CONDITIONING OF SPENT ION EXCHANGE RESIN USING HIGH PERFORMANCE CEMENT

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ABSTRACT

A new cementitious material, high performance cement, has been developed for conditioning of spent ion exchange resin. The cement contains reinforcing fiber and natural zeolite. These additives effectively raise waste loading and improve properties of the waste form.

Laboratory-scale experiments were performed to estimate such long-term properties as water resistance, radiation stability and leachability of the waste form. Their results showed that the high performance cement provided high-quality waste forms even when waste loading was double that with conventional cement. Full-scale pilot plant tests were subsequently carried out to demonstrate that the new cement could be applied industrially.

INTRODUCTION

Cement solidification is widely used for conditioning of spent ion exchange resin generated from nuclear facilities, because of the simplicity of the system and the low amount of secondary wastes generated. Hitachi has developed a high performance cement (HP-cement) which consists mainly of slag cement, reinforcing carbon fiber and natural zeolite (1). It provides the following features.

1. High waste loading: The resin content in a cementitious waste form is typically controlled below 25kg-dry resin/200 l, because the waste form tends to deteriorate in water when resin content is higher. The basic aspects of the deterioration mechanism were examined and this led to the development of fiber reinforced cement (2). It was confirmed that the waste loading could be doubled by use of the HP-cement.
2. Low leachability: Leachability of radiocesium from the cementitious waste form is relatively high compared with other radioactive nuclides such as Co-60, Sr-90 and C-14. Therefore, Cs adsorbents were surveyed and natural zeolite was selected from among them (3). The Cs leachability was reduced to about 1/10 by adding zeolite to the cement.

Laboratory-scale experiments were first performed to evaluate properties of the waste form using the HP-cement. Emphasis was laid on such long-term properties as water resistance and radiation stability. A pilot plant was subsequently constructed and full-scale experiments were carried out to demonstrate that the new cement could be industrially applied. This paper summarizes these experimental results.

WASTE FORM PROPERTIES

Bead and powdered ion exchange resins were solidified into waste forms (45ϕ x 40mmH) using the HP-cement. These were cured under a sealed condition at ambient temperature for one month and the following properties were examined.

Compressive Strength

Mechanical strength is one of the most important parameters from the viewpoint of final disposal. Figure 1 plots the changes in compressive strength as a function of resin content. The maximum waste loadings were found to be about 60 and 50kg-dry resin/200 l for bead and powdered resins, respectively. It was quite difficult to get uniform mixing of the cement and resin above the respective maximum loading. The minimum compressive strength, 4.0MPa, was observed at the maximum loading value of the powdered resin. This value is much larger than the minimum requirement (0.414MPa) set for final disposal of low level radioactive wastes in the USA.

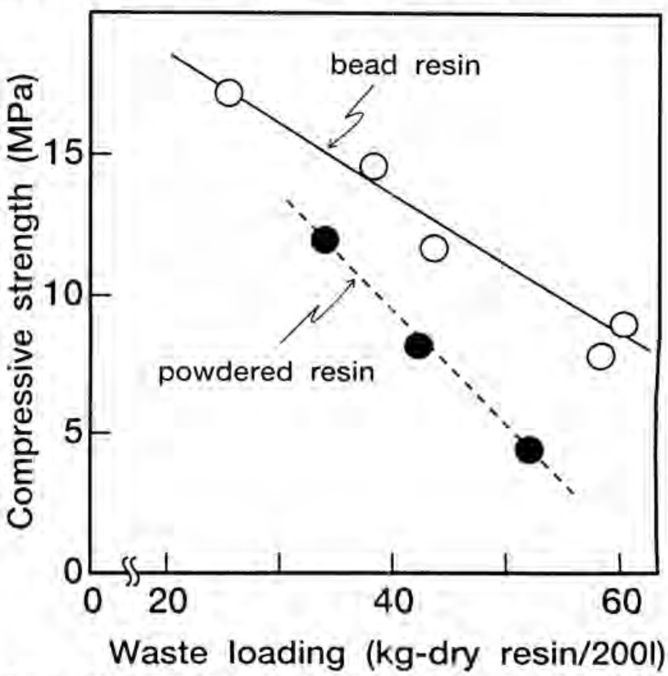
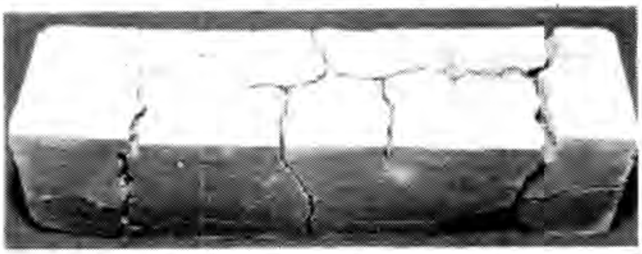


Fig. 1. Effect of waste loading on compressive strength for bead and powdered resins.

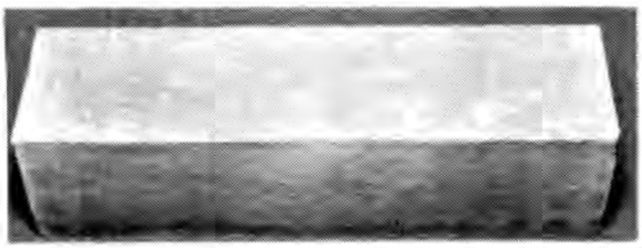
Water Resistance

Excessive loading of resin, particularly of bead resin, may lead to deterioration of the waste form under a water immersion condition (4,5). This is because the resin tends to swell on contact with water, thereby creating large internal stresses in the waste form (5). The HP-cement contains reinforcing carbon fiber to prevent resin swelling (2). Water immersion tests were carried out for 90 days to examine the effect.

Figure 2 and Table I summarize the results. The conventional cementitious form cracked in water (Fig. 2 (a)) and its strength decreased to ~0MPa within a few days. The waste form using the HP-cement, on the other hand, did not deteriorate even at such a high resin content as 60kg-dry resin/200 l. Its strength increased by approximately 15% during the water immersion, as in Table I. This was probably because hydration reaction of cement progressed during the immersion. These results suggested that the waste loading could be increased from 25 to 60kg/200 l by using the HP-cement.



(a) Conventional cement



(b) High performance cement

Fig. 2. Improvement of water resistance using HP-cement (Resin content = 60kg-dry resin/2001.)

TABLE I

Results of Water Immersion Tests for 90 Days

Cement type	Compressive strength (MPa)	
	before immersion	after immersion
Conventional	7.1	~0
HP-cement	8.3	9.4

Radiation Stability

A great number of chemical reactions occur in irradiated waste forms. Various gases (H_2, CH_4, SOx etc.) are generated by radiolysis of water and ion exchange resin (6). These materials may influence the mechanical properties, hence radiation stability tests were carried out using a Co-60 γ-ray source.

Waste forms, having a bead resin content of 55kg/200 l, were irradiated at a dose rate of ~ 10^4Sv/h. Table II shows the results. Deterioration, such as cracking, was not observed and compressive strength was constant in the region of 0-10^6Sv (0-10^8rad) irradiation. Density of the waste form was also stable at about 1.5g/cm^3.

TABLE II

Results of Radiation Stability Test

Total Dose (Sv)	Comp. Strength (MPa)	Density (g/cm^3)
0	8.6	1.51
10^4	8.9	1.50
10^6	8.8	1.51

Leachability

The high performance cement contains natural zeolite, whose main constituent is clinoptilolite, to reduce Cs leachability. Excessive Ca exists in cementitious waste forms. The clinoptilolite selectively adsorbs Cs ion in Cs/Ca mixed solution, so that it was selected for Cs adsorbent (3).

Waste forms were prepared using both conventional slag cement and the HP-cement. Their resin contents were 25 and 60kg-dry resin/200 l, respectively. Leachability of Cs-137 was subsequently measured based on the IAEA standard method. These results are compared in Fig. 3. In spite of the high waste loading, the HP-cement could reduce the Cs release fraction to about 1/10 as compared with the conventional cement. The leachibility index (LIX) was calculated from Fig. 3 (7). It was 11.9 for the HP-cement waste form. This value is much larger than the minimum requirement (LIX = 6.0) set in the USA.

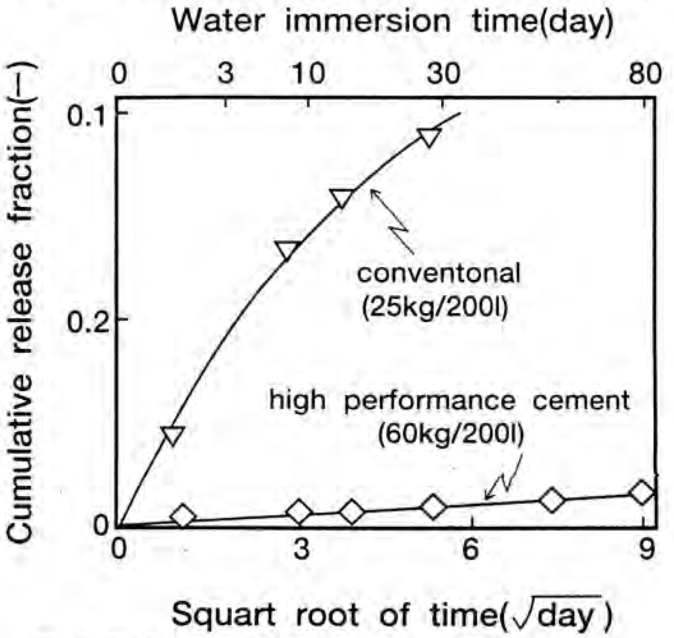


Fig. 3. Reduction of Cs leachability using HP-cement.

PILOT PLANT TEST

A full-scale pilot plant, shown in Fig. 4, was constructed to demonstrate that the HP-cement could be applied

Fig. 4. View of full-scale pilot plant.

industrially. An outline of the pilot plant and typical test results are given in this section.

Outline of Pilot Plant

Figure 5 shows a schematic diagram of the pilot plant. Spent resin, in a slurry condition, is first dewatered to a water content of about 50% using a centrifugal liquid/solid separator. Its maximum capacity and rotation number are 1500 l-slurry/hour and 3900 rpm, respectively. The resin is then transported into a mixer by use of a screw-feeder and mixed with the HP-cement and water. Typical mixing ratio is:

resin/water/cement = 100/60/140,

where the resin weight is on a wet basis. The mixing ratio is controlled using load cells. Finally, the mixture is fed into a 200 l drum and cured at room temperature after capping. The reinforcing carbon fiber and natural zeolite are uniformly mixed in the HP-cement in advance. Therefore, such special equipment as a high-shear mixer is unnecessary.

Test Results

The temperature in the waste form increases during cement hydration, because this is an exothermic reaction. Figure 6 shows a temperature profile at the drum center as a function of time after mixing. The maximum value (45°C after 21 hours) was relatively low and undesirable effects, such as dimensional changes and cracking, were not observed.

A long-term water resistance test was performed using a 200 l waste form. The steel drum was removed from the waste form, after curing for three months at room temperature. It was then put into a 1m^3 water vessel and changes in its volume, weight and compressive strength were measured for more than two years. The strength was estimated from the propagation velocity of ultrasonic waves in the waste form. Figure 7 shows experimental results. Its weight gradually increased with time and became saturated at an increased value of 3.5wt% after immersion for about 100 days, indicating water penetration into the waste form. Deterioration features such as cracking and swelling were not observed. Its volume change was less than the experimental error of 0.1%, and compressive strength was more than 8.0MPa before and after the water immersion. These findings agreed with the results of laboratory-scale experiments.

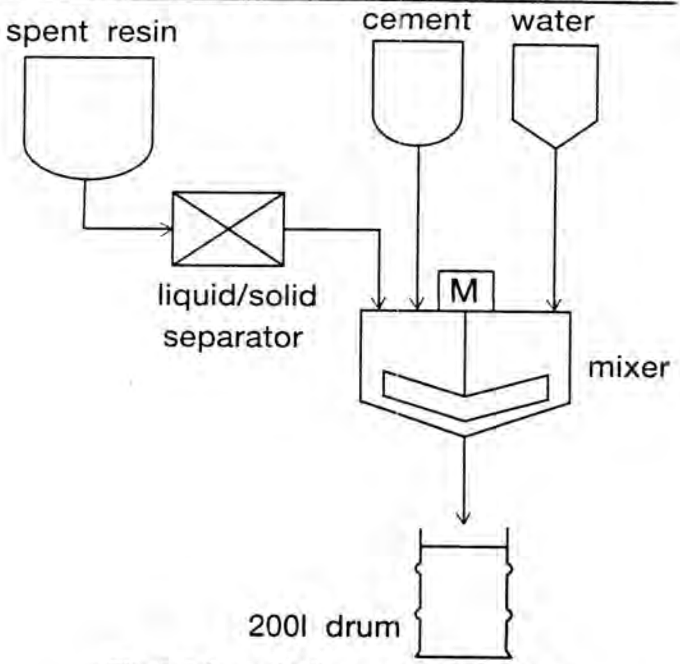


Fig. 5. Schematic diagram of pilot plant.

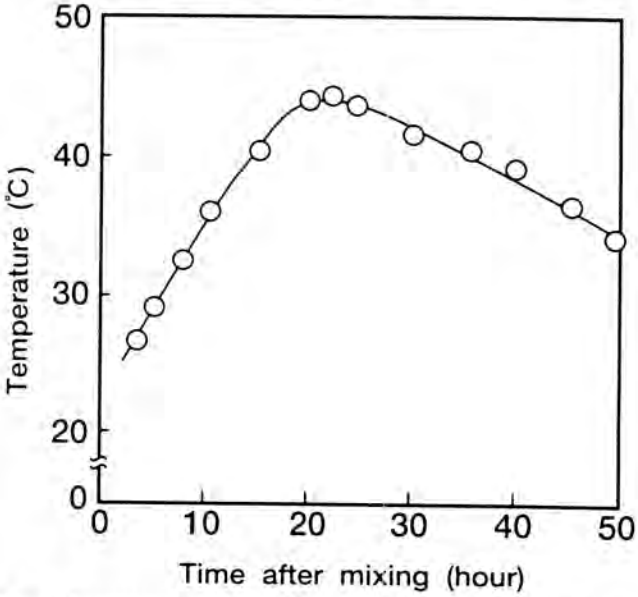


Fig. 6. Increase in temperature at drum center by cement hydration reaction.

CONCLUSIONS

A high performance cement (HP-cement) has been developed for conditioning of spent ion exchange resin. Laboratory- and full-scale experiments were carried out to examine

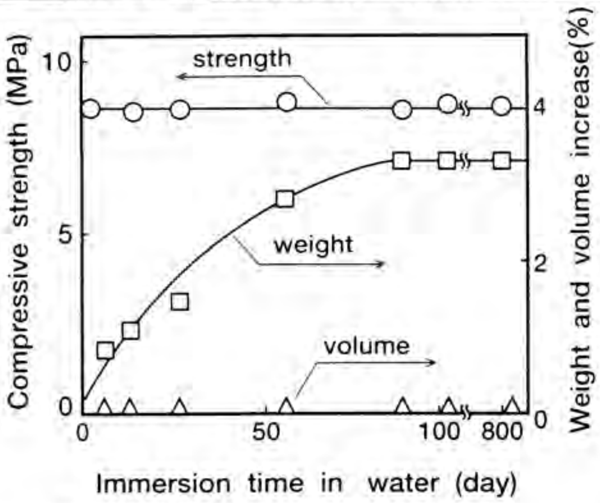


Fig. 7. Water resistance of 2001 waste form.

properties of the waste form. The following results were obtained.

1. Carbon fiber in the HP-cement improved water resistance of the waste form. This enabled waste loading to be increased from 25 to 60kg-dry resin/200 l, hence reducing the number of waste packages to about half.
2. Natural zeolite in the HP-cement functioned as cesium adsorbent. The cesium leachability was, therefore, reduced to about 1/10. Radiation stability tests showed that the waste form was stable even at a high irradiation of 10^8rad.
3. A full-scale pilot plant was constructed and 200 l waste forms were produced. Temperature rise during the cement hydration reaction was only 25°C at the drum center and no undesirable effects were observed. The water immersion test was subsequently carried out for two years using the 200 l waste form. No deterioration such as swelling was observed. These results suggested that the HP-cement was applicable industrially.

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