HIGH VOLUME REDUCTION AND CEMENT SOLIDIFICATION TECHNIQUE FOR PWR CONCENTRATED WASTE

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ABSTRACT

The hyper-Cement solidification technique was developed, which reduced the volume of concentrated liquid wastes from PWR plant by means of stable cement solidification. Drying the liquid wastes into powder using a wiped film evaporator and then solidifying the large amount of powdered wastes attained high volume reduction of the wastes due to the special cement paste with low viscosity. Using this technique, The volume reduction ratio of the wastes was larger than in the case of using bitumen technique, which is conventionally employed to solidify the concentrated liquid wastes in PWR plant. This paper presents the outline of the hyper-cement technique and discusses the mechanical and chemical properties of the cement solidification.

INTRODUCTION

Cement materials are known to be attractive for solidifying radioactive wastes because of its low water permeability after hardening and the high absorbability of some radioactive species onto hardening materials. In view of the simplicity of the solidification process using these materials, cement solidification systems are operating at many nuclear facilities. However, its hardening is sometimes hindered by the presence of certain components such as boric acid and phosphate acid because they impair the hydration reactions of cement. These impairments are of particular concern in the case of the solidification of concentrated liquid wastes from pressurized water reactor (PWRs), since their main components is boric acid. To avoid these impairments, it is necessary to reduce the amount of these components in cement solidification, but this causes the increase of the volume of the products of waste solidification. For this reason, the bitumen technique in which both salts of boric compounds and radioactive elements are mixed into molten asphalt is introduced to reduce the generation of the products of waste solidification in PWR power plants. But this solidification process is complicated and sometimes it is necessary to repair equipment because the activation of molten asphalt at high temperature results in the corrosion of metals. Thus, there is a need to develop a solidification technique using cement materials that increases the borate content in products.

We have already developed a new cement solidification technique that realizes high volume reduction of waste. This technique consists of two processes: a drying process to reduce the volume of liquid waste, and a cementation process to solidify a large amount of the dried product with a given cement. Using this technique, The volume reduction ratio of the wastes was larger than that in the case of using the bitumen technique.

This paper presents the outline of a new cement solidification technique for concentrated liquid waste generated from PWR power plants and investigates the detailed properties of the products solidified by the technique.
SYSTEM FLOW

Figure 1 shows the cement solidification process we developed for concentrated liquid waste from PWR plants (1,2).

First, a pre-treatment technique is applied to convert the soluble borate into non-soluble borate by adding a chemical agent to the solution before drying. The chemical agent is Ca(OH)2. By adding Ca(OH)2 to the liquid waste, crystal calcium and boron compound precipitate in the liquid waste. Because they are insoluble in water, they do not affect the hydration reaction of cement.

In the second process, in order to reduce the volume of liquid waste from PWR plants, the pretreated liquid is reduced to a powder by a drying method. Toshiba has already developed evaporation equipment for liquid waste and spent resins, which is called the wiped film evaporator. The optimum condition for drying of PWR concentrated liquid waste was concluded to be from 0.4 to 0.6 of calcium/boron (Ca/B) mole ratio. The decontamination factors (DFs) of the wiped film evaporator under this condition were from 300 to 400 and these values were found to be sufficiently high in comparison to the target value (100) (3).

In the next process, the powdered waste is solidified by cement. This cement contains a special admixture that disperses the particles of both cement and powdered waste in mixing water, and, as a result, the viscosity of this mixture is low. Consequently a large amount of powdered waste can be mixed homogeneously and the volume reduction ratio of waste is six to seven times higher than that for conventional cement solidification.
The details of the solidification technique and the properties of this solidification are presented below.

BORON-ACID CONTENT IN CEMENT SOLIDIFICATION

Experimental
The Ca/B mole ratio of the powdered waste was selected to be 0.5 to 0.6 and the cement material used to solidify this powder was the mixture of ordinary Portland cement and blast furnace slag; these conditions are the same as those in our previous study (3).

In order to increase the amount of powdered waste that is solidified in 200 L drum can in comparison to the case for bitumen, we studied the relation between the amount of solidified boric acid and two properties, namely the viscosity of mixture and the compressive strength after hardening. We selected the optimum condition for the cement solidification, namely low viscosity of the mixture (< 50 dPa.s), which a view to obtaining high compressive strength (>5MPa).

Result and Discussion
Figure 2 shows the relation between the boron-acid content in cement solidification for 200L drum size and the viscosity of the mixture. It was found that the mixture keeps a low viscosity even though it includes about eight times as much boric-acid (about 110kg in 200L drum) as the conventional cement. Because the admixture enhances the zeta potential of powder in the water, the particles repulse one another, thereby reducing the viscosity of the mixture.

Fig.2 The relation between the boric-acid content in cement solidification for 200L drum size and the viscosity of the mixture.
Table I shows the compressive strength of solidified products at 28 days curing time. It was found that the mixture keeps a high compressive strength of over 5 MPa even though it includes about eight times as much boric-acid (about 110kg in 200L drum) as the conventional cement.

<table>
<thead>
<tr>
<th>boron-acid</th>
<th>Compressive Strength (MPa)</th>
<th>new cement solidification</th>
<th>The optimum condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>100kg</td>
<td>10.0</td>
<td></td>
<td>&gt;5</td>
</tr>
<tr>
<td>110kg</td>
<td>6.7</td>
<td></td>
<td></td>
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</tbody>
</table>

These results confirmed that it is possible to increase the boron-acid content in solidified products. Compared with the conventional cement solidification technique, our cement solidification technique realizes about an eight times increase in the amount of boric-acid contained in the solidified products.

**LEACHABILITY OF SOLIDIFIED PRODUCTS**

**Experimental**

A study on the leachability of important radionuclides of the solidified products was carried out in order to confirm the radioactive containment of the products. The leachability of solidified low-level radioactive wastes was measured by a short-term test procedure (ANL method)(4). The radionuclides used were Cs-137 and Co-60. The specimen is a circular cylinder with a diameter of 1.8 cm and a length of 1.4 cm. The leachability index is calculated on the basis of diffusivity.

**Results and Discussion**

Figure 3 shows the relation between the leaching times and the diffusivity of Cs-137 and Co-60. Table II shows the leaching indices obtained from these results.
Table II. The leaching indices (Cs-137, Co-60)

<table>
<thead>
<tr>
<th>boron-acid</th>
<th>Leachability Index</th>
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<tbody>
<tr>
<td></td>
<td>Cs-137</td>
</tr>
<tr>
<td>100kg</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>110kg</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
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</table>

The leachability indices for important nuclides obtained by the ANL method were about 9 for Cs-137 and about 12 for Co-60.

These results showed that the products produced by our technique satisfied the low-level waste disposal regulations of the USA.

DEMONSTRATION TESTS

Experimental

The simulated liquid waste containing sodium and boron compound (21000 ppm of boron) and
Ca(OH)₂ powder (Ca/B mole ratio 0.5) were mixed at 80 °C, and the mixture was dried by the wiped film evaporator.

The mixture condition of the demonstration tests was to contain 100kg of boron-acid in 200L drum. The volume of solidified waste was reduced to one eighth of that in the case of using the conventional cement solidification technique. Figure 4(a) shows a photograph of the full-scale equipment.

![Image](image1.png)

(a) 

(b)

**Fig. 4** The full-scale equipment and the 200L drum size product

**Results and Discussion**

It was measured the motor power consumption changes during operation. The average value of motor power consumption during operation was about 2kWhrs. The peak value was about 2.5kWhrs. The relatively small fluctuation of motor power consumption during operation is due to the smooth downward motion of thin films formed on the inner surface of heating wall to the bottom of the wiped film evaporator. The powder was found to have less than 10-weight % moisture.

This result satisfied the target value (50dPₜₚₜ). It was confirmed that there was no massive matter in the cement solidification equipment.

The peak temperature in the core of the product was about 60 °C at 6 hours after mixing. Figure 4(b) shows a photograph of 200L drum size product, which was produced using the full-scale cement solidification equipment. No bleeding, cracks, voids or sedimentation of contents was found.

These results confirmed that the concentrated liquid waste of PWR plants was successfully
solidified using our solidification technique. The volume of waste was found to be one eighth of that in the case of using the conventional solidification.

CONCLUSION

A new cement solidification technique for the concentrated liquid waste generated from PWR plants was developed.

The volume of waste was reduced to one eighth of that in the case of using the conventional cement solidification technique.

The solidified products had good properties and they satisfied the low-level waste disposal regulations of the USA.

REFERENCES