HIGH STRENGTH CEMENTIZED DRIED RESINS

R. L. Gay and L. F. Grantham

Rockwell International Corporation
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, CA 91304

ABSTRACT

One common method for disposal of radioactive resins is to mix them with cement and cast them into monolithic blocks in rigid liners (containers). In some cases, cementized resin samples have reabsorbed water and swelled until the cement crumbled. Therefore, the NRC Branch Technical Position on waste forms requires cementized bead resin to undergo a 0.34 MPa (50 psi) compressive strength test after immersion in water for 90 days in order to qualify as an acceptable radioactive waste disposal form. Many cementized resin waste forms cannot achieve high radioactive waste loading and still qualify as a waste form after the 90-day immersion strength test.

It was found that chemically spent resins pretreated in a high efficiency dryer are nearly impermeable to water and will not reabsorb and swell when immersed. The chemical form of the resins was found to be an important factor in water reabsorption. Fresh resins in the H^+ or OH^- form were susceptible to water reabsorption after high-efficiency drying. However, depleted resins were found to be well-suited for cement solidification and high-strength waste forms were produced with loadings as high as nearly 28 wt. % dried resins (equivalent to 70 wt. % dewatered resins). These waste forms easily withstood the compressive strength test after initial curing and after 90 days of immersion in water.

Substantial volume reduction and cost savings can be achieved by disposal of cementized dried resins. Cement solidification of 0.028 m^3 (1 ft^3) of dewatered resins yields 0.045 m^3 (1.6 ft^3) of solid monolith whereas cement solidification of the equivalent dewatered resins with resin drying before solidification yields 0.030 m^3 (1.06 ft^3) of solid monolith. Drying of the resins before solidification is projected in 1986 to save $\$750/m^3$ ($\$21/ft^3$) of dewatered resin at 3.5 μCi/ml (0.1 Ci/ft^3) activity and $\$1,710/m^3$ ($\$48/ft^3$) at 35 μCi/ml (1.0 Ci/ft^3) activity. These cost savings will increase to at least $\$1,390/m^3$ ($\$39/ft^3$) and $\$2,360/m^3$ ($\$66/ft^3$) respectively in 1990 solely due to recently legislated burial surcharges. Additional cost savings can be anticipated if burial charges continue to increase at 10 to 15% per year.

BACKGROUND

At a nuclear reactor powdered and bead ion exchange resins are used to cleanup waste water by exchanging ions in solution with hydrogen and hydroxide ion in the resin. Some of the ions in the water are radioactive activation products and corrosion products from the reactor core and thus render the resins radioactive. As the resins reach their exchange capacity, fresh resins are used for replacement, and the spent resins must be disposed of as radioactive waste. Although the generation of spent resins varies with each reactor, a typical BWR or PWR generates 70 to 140 m^3 (2500 to 5000 ft^3) of spent resin each year.

In order to meet the waste form stability requirements of 10 CFR 61, [1] spent resins are commonly disposed of in two possible ways: (1) by removal of all of the free-standing water (dewatering) and burial in high-integrity containers or (2) by solidification or encapsulation in an approved medium such as cement, bitumen, or polymer. Solidification in cement is widely used and accepted at all of the burial sites.

The NRC Branch Technical Position [2] on waste forms provides guidance on the processing of wastes into an acceptable, stable waste form. Wastes that are classified as Classes B and C wastes are required to have stability. Stability requires that the waste form maintain its structural stability under the expected disposal conditions. Among the conditions that must be met to ensure stability is the requirement that the waste should remain stable if exposed to moisture or water after disposal. Cement waste forms that are improperly mixed may be susceptible to absorption of water and thus crumble and lose their stability. Acceptable solidified waste specimens should have a compressive strength of at least 0.34 MPa (50 psi) immediately after curing and after 90 days of immersion in water.

WATER CONTENT AND WASTE VOLUME

Ion exchange resins are usually composed of styrene-divinylbenzene copolymer with various degrees of cross-linking. The resins have a complex pore structure and have a large affinity for water absorption. In practice, the resins are slurried in water and three "categories" of water may be described: absorbed water in the pore structure, adsorbed water on the resin particle surface, and interstitial water between the resin particles. [3] Decanting and dewatering by pumping or centrifuging will remove nearly all of the interstitial water. Resins that have been dewatered to less than 1 vol % free-standing water may be disposed of in high-integrity containers. However, these resins still contain all of the absorbed water and most of the adsorbed water and tend to form loose-fitting solids of low-density. Typical dewatered resins contain 50 to 75 wt. % water and have a tap density of 0.6 to 0.9 g/ml. In addition, a significant portion of the volume of the high-integrity container used for burial is occupied by void space and dewatering equipment. Thus, a premium is paid in unused volume for burial of dewatered resins in high-integrity containers.

Less expensive than high-integrity containers are disposal liners. Spent resins that have been incorporated into cement are solidified in large volume liners, typically 3 to 9 m^3 (100 to 300 ft^3). The cured cement will meet waste form stability criteria if the resin loading is carefully limited. The highest limits for resin loading (about 20 wt. % dewatered resins) still produce a 50 to 60% increase in volume as compared to the dewatered resin volume. This increase in volume is the premium that is paid for disposal with cement solidification.

New technologies have become available that recognize the expanded resin pore structure and water affinity and take advantage of these properties for volume reduction.[4-6] High-efficiency dryers are capable of removing much more of the water from resin slurries than standard dewatering techniques. For example, spray-drying of bead resins or powdered resins can produce a virtually dry product of less than 10% absorbed water. The resin particles shrink on drying and a final volume of 1/2 to 1/3 the dewatered resin volume can be achieved. These dried resins are disposed of in high-integrity containers at substantial cost savings.

Legislation in progress for the disposal sites operated by individual state compacts suggests that more stringent requirements than 10 CFR 61 may be imposed on waste form stability. In addition, the costs of disposal are also anticipated to increase. Thus, we have begun studies of the incorporation of high-efficiency dried resins in cement. Significant reduction in the final cement volume is potentially possible through this approach. Following are results of laboratory cement solidification tests with simulated spent resins.

TESTS WITH H^+ AND OH^- RESINS

Initial tests were done with ion exchange resins in the hydrogen (H^+) and hydroxide (OH^-) form. Strong cation (H^+) resins, Gravex GR-2 and strong anion (OH^-) resins, Gravex GR-1 were procured from Ecodyne Corp. These resins were tested in the "as-received" condition: no chemical loading was done. The high-efficiency dryer used in these tests consisted of a feed system, spray dryer, baghouse, blower, and controls. This system has been described previously in several publications[4,5] and will not be described further. The resins were slurried in water and dried to near bone-dry condition (less than 5 wt. % absorbed water). Separate batches of dried cation and anion resins were prepared for cement solidification.

The results of cementation of dried H^+ and OH^- resins are presented in Table I. High waste loading (45 wt. %) of anion (OH^-) resins was achieved in a limited number of samples (2 out of 3). The cation (H^+) resins did not produce good cement waste forms in any sample. The cation resin samples got very warm on mixing with the cement-water mixture. We believe this is due to hydration of the sulfonic acid ($R-SO_3$) group on these resins. This tendency for water re-adsorption interfered with the cement solidification chemistry. Solidification of dried cation resins in the H^+ form is possible, but high waste loadings (near 30 wt. % dried resins) were not achieved in these tests.

TABLE I

Cementation of Dried Bead Resins, H^+ and OH^- Form

Composition (wt. %)			Results of Compression Test[a] (After Curing)	Type of Resins
Dried Resins	Cement	H_2O		
40.9	40.6	18.5	Failed	Anion (OH^-)
40.9	38.9	20.2	Passed	Anion
45.2	28.1	26.7	Passed	Anion
30.0	21.2	48.8	Failed	Cation (H^+)
30.7	30.8	38.4	Failed	Cation
30.7	20.7	48.7	Failed	Cation
33.2	21.8	45.0	Failed	Cation
34.4	21.6	44.0	Failed	Cation
35.9	24.2	39.9	Failed	Cation

[a] Cured at room temperature overnight in open plastic pans; compression test by hand examination.

PREPARATION OF DEPLETED RESINS

Typical spent resins for waste disposal are chemically depleted to 80 to 100% of their exchange capacity. Thus, strong ion exchange resins in the H^+ or OH^- form have been converted to other ionic species before disposal. Depleted resins were prepared in our laboratory from Amberlite nuclear grade resins that were procured from Epicor in the H^+ and OH^- form. The resins were depleted 80 to 100% by stirring overnight in separate water solutions containing sufficient cations and anions to exchange with the H^+ and OH^-. The depleted resins were washed thoroughly before drying.

A mixture of depleted cation and depleted anion resins was used for these tests. The slurry contained 3.1 kg of dewatered cation resin and 1.9 kg of dewatered anion resin in 6.6 kg of water. The physical properties of the feed materials are given in Table II. The density of the feed slurry was approximately 1.02 g/ml. The densities of the dewatered cation and anion resin were approximately 1.06 and 0.99 g/ml, respectively. These dewatered resin densities are about 20% higher than those obtained in

TABLE II

Properties of Feed and Product Material

Material	Density (g/ml)		Content[a] Water (wt. %)
	Bulk	Tap	
Dewatered cation	1.06	-	57.0
Dewatered anion	0.99	-	64.4
Slurry	1.02	-	83
High-efficiency dryer product	0.64	0.84	7.0

[a] Compared to resin oven-dried at 120°C for 600 h, i.e., bone-dry resin

the field at nuclear power plants. Thus, a 20% improvement in volume reduction would be expected if actual spent power plant resins were tested.

The dried resin was collected in the baghouse hopper. The dry product had a moisture content of only 7 wt. % and bulk and tap densities of 0.64 and 0.84 g/ml respectively.

CEMENTATION

Samples of the dried resins were mixed with cement in screw top jars (8-cm diam, 225-ml vol). Sufficient water was added and stirred into the mixture to obtain a typical concrete thixotropic mixture. After mixing for 1 min and tapping to settle the cement to the bottom of the jar, the jars were sealed and placed in an oven at 60°C to cure for 84 h. The plastic jars were cut to remove the concrete specimens for mechanical compression tests and volume measurements.

The mixtures used in the cementation samples of dry product are given in Table III. The mixtures used for cementation samples of dewatered mixed resins are given in Table IV. From these data the weight percent of dry product and dewatered resins in the cement was calculated and is also given in Tables III and IV, respectively. The volume of cement product was measured by a water displacement method in which water was forced to flow out of a container by cement immersion. The overflow water was collected and weighed. A maximum waste loading

TABLE III

Cementation of Dried Depleted Bead Resins

Composition (wt. %)			Dried Resin[c] (vol %)	Cement Sample Density (g/cc)	Results of Compression Test[a] (After Curing)	Results of Compression Test[b] (After Immersion)
Dried Resin	Cement	H_2O				
13.9	55.6	30.5	37.2	1.64	Passed	Passed
13.5	54.1	32.4	36.8	1.60	Passed	Passed
15.8	52.6	31.6	42.3	1.66	Passed	Passed
14.2	55.2	30.7	37.2	1.62	Passed	Passed
15.4	51.3	33.3	39.5	1.58	Passed	Passed
17.5	50.0	32.5	44.8	1.56	Passed	Passed
17.1	48.8	34.1	44.5	1.51	Passed	Passed
18.6	46.5	34.9	45.1	1.50	Passed	Passed
18.2	45.4	36.4	45.2	1.49	Passed	Passed
17.8	44.4	37.8	42.1	1.45	Passed	Passed
17.7	44.2	35.8	48.7	1.49	Passed	Passed
19.6	43.5	36.9	46.1	1.46	Passed	Passed
21.3	42.6	36.2	50.8	1.46	Passed	Passed
20.8	41.7	37.5	49.7	1.46	Passed	Passed
23.6	39.4	37.0	54.4	1.33	Passed	Passed
23.9	39.9	36.2	55.1	1.49	Passed	Passed
26.3	35.1	38.6	58.6	1.40	Passed	Passed
25.0	31.2	43.8	62.5	1.16	Failed	Failed
27.8	27.8	44.4	69.5	1.45	Passed	Passed

[a] Compression test made after cement set up at 60°C for 84 h in closed container; 0.48 MPa (69 lb/in.^{2}) applied.

[b] Compression test made after 90 days immersion in water; 0.48 MPa (69 lb/in.^{2}) applied.

[c] Volumetric loading based on ratio of volume of dried resin at tap density to volume of cement waste form.

TABLE IV

Cement Prepared from Dewatered Mixed Resin

Composition (wt. %)			Cement Sample Density (g/cc)	Results of Compression Test[a] (After Curing)	Results of Compression Test[b] (After Immersion)
Dewatered Resin	Cement	H_2O			
19.9	60.6	19.5	1.70	Passed	Passed
41.7	50.0	8.3	1.51	Passed	Passed
42.8	42.8	14.4	Cracked	Failed	Failed

[a] Compression test made after cement set up at 60°C for 84 h in closed container; 0.48 MPa (69 lb/in.^{2}) applied.

[b] Compression test made after 90 days immersion in water; 0.48 MPa (69 lb/in.^{2}) applied.

of 28 wt. % of dry product in cement was obtained. This corresponds to an equivalent loading of 70 wt. % of the original dewatered resin.

Compression tests on the cement product were made by setting a round 2.5-cm-diam (1-in.) piece of metal on the cement product and placing 24.5 kg (54 lb) of lead bricks on it. Only two of the cement samples cracked as indicated in Tables III and IV. These cement specimens were immersed in water at ambient temperatures for 90 days and retested to determine the integrity of cement as required. All of the cement samples which passed the first compression test also passed the compression test after immersion.

A maximum waste loading of 27.8 wt. % was tested in these samples and passed the compression test both before and after water immersion. Higher waste loadings above 28 wt % may be possible, but were not tested here.

VOLUME REDUCTION AND ECONOMICS

The disposal volumes of dewatered resins with options of drying and cementation are given in Table V. Using 0.028 m^3 (1 ft^3) of dewatered resins as the starting material, 0.045 m^3 (1.59 ft^3) of cemented dewatered resins would be obtained. However, if the same volume of dewatered resins was dried in a high-efficiency dryer, and then cemented, a volume of 1.06 ft^3 would result. Thus, using a high-efficiency dryer to process the resins produces only 66% of the disposal volume on cement solidification.

TABLE V

Disposal Volumes of Waste Resins*

Waste Resin Description	Dewatered	Solidified in Cement
Waste resins without drying	1.00	1.59
Waste resins with drying	1.00	1.06

*Volume units are normalized.

This volume reduction by high-efficiency drying produces significant cost savings. An economic estimate is given here for the disposal cost savings for four cases:

1) 3.5 μCi/ml (0.1 Ci/ft^3) dewatered resins, disposal at Hanford.
2) 3.5 μCi/ml (0.1 Ci/ft^3) dewatered resins, disposal at Barnwell.
3) 35 μCi/ml (1.0 Ci/ft^3) dewatered resins, disposal at Hanford.
4) 35 μCi/ml (1.0 Ci/ft^3) dewatered resins, disposal at Barnwell.

These two levels of radioactivity correspond to resins from secondary and primary coolant streams. The following assumptions were made:

1) Waste Preparation
   - Cement costs \$0.09/kg (\$0.04/lb).
   - 55-gal drums cost \$30.00 each.
   - Labor costs \$25.00/h.
   - Dewatered resins contain 60 wt. % water.
   - Dried resins contain 7 wt. % water
   - Dewatered resins are solidified at 41.7 wt. %
   - Dried resins are solidified at 27.8 wt. % (70 wt. % dewatered equiv.).
2) Surface Activity
   - Dewatered resins are 50% Co-60, 50% Cs-137.
   - 1.0 Ci/ft^3 resins have 23 R/h on the surface of the dewatered resin-cement monoliths, 35 R/h on the surface of the dried resin-cement monoliths.
   - Surface activity is proportional to resin activity.
3) Transportation
   - 1300 km (800 miles) to disposal site, \$0.93/km (\$1.50/mile).
   - 44 drums/truckload for 0.1 Ci/ft^3 cases.
   - 14 drums/cask for 1.0 Ci/ft^3 cases
   - \$500 cask rental fee.
4) Burial Charges
   - 1986 Barnwell site schedule.
   - 1986 Hanford site schedule.
5) Burial Surcharge
   - 1986-1987--\$10/ft^3.
   - 1990-1992--\$40/ft^3.

The results of the economic calculations are given in Table VI for disposal of 3.5 μCi/ml (0.1 Ci/ft^3) resins and in Table VII for disposal of 35 μCi/ml (1.0 Ci/ft^3) resins. In all cases, the largest portion of the disposal costs is in burial. Disposal of cement solidified 3.5 μCi/ml (0.1 Ci/ft^3) resins at Barnwell will cost \$4,080/m^3 (\$114/ft^3) for dewatered resins and \$3,350/m^3 (\$94/ft^3) for dried resins. Corresponding values at Hanford are \$3,540/m^3 (\$99/ft^3) and \$2,780/m^3 (\$78/ft^3). At each disposal site, a cost savings of \$750/m^3 (\$21/ft^3) can be achieved by drying. This cost savings will increase to \$1,390/m^3 (\$39/ft^3) in 1990 as burial surcharges increase.

As seen in Table VII, disposal of cement-solidified, 35 μCi/ml (1.0 Ci/ft^3) resins at Barnwell will cost \$8,870/m^3 (\$248/ft^3) for dewatered resins and \$7,240/m^3 (\$203/ft^3) for dried resins. Corresponding values at Hanford are \$6,330/m^3 (\$177/ft^3) and \$4,600/m^3 (\$129/ft^3). A cost savings of \$1,710/m^3 (\$48/ft^3) can be achieved by resin drying. These savings will increase to \$2,360/m^3 (\$66/ft^3) by 1990. Thus, drying of resins and solidification in cement can be expected to yield a 20% reduction in overall disposal costs in 1986 and greater reduction in later years.

CONCLUSION

The chemical form of ion exchange resins that have been treated by high-efficiency drying was found to be an important factor influencing monolith strength during cement solidification of dried resins. Resins in the H^+ or OH^- form (the as-received form from the manufacturer) did not produce high-strength cement waste samples at dried resin loadings of 35 to 45 wt. %. Chemically spent resins that were dried produced high-strength cement waste forms that passed the compressive strength test immediately after curing and after 90 days of water immersion. Dried resin loadings of up to 28 wt. % were tested and passed the immersion test.

Drying of the resins before cement solidification produced a final volume equal to 66% of the volume of the equivalent cementized dewatered resins. The volume of the cementized dried resins was 6% greater than the original dewatered resin volume. The volume of the cementized dewatered resins was 59% greater than the original dewatered resin volume.

TABLE VI

Comparison of Disposal Costs for Spent Resins Having 3.5 μCi/ml (0.1 Ci/ft^3) Activity, $\$/\text{m}^3$ ($\$/\text{ft}^3$)

	Barnwell Site		Hanford Site	
	Dewatered Resins in Cement	Dried Resins in Cement	Dewatered Resins in Cement	Dried Resins in Cement
Waste preparation	790 (22)	960 (27)	790 (22)	960 (27)
Transportation	250 (7)	140 (4)	250 (7)	140 (4)
Burial	2,430 (68)	1,860 (52)	1,890 (53)	1,290 (36)
Surcharge, 1986	610 (17)	390 (11)	610 (17)	390 (11)
1990	2,430 (68)	1,570 (44)	2,430 (68)	1,570 (44)
Total, 1986	4,080 (114)	3,350 (94)	3,540 (99)	2,780 (78)
1990	5,900 (165)	4,530 (127)	5,360 (150)	3,960 (111)
Cost savings by resin drying				
1986		730 (20)		750 (21)
1990		1,370 (38)		1,390 (39)

TABLE VII

Comparison of Disposal Costs for Spent Resins Having 35 μCi/ml (1.0 Ci/ft^3) Activity, $\$/\text{m}^3$ ($\$/\text{ft}^3$)

	Barnwell Site		Hanford Site	
	Dewatered Resins in Cement	Dried Resins in Cement	Dewatered Resins in Cement	Dried Resins in Cement
Waste preparation	790 (22)	960 (27)	790 (22)	960 (27)
Transportation	1,040 (29)	680 (19)	1,040 (29)	680 (19)
Burial	6,430 (180)	5,210 (146)	3,890 (109)	2,570 (72)
Surcharge, 1986	610 (17)	390 (11)	610 (17)	390 (11)
1990	2,430 (68)	1,570 (44)	2,430 (68)	1,570 (44)
Total, 1986	8,870 (248)	7,240 (203)	6,330 (177)	4,600 (129)
1990	10,690 (299)	8,420 (236)	8,150 (228)	5,780 (162)
Cost savings by resin drying				
1986		1,610 (45)		1,710 (48)
1990		2,250 (63)		2,360 (66)

Disposal of cementized dried resins was projected to save $\$750/\text{m}^3$ ($\$21/\text{ft}^3$) of dewatered resins at 3.5 μCi/ml (0.1 Ci/ft^3) and $\$1{,}710/\text{m}^3$ ($\$48/\text{ft}^3$) at 35 μCi/ml (1.0 Ci/ft^3) activity, if disposal occurred in 1986. These cost savings will increase to $\$1{,}390/\text{m}^3$ ($\$39/\text{ft}^3$) and $\$2{,}360/\text{m}^3$ ($\$66/\text{ft}^3$) respectively in 1990 solely due to recently legislated burial surcharges. Additional cost savings are very probable if burial site charges continue to increase at 10 to 15% per year and state-imposed burial surcharges are increased for out-of-state waste generators.

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