ADVANCED CEMENT-SOLIDIFICATION PROCESS FOR SPENT ION-EXCHANGE RESINS

K. Sauda, F. Todo, T. Nakashima, T. Kagawa, H. Kuribayashi
JGC Corporation
Yokohama, Japan 232

ABSTRACT

JGC has developed an advanced cement-solidification process (AC-Process) for the treatment and stabilization of radioactive spent ion-exchange resins generated at nuclear power plants. The AC-Process can produce excellent products in comparison with other existing cement solidification processes. In addition, this process requires a lower operating cost than that of the HIC system.

In general, cement-solidification products derived from spent ion-exchange resins tend to swell in water. Such swelling is caused by the expansion of resins in water due to the absorption of water and by the adsorption of soluble contents in the cement matrix. In order to solve this problem, JGC has developed a new pretreatment technique for obtaining cement-solidified products which will meet the requirements for final disposal. Extensive tests were conducted to determine pretreatment conditions. The properties of obtained products were evaluated to verify that they met the requirements for final disposal. The results of the tests and evaluation are reported below.

INTRODUCTION

JGC has carried out research and development work on cement solidification technologies for radioactive wastes for a long time. Such wastes as PWR evaporator concentrates, incineration ashes, etc., were difficult to cement-solidify using existing technologies. To stabilize such wastes, JGC has already established a new technology for obtaining highly volume-reduced solidified products excellent in water resistivity and other properties by using a JGC-developed unique pretreatment method (USP 4800042).

Also for ion-exchange resins, JGC has succeeded in solving problems associated with existing cement-solidification processes by pretreating ion-exchange resins before mixing them with cement.

The advanced cement-solidification technology for spent ion-exchange resins, developed by JGC, is described below with respect to the pretreatment method, process control program, Technical Position tests for cementitious waste forms.

PRETREATMENT OF SPENT ION-EXCHANGE RESINS

A problem associated with existing well-known cement-solidification processes for spent ion-exchange resins is that the matrix of the cement-solidified products obtained is disrupted when immersed in water for a long time. Cement-solidified products derived from spent bead resins particularly exhibit such a phenomenon. For this reason, the pretreatment of spent ion-exchange resins has been actively discussed at the Workshop on Cement Stabilization of LLRW" held by the U.S. Nuclear Regulatory Commission (1).

This report describes the concept of the spent ion-exchange resin pretreatment method developed by JGC in comparison with other pretreatment methods. The mechanism of the matrix disruption of cement-solidified spent ion-exchange resin products in water has not yet been clarified. However, such a disruption is said to be caused by the adsorption of soluble cement components by resins during the curing and by the swelling and contraction of resins due to the reactions between cement-water and resin-water.

Various methods have been proposed to prevent such a disruption of the matrix and they can be classified roughly as follows:

1) Adsorption of such ions as Na, Ca, etc., by cation exchange resins (2).
2) Improvement of cement binders (3).
3) Coating of resins with polyester or similar materials (4).
4) Pretreatment to raise the water content (1).

Concerning method 1, the following problem exists: When spent ion-exchange resins are pretreated by NaOH, the adsorbed Na ions are replaced after a long period of time by Ca ions contained in cement. As a result, the matrix of the cement-solidified product is disrupted. The pretreatment of spent ion-exchange resins by lime (CaO) cannot prevent an increase in the anion exchange resin volume, though it is very effective in preventing an increase in the cation exchange resin volume.

According to our test results, it is revealed that when a cement-solidified product derived only from anion exchange resins is subjected to a water immersion test, the volume of the product gradually increases and finally disruption of the matrix and cracking occurs. Figure 1 shows the immersion test results.

On the other hand, the following problems are associated with methods 2 and 3: As methods for improving cement binders, examples exist of using slag cement, alumina cement, polymer gypsum cement, or sulfur cement. However, these methods do not differ from the use of

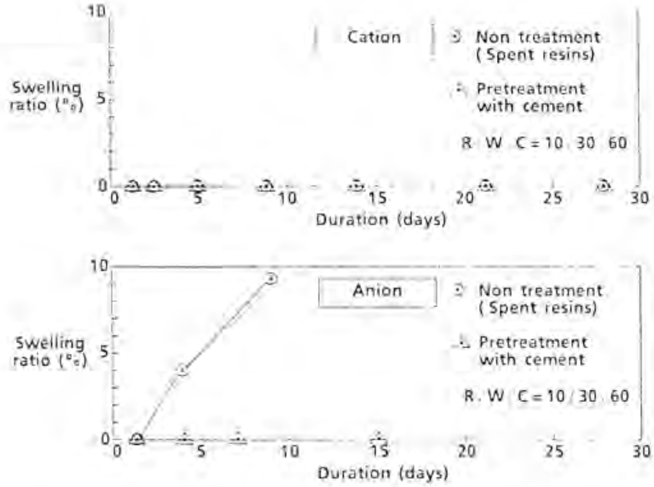

Fig. 1. Swelling of Solidified Spent Resin Products During Immersion Tests.

ordinary Portland cement. In method 3, spent ion-exchange resins are coated with an organic high-viscosity liquid such as polyester which requires a special chemical or heating for hardening to occur. This complicates the solidification process. Therefore, this method is undesirable although is effective.

Alternatively, as listed as method 4, spent ion-exchange resins can be cement-solidified under water-containing conditions. However, this method is not very effective because spent resins become dry during the curing.

As described above, the spent ion-exchange resin pretreatment methods reported up to the present time have both advantages and disadvantages. The development of a new cement solidification technology has therefore been desired. Considering such circumstances, JGC conceived the following pretreatment.

After the addition of a certain amount of cement and water, dewatered spent ion-exchange resins are agitated at a high speed in a highly alkaline cement slurry. Cement hydration of the spent resins after mixing with cement can thereby be prevented.

On the basis of this concept, JGC studied the spent ion-exchange resin pretreatment conditions, especially the amount of cement to be added, pretreatment time, and agitator revolutions. As a result of the study, it was revealed that satisfactory pretreatment effects could be achieved by high-speed agitation at 350 rpm using a high shearing mixer, cement addition of 20 wt% on a dry resin basis, agitation for more than 10 minutes, and curing for more than 3 hours. As shown in Fig. 1, application of the cement pretreatment could also prevent matrix disruption of cement-solidified anion resin products.

TECHNICAL POSITION TESTS ON SOLIDIFIED PRODUCTS

Technical Position tests were conducted to verify that cement-solidified products obtained by applying this new pretreatment method met the technical requirements of 10 CFR 61, Technical Position (1983). The tests were comprised of a compressive strength test, radiation stability test, biodegradation test, leachability test, immersion test, thermal cycling test, free liquid test, and a full-scale test.

Preparation of test products

Non-radioactive spent ion-exchange resins were used to prepare solidified products for laboratory and full-scale tests. For leachability tests, the radionuclides, Co and Cs, were added to resins. For field tests, spent ion-exchange resins actually generated at a PWR plant in Japan were used.

Spent bead and powdered resins were both used as ion-exchange resins and the standard mixing ratio of cation to anion exchange resins was 1:1.

Test procedure

Compressive strength tests were conducted in accordance with ASTM C 39. Test specimens were cured in water-saturated air for 30, 60, and 90 days.

For radiation stability tests, specimens were irradiated with gamma rays of 10^8 rads at the Japan Atomic Energy Research Institute. Biodegradation tests were conducted in accordance with ASTM G21 and ASTM G22.

Leachability tests and immersion tests were conducted in accordance with ANSI 16.1. Test specimens cured in water-saturated air for 30 days were used for all the tests.

Thermal degradation tests were conducted in accordance with ASTM B553 and free liquid tests were conducted using full-size (55-gal drum) solidified products prepared by a demonstration pilot plant (Fig. 2) at JGC Oarai Research and Development Center.

Full-scale tests were conducted using specimens taken from a 55-gallon drum size solidified product prepared by the pilot plant, using a core boring machine.

Physical properties of products

The physical properties of cement-solidified products obtained are shown in Table I. All the data satisfied the criteria required by the Technical Position on Waste Form. From the test data, it is concluded that the cement-solidified

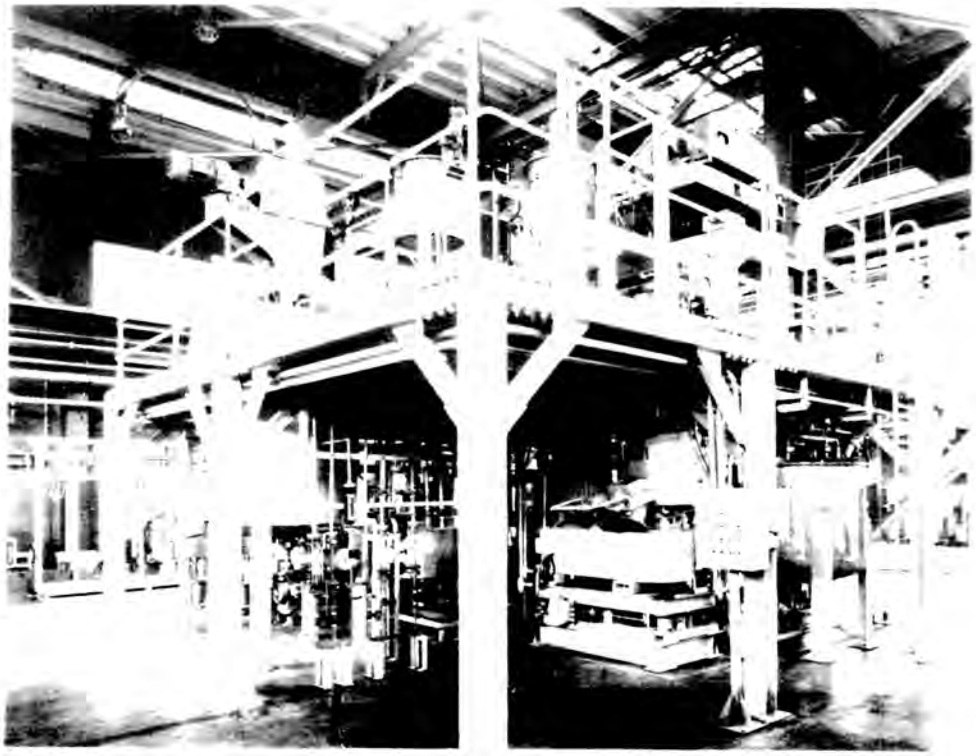

Fig. 2. Demonstration Pilot Plant at JGC Oarai Research and Development Center.

TABLE I

Physical Properties of Solidified Products Obtained by AC - Process

NO	Test Item	Regulatory Position (NRC)		JGC's Data			
		Standard	Acceptance Criteria	Spent Bead Resins		Spent Powder Resins	
				18 / 36 / 46	20 / 40 / 40	18 / 36 / 46	20 / 40 / 40
1	Compressive strength	ASTM C 39	More than 60 psi	1,390 ± 480	1,390 ± 80	3,070 ± 120	1,910 ± 80
2	Radiation stability	ASTM C 39 (after10^8rads)	More than 60 psi	1,080 ± 10	——	2,550 ± 250	——
3	Biodegradation	ASTM G21 ASTM C39	No growth More than 60 psi	No growth 1,440 ± 0	——	No growth 2,920 ± 60	——
		ASTM G22 ASTM C39	No growth More than 60 psi	No growth 1,550 ± 60	——	No growth 2,550 ± 550	——
4	Leachability	ANS 16.1 DW Co	More than leach index of 6	14.89 ± 0.33	12.58	15.42 ± 0.25	12.70
		ANS 16.1 DW Cs		7.33 ± 0.02	——	7.12 ± 0.07	——
		ANS 16.1 DW Sr		9.68 ± 0.03	7.80	8.32 ± 0.08	7.59
		ANS 16.1 SW Co		15.51 ± 0.04	——	15.88 ± 0.19	——
		ANS 16.1 SW Cs		7.37 ± 0.11		7.30 ± 0.08	
		ANS 16.1 SW Sr		9.57 ± 0.18		8.53 ± 0.09	
5	Immersion	ASTM C 39	More than 60 psi after 90 days	1,300 ± 230	330 ± 20	2,650 ± 80	2,000 ± 90
6	Thermal Cycling	ASTM B 553	More than 60 psi after 30 cycles	1,190 ± 120	——	1,970 ± 10	——
7	Free liquid	ANS 55.1	No more than 0.5 vol%	0 vol%	——	0 vol%	——
8	Full - scale test	ASTM C 39	More than 60 psi	1,530 ± 200	——	2,140 ± 130	——

DW : Demineralized water SW : Sea water

products obtained by this process meet the requirements for Class B and Class C waste forms.

System Description

JGC's advanced cement-solidification process, for the effective pretreatment of spent ion-exchange resins, is shown in Fig. 3. Spent ion-exchange resins are received in a spent resin receiving tank, then sent to a dehydrator or centrifugal separator for dehydration purposes. The supernatant is returned to a spent resin storage tank and the dewatered resins are received in a mixer, where the resins are mixed with the specified amount of cement and water. After the specified amount of cement is added, the pretreated resins are sufficiently mixed, then filled into drums.

Control parameters

The following parameters are controlled to obtain satisfactory cement-solidified products. The amount of cement to be added for pretreatment is more than 20 wt% on a dry resin basis. Resins are mixed for more than 10 minutes at an agitation speed of 350 rpm and cured for more than 3 hours. In addition, when the pretreated resin is mixed in the mixer, the weights are controlled so as to enable the following mixing ratio:

Resin/Water/Cement = 18/36/46

Resin : Dry resin (lb)

Water : Water contained in resin + Free water (lb)

Cement: Portland cement (lb)

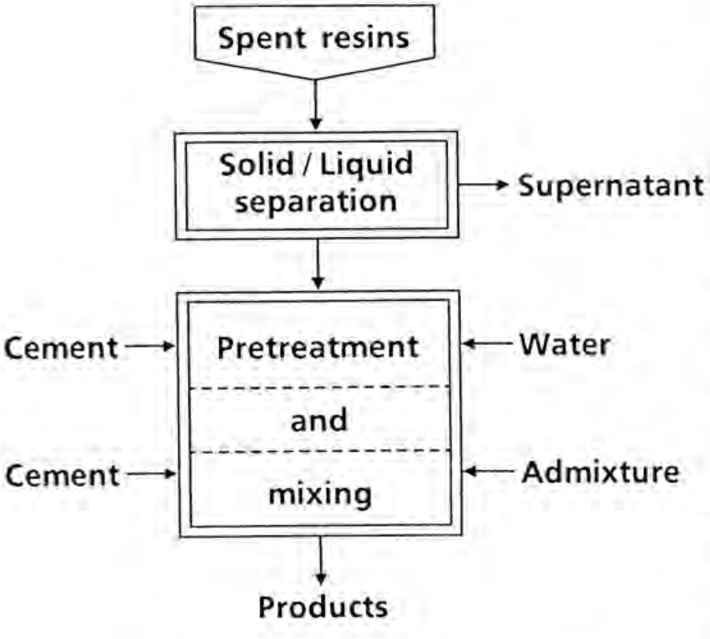

Fig. 3. Basic Flow Diagram of AC - Process.

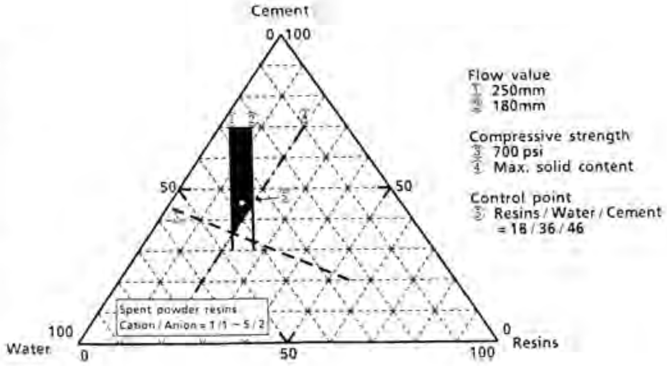

Fig. 4. Relation Between Mixing Ratios (R/W/C) and Bounding Limits.

When the amount of water increases beyond the No. 1 line in Fig. 4, bleeding occurs, and when the amount of water decreases below the No. 2 line, the dischargeability from the mixer is lowered. An increase in the amount of resin lowers the compressive strength of cement-solidified products and causes disruption of the matrix in immersion tests. The No. 3 line indicates the condition under which cement-solidified products cured in water-saturated air for 30 days show a compressive strength of 700 psi. When the amount of resin is increased above the No. 4 line, cracks develop on the surface of cement-solidified products in 90-day immersion tests.

ECONOMICAL EVALUATION

This advanced cement solidification process eliminates the need for using expensive HIC liners because spent ion-exchange resins are stabilized by cement. A large reduction of direct expenses such as container cost, disposal cost, etc., can therefore be achieved.

CONCLUSION

In the advanced cement solidification process developed by JGC, solidified products obtained are excellent in physical properties because spent ion-exchange resins are sufficiently pretreated before being cement-solidified. Therefore, the products can satisfactorily meet the waste form criteria required by 10 CFR 61 and Technical Position. In addition, direct expenses can be largely reduced because there the use of expensive HIC liners is not required.

REFERENCES

1. U.S. NRC, "Workshop on Cement Stabilization of Low-Level Radioactive Waste," NUREG/CP-0103, NISTIR 89-4178.
2. T. TSUTSUI and K. NISHIMAKI, "Evaluation Method for Cement-Solidified Products of Radioactive Waste," Vol. 9, P87 94, Health Physics, (1974).
3. Brookhaven National Laboratory "Waste Form Development Program Annual Report," BNL 51614, (1982).
4. Brookhaven National Laboratory, "Waste Form Development Program Annual Report," BNL 51756, (1983).