SOLIDIFICATION OF ION EXCHANGE RESIN USING FIBER REINFORCED CEMENT

Authors were unable to present this paper due to their concern over traveling during the Gulf War.

Masami Matsuda, Koichi Chino and Takashi Nishi
Energy Research Laboratory, Hitachi, Ltd.
1168 Moriyama, Hitachi, Ibaraki, 316 Japan

Makoto Kikuchi
Hitachi Works, Hitachi, Ltd.
3-1-1 Saiwai, Hitachi, Ibaraki, 317 Japan

ABSTRACT

A fiber reinforced cement has been developed to improve volume reduction efficiency for spent ion exchange resin. The resin content in a cement package is controlled, typically, below 20 vol%, because the package tends to crack and deteriorate in water when resin content is higher. The deterioration mechanism was quantitatively investigated in this study. The package was found to crack in water when swelling pressure of the resin exceeded tensile strength of the cement. This finding led to the development of a fiber reinforced cement. The tensile strength of the cement was almost doubled by adding steel fiber and the resin content could be increased from 20 to 42 vol%.

INTRODUCTION

Ion exchange resin is widely used for water treatment in nuclear power plants because of its ability to remove ionic and solid impurities from reactor water. Spent ion exchange resin comprises a major fraction of the low and intermediate level radioactive wastes.

Cement solidification is a common technique to solidify the spent resin. The resin content in a cement package is conventionally controlled, typically, below 20 vol%, because the package tends to swell and crack in water when resin content is higher (1). While the deterioration mechanism has not yet been clarified, it is inferred to be caused by the interaction between cement and resin in the package. Sauda et al. (2) have developed a new pretreatment technique to prevent the interaction. This is a very effective method to improve the resin content, but it complicates the solidification process.

The objectives of this study were to clarify the deterioration mechanism quantitatively and identify its preventive measures without any pretreatment even at a high resin content of 40 vol%. Pilot plant tests were, subsequently, carried out to confirm its availability for increasing the resin content.

DETERIORATION MECHANISM

Preliminary water immersion tests were performed for cement packages with resin contents of 20 and 42 vol%. The changes in their compressive strength were measured and are summarized in Fig. 1. The package with 20 vol% resin did not deteriorate in water and its compressive strength was maintained above 150 kg/cm^2 after immersion for 90 days. The package with 42 vol% resin, on the other hand, cracked in water within a few days and its strength decreased very quickly.

It was presumed that such deterioration was caused by the swelling property of resin. Ion exchange resin tends to expand, or "swell" by absorbing water, as in Fig. 2, when it is in a dry condition (3). If the expansion is obstructed by a material, swelling pressure is exerted on the material.

Figure 3 indicates the deterioration mechanism inferred in this study. In the case of cement solidification, wet resin is mixed with cement and water. THe small amount of water in the resin moves to the cement, because water content in the resin (~ 50 wt%) is ordinarily higher than that in cement (25 - 35 wt%). Therefore, the resin particles become dry and shrink during the cement curing process. When such a package is immersed in water, the water penetrates into the package and the resin particles tend to expand or swell. The cement matrix, however, obstructs this expansion. Therefore, tensile stress, induced by swelling pressure of the resin, is exerted on the cement. It was presumed in this study that the resin package deteriorated

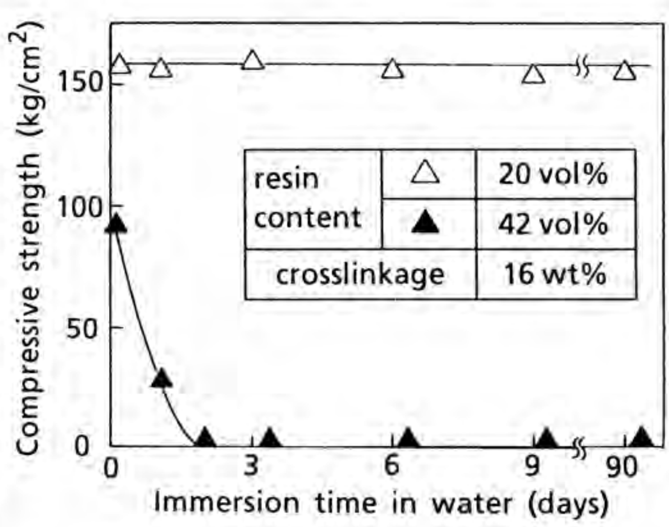

Fig. 1. Effect of resin content on water resistance of cement package.

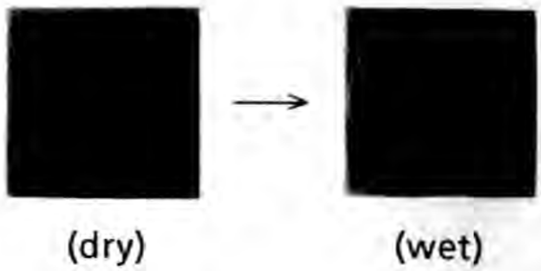

Fig. 2. Swelling property of resin by absorbing water (X50).

in water, if its stress was higher than the tensile strength of the cement matrix.

It was expected from the above deterioration model that water resistance of the cement package depended on swelling pressure of the resin and tensile strength of the cement. Therefore, the following experiments were carried out.

EXPERIMENTAL

Water Immersion Test

Five kinds of bead cation exchange resin with different cross-linkage were used in this study, because swelling pressure depended on this. Tensile strength of cement was changed by adding reinforcing steel fiber (90 umΦ X 3 mm) to the cement. Each slurry resin was first filtered by suction for ten minutes, and then solidified into a cement package under the conditions listed in Table I. After curing each package in a sealed container for 28 days, it was immersed into water at room temperature for 30 days. Changes in its weight were measured to estimate the amount of water penetrated into the package. Compressive strength was also measured by use of a compression tester.

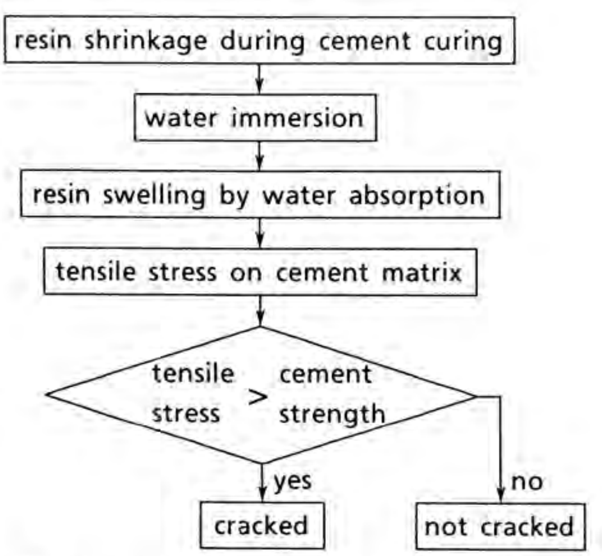

Fig. 3. Deterioration mechanism of resin package inferred in this study.

TABLE I

Experimental Conditions

Cement	Type	Slug Cement
	Fiber Content	0-15wt%
Resin	Type	Cation Exchange
	Particle Size	~500μm
	Crosslinkage	4-16wt%
Water/cement ratio		0.3
Maximum Resin Content		39wt%(42vol%)
Package Size		45∅ x40mmH

Measurement of Swelling Pressure

An experimental method to determine swelling pressure has not been reported in the literature. Then a method was developed in this study.

Figure 4 shows a schematic of the experimental apparatus. After curing for 28 days, each cement package was ground into pieces and the resin picked out. Resin (~ 0.3 g each) was then charged in a cylindrical die (13 mmΦ) as in

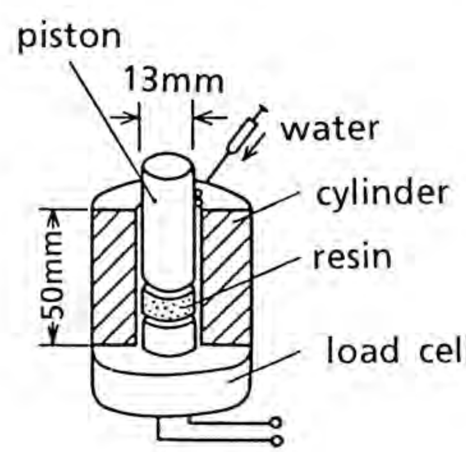

Fig. 4. Cylindrical die to measure swelling pressure of resin.

Fig. 4 and pelletized under a compacting pressure of 4,000 kg/cm^2 to eliminate pores between the resin particles. After removing the pressure, the piston was fixed in a position to contact with the pellet surface. Subsequently, water was injected into the pellet through the clearance (~5-μum) between the piston and cylinder using a syringe. The pressure increase in the cylindrical die was measured by use of a load cell to estimate the swelling pressure.

Measurement of Tensile Strength

Tensile strength of cement matrix was measured based on the method of ASTM C190 (4). Slug cements with and without reinforcing fiber were mixed with water in the water/cement ratio of 0.3 and poured into briquet-shaped containers (42W X 76 X 26mmt). After curing them for 28 days, each sample was set in a tensile tester and pulled with a speed of 0.1 mm/min to measure its tensile strength.

RESULTS AND DISCUSSION

Deterioration Condition

Cement packages were immersed in water and changed in their weight and compressive strength were measured for 30 days. All packages showed weight increases of 3 - 6%, indicating water penetration in to the packages. Some packages cracked and their strength decreased. This deterioration depended on resin content and cross-linkage.

When resin content was 20 vol%, no deterioration was observed for any packages regardless of the resin cross-linkage. For packages with 42 vol% resin, deterioration occurred depending on the cross-linkage, as is shown in Fig. 5. In the case of slightly cross-linked resins (cross-linkage > 12 wt%), on the other hand, their packages cracked in water and compressive strength decreased remarkably. Swelling pressure was measured next to understand these results.

Figure 6 summarizes the swelling pressure of resin picked out from the cement package. It was observed that the pressure increased with cross-linkage of the resin. This was in agreement with the results in Fig. 5; the higher the cross-linkage, the less the water resistance. Stress analysis was carried out using these pressure data, to verify the deterioration mechanism inferred in Fig. 3 quantitatively.

Stress analysis was performed by use of a shell model shown in Fig. 7. It was assumed that the spherical resin particles (radius = a) were closely covered by cement with a uniform thickness (b-a) in the package. When such a resin

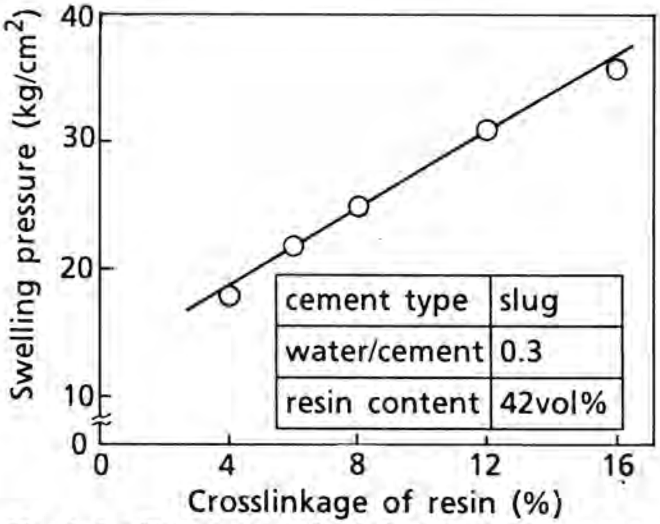

Fig. 6. Swelling pressure of resin in cement package as a function of crosslinkage.

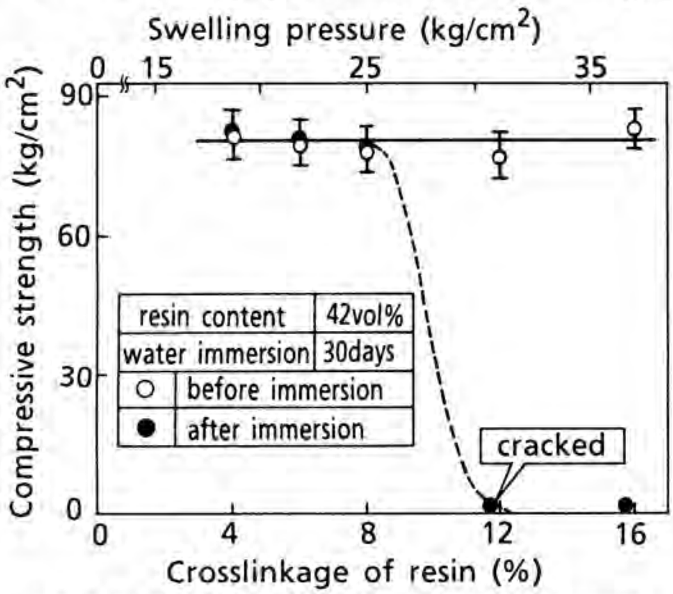

Fig. 5. Effect of resin cross-linkage on water resistance of cement package.

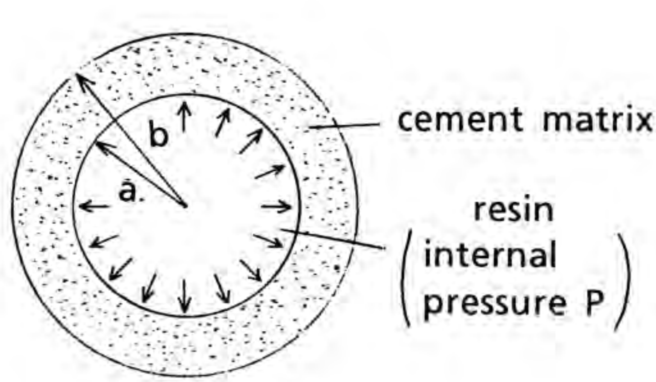

Fig. 7. Shell model to analyze tensile stress in cement package by resin swelling.

absorbs water, tensile stress is exerted on the cement matrix corresponding to the swelling pressure. The maximum tensile stress σ can be evaluated by Eq. (1), based on the elastic theory (5):

$$\sigma = P\cdot(1+2k)/2(1-k), \quad \text{Eq. (1)}$$

$$k = a^3/b^3, \quad \text{Eq. (2)}$$

where P is the swelling pressure and k corresponds to the voluminal resin content in a package.

The solid and broken lines in Fig. 8 are the results calculated using Eq. (1). The tensile stress on the cement using Eq. (1). The tensile stress on the cement matrix increased with the swelling pressure P and resin content k. Circles superimposed on the same figure are the results of the water immersion tests in Fig. 5. The black circles mean the packages cracked and deteriorated in water, while the open ones show no deterioration. Tensile strength of the cement used in this study (38 ± 5 kg/cm^2) is also shown in Fig. 8. It was found that only the packages whose tensile stress was higher then the above tensile strength cracked in water, as expected. Therefore, the deterioration model inferred in Fig. 3 was considered to be reasonable.

Increase in Resin Content

The results in Fig. 8 suggested that water resistance of the package could be improved by increasing the cement strength or by reducing the swelling pressure. The former countermeasure was examined in this study.

The maximum tensile strength exerted by the resin swelling was less than 60 kg/cm^2 even at a high resin content of 42 vol%. Deterioration could be prevented at such high content if the tensile strength was higher than the above maximum stress.

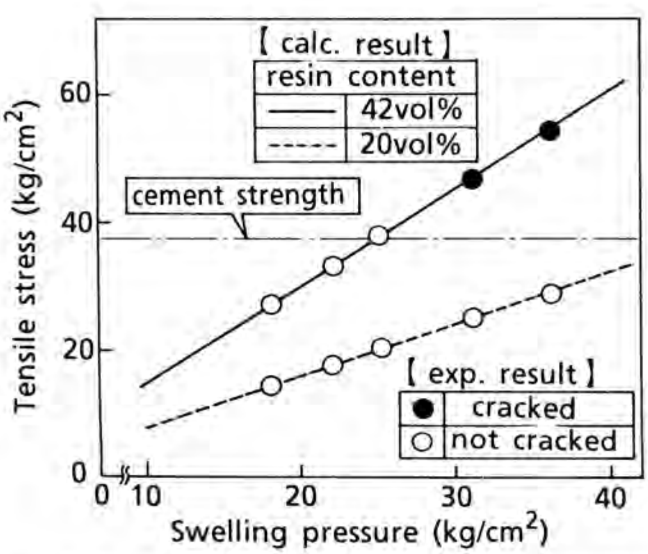

Fig. 8. Comparison between calculated and experimental results.

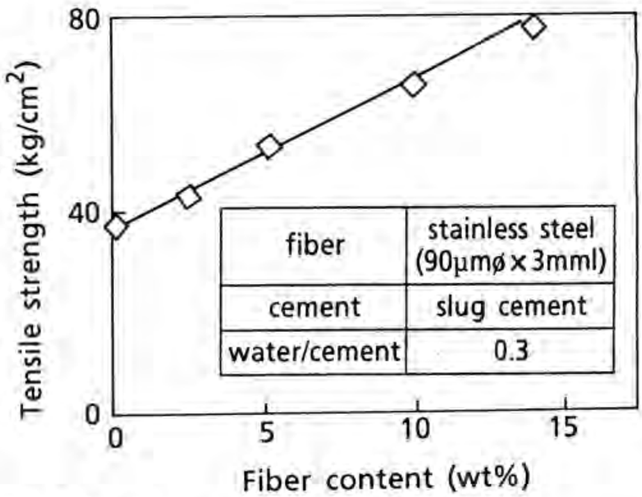

Fig. 9. Tensile strength of fiber reinforced cement.

Fiber reinforcement is a known, effective method to increase the tensile strength of cement (6). Various materials such as glass, carbon and steel are used as fibers. Glass fiber in the cement, however, tends to dissolve and deteriorate in water, because the water in a cement package is highly alkaline and it is difficult to disperse carbon fiber uniformly into the cement. Therefore, steel fiber was selected for the material.

Figure 9 shows the changes in cement strength as a function of steel fiber content. The tensile strength increased in proportion to the fiber content and almost doubled (~70 kg/cm^2) by adding 10 wt% fiber, while the sufficient strength for increasing the resin content to 42 vol% was 60 kg/cm^2 as discussed previously.

Table II summarizes the effect of the fiber on the cement package with resin. The package using the fiber reinforced cement did not crack and its compressive strength was maintained above 80 kg/cm^2 even in such a high resin content as 42 vol%, which corresponded to 55 kg - dry resin/200 drum, during the water immersion test for three months. The packages without fiber, on the other hand, tended to deteriorate in water when resin content was higher than 20 vol%. These findings predicted that the number of waste packages would be reduced by about half by use of the reinforced cement, as compared with the conventional cement solidification method.

TABLE II

Results of Water Immersion Tests

Experimental Condition		Test Result	
Steel Fiber in Cement	Resin Content	Appearance	Compressive Strength
0wt%	42vol%	Cracked	~ $0kg/cm^2$
10wt%	42vol%	Good	> $80kg/cm^2$

PILOT PLANT TEST

A full-scale pilot plant was constructed to demonstrate availability of the fundamental experiments. Simulated spent ion exchange resin, generated from a thermal power plant, was solidified into a 200 package with a resin content of 42 vol% (55 kg - dry resin/200) using the fiber reinforced cement. After the curing, it was put into a 1 cm^3 water vessel (Fig. 10), and changes in its compressive strength, package volume and weight were measured during the last nine months. The strength was estimated from propagation velocity of ultrasonic waves in the package.

Figure 11 shows the results of the water immersion test for a 200 cement package. Its weight gradually increased with time and was saturated at the increase of 3.5 wt% after immersion for about 100 days, indicating water penetration into the package. Deterioration such as cracking and swelling was not observed. Its volume change was less than the experimental error of 0.1%, and compressive strength was more than $80kg/cm^2$ before and after the water immersion. These findings agreed with the results of fundamental experiments.

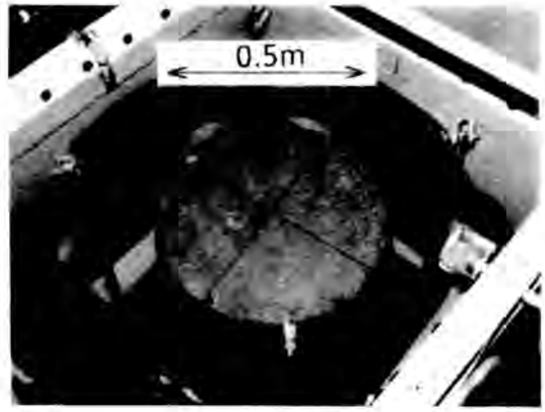

Fig. 10. Water immersion test of 200l cement package.

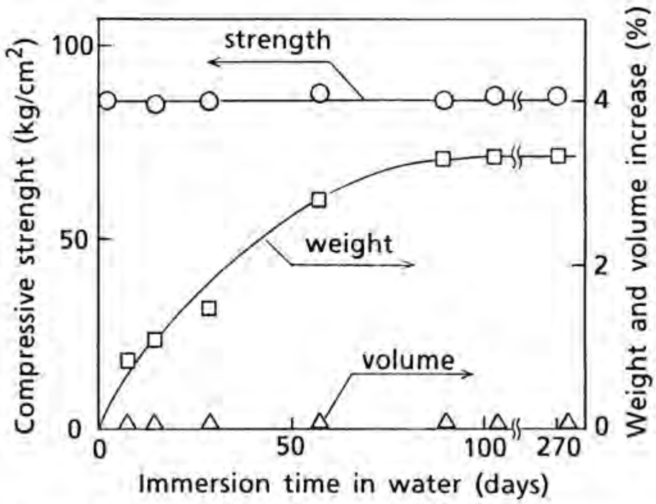

Fig. 11. Results of water immersion test for 200l cement package with resin content of 42 vol%.

CONCLUSIONS

Conventional cement packages tend to deteriorate in water when their resin content is high. The deterioration mechanism was first investigated in this study. Subsequently, prevention measures against the deterioration were studied, to improve volume reduction efficiency. The following results were obtained:

1. Ion exchange resin in the cement package tended to swell under a water immersion condition and tensile stress was exerted on the cement matrix. The package was cracked and deteriorated in water when its stress was higher than the tensile strength of the cement.
2. Tensile strength was almost doubled by adding 10 wt% reinforcing steel fiber to the cement. This enabled resin content to be increased from 20 to 42 vol%, hence improving volume reduction efficiency.
3. Pilot plant tests were performed to confirm availability of the fundamental experiments. Full-scale cement package (200) has not deteriorated in water after nine months even at a high resin content of 42 vol% when fiber reinforced cement was used.

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