

*Cement Waste-Form Development for
Ion-Exchange Resins at the Rocky Flats Plant*

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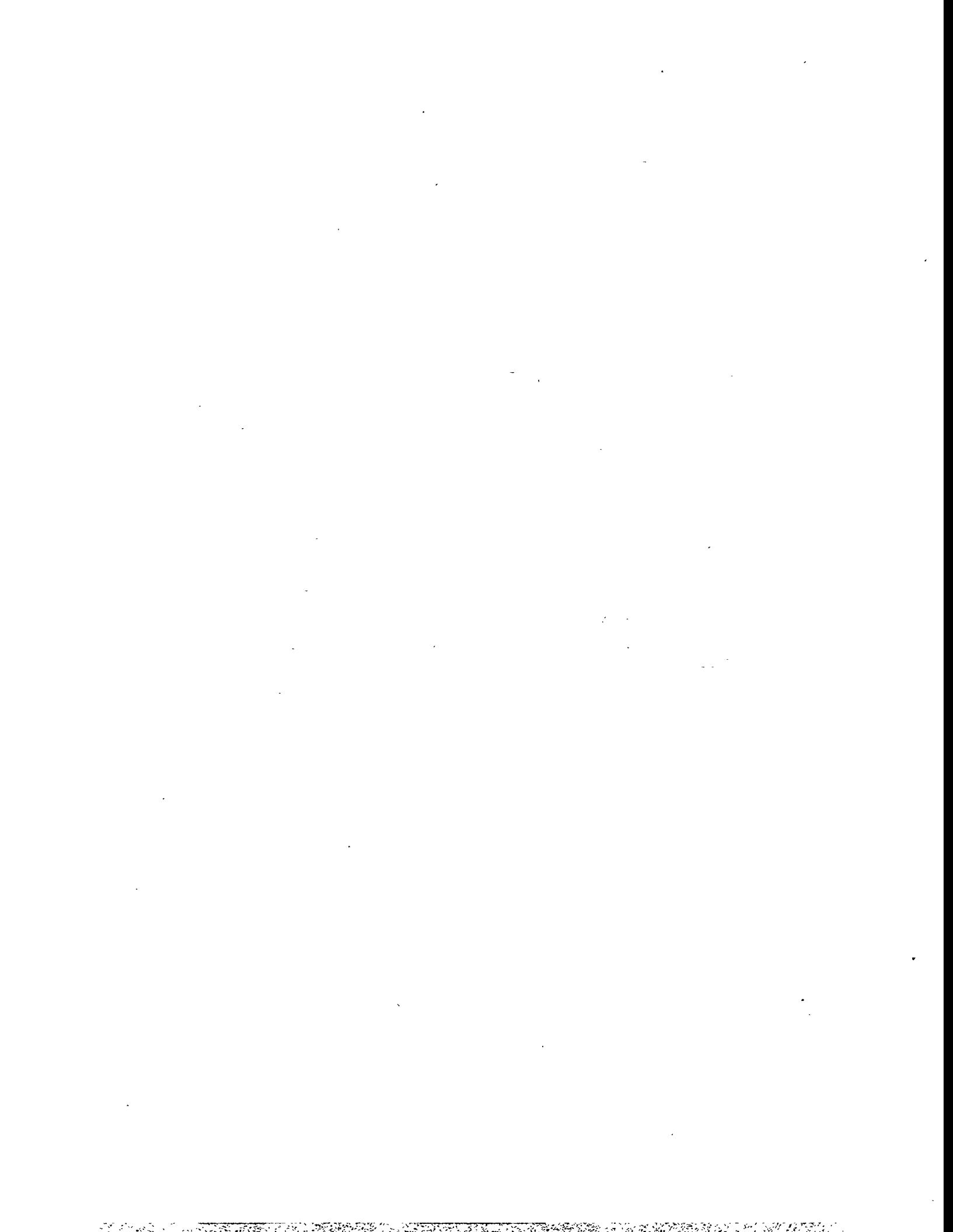
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CEMENT WASTE-FORM DEVELOPMENT FOR ION-EXCHANGE RESINS AT THE ROCKY FLATS PLANT

by

G. W. Veazey and R. L. Ames

ABSTRACT

This report describes the development of a cement waste form to stabilize ion-exchange resins at Rocky Flats Environmental Technology Site (RFETS). These resins have an elevated potential for ignition due to inadequate wetness and contact with nitrates. The work focused on the preparation and performance evaluation of several Portland cement/resin formulations. The performance standards were chosen to address Waste Isolation Pilot Plant and Environmental Protection Agency Resource Conservation and Recovery Act requirements, compatibility with Rocky Flats equipment, and throughput efficiency. The work was performed with surrogate gel-type Dowex cation- and anion-exchange resins chosen to be representative of the resin inventory at RFETS. Work was initiated with nonactinide resins to establish formulation ranges that would meet performance standards. Results were then verified and refined with actinide-containing resins. The final recommended formulation that passed all performance standards was determined to be a cement/water/resin (C/W/R) wt % ratio of 63/27/10 at a pH of 9 to 12. The recommendations include the acceptable compositional ranges for each component of the C/W/R ratio. Also included in this report are a recommended procedure, an equipment list, and observations/suggestions for implementation at RFETS. In addition, information is included that explains why denitration of the resin is unnecessary for stabilizing its ignitability potential.

INTRODUCTION

The purpose of this project was to develop a cement-based waste form that would reduce a significant safety concern posed by actinide-containing, nitrated ion-exchange resins stored at Rocky Flats Environmental Technology Site (RFETS). Cementation was chosen, based on a literature survey of available stabilization technologies,^{1,2} as the technology best able to meet the set of desirable characteristics listed in the statement of work for this project.³ These characteristics include timely demonstration, simplicity, and applicability to other wastes. The safety concern stemmed from the ignitability potential of the dry, nitrate-form, polystyrene-divinylbenzene (DVB) resins given a heat source such as that from radioactive decay.³ This concern is well substantiated through several incidents in which such a resin at an elevated temperature was involved in an exothermic, exponential reaction that resulted in rupture of the containment vessel.⁴ In fact, such an incident occurred at RFETS in 1963 with a resin (Dowex 1-x4) that is contained in the current RFETS resin inventory.^{5,6} The generation of H₂ gas from

radiolysis further intensified the safety concern, especially since some of the drums used to store these resins were unvented.³ Because of the potential catastrophic nature of this scenario, this project was to be completed and implemented with all possible dispatch.

The stabilization operation at RFETS is to be conducted in relatively small batch sizes with existing gloveboxes and equipment. The intention is to use a Hobart-type mixer with batch sizes of 3 liters. Small batches are appropriate because the resin is contained in small containers within the 55-gallon drums. The small batches will also simplify handling and allow fine-tuning of the loading of the containers in the drums to meet the wattage limits for the Transuranic Package Transporter (TRUPACT-II).⁷ The equipment and techniques used in the work presented in this report were selected to be compatible with the existing RFETS equipment and conditions. The equipment used in this project is described in Appendix A.

SURROGATE RESIN SELECTION

An early task was to identify surrogate resins that would imitate the RFETS resins in the experiments to be conducted at Los Alamos National Laboratory (LANL). The selection process was hampered because the RFETS resin inventory was composed of varying (but unknown) blends of (1) cation- and anion-exchange resins, (2) resins from several manufacturers, and (3) gel and macroporous resin types.^{8,9} The literature cited problems with the cementation of both cation- and anion-exchange resins. Cation-exchange resins are capable of removing structural-forming cations such as Ca^{2+} and Al^{3+} from the Portland cement structure.¹⁰ The inclusion of anion-exchange resins in cemented waste forms has been known to produce excess free liquid.¹¹ Gel-type resins can produce problems because their structure generally has a lower degree of cross-linkage and, thus, rigidity. Gel-type resins therefore have a greater tendency than macroporous-type resins to change physical size after cementation because of interaction with ions in the media.¹² Change in physical size can damage the structural integrity of the waste form. To obtain the most extreme evaluation of the formulations, the surrogate resins were chosen to be a gel-type cation-exchange and a gel-type anion-exchange resin. These resin types were also chosen because of their prevalence in the RFETS resin inventory to be stabilized. Dowex 50w-x8 (H⁺ form) was selected as the cation-exchange resin, and Dowex 11 (nitrate form) was selected as the anion-exchange resin.

WASTE FORM PERFORMANCE CRITERIA

The performance criteria were designed to produce a waste form able to address (1) the Waste Acceptance Criteria for the Waste Isolation Pilot Plant (WIPP-WAC), (2) the Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) regulations defining hazardous waste, (3) throughput requirements, and (4) equipment compatibility. The performance criteria are listed below:

1) No free liquid at 24 hours after cementation

The requirement for a dry-surface waste form was necessary to meet WIPP-WAC restriction on free liquid.¹³ The 24-hour time limit was chosen as a reasonable time frame to ensure satisfactory process throughput.

2) Compressive strength of ≥ 500 psi at 28 days after cementation

A minimum compressive strength was not needed to meet any WIPP or EPA requirement but as a way to ensure that the physical stability of the waste form would be durable enough to resist breakdown to a particulate size prohibited by the WIPP-WAC.* The minimum compressive strength of 500 psi for this study was adopted from the National Regulatory Commission's use of this standard for low-level cemented waste as the best indicator of general physical stability.¹⁴ The compressive strength of both the nonactinide and the actinide waste forms was determined in accordance with the American Society for Testing and Materials (ASTM) method for compressive-strength determination.¹⁵

3) No significant decrease in compressive strength over a 28-day period

Previous cementation work by Veazey identified an expansive phenomenon that allowed satisfactory early strength development but caused complete structural failure after a few weeks.¹⁶ The concern in the RFETS project was that this phenomenon could potentially result in cement forms that were still above the minimum compressive-strength requirement at 28 days but would experience expansion failure at a later time. In previous work, this phenomenon was detected at the 14- or 28-day strength determinations by a significant decrease (>50%) in strength from the previous strength value. This method of detection was adopted for this project.

4) Adequate mixability to ensure homogeneity

It is important to attain a homogeneous mixture of the cement powder, liquid, and resin to ensure that the final waste form is consistent with the design formulation. Therefore, the viscosity of the mixture must not be above the maximum viscosity at which the mixing equipment can provide thorough mixing. This failure viscosity was defined as the viscosity at which the paste began to lose its fluidity so that fissures appeared on the surface.

5) Penetration resistance of ≥ 500 psi at 24 hours after cementation

Penetration resistance was determined by the ASTM method for determining the initial set of a cement sample.¹⁷ The ASTM standard for the initial setting of a cement sample is a penetration resistance of 500 psi. Achievement of the initial set within a 24-hour period was chosen as a desirable condition for purposes of throughput efficiency.

6) Pass TCLP for RCRA metals

EPA regulations govern the on-site storage of mixed (radioactive with RCRA-hazardous constituents) waste. Since mixed waste is much more costly to store than nonhazardous

*This work was performed under Revision 4 of the WIPP-WAC. Since this time, Revision 5 of the WIPP-WAC has been issued. Revision 5 does not require the immobilization of particulates, although it does not prohibit their immobilization.

radioactive waste, it is advantageous for a waste form to pass the RCRA leaching standard for nonhazardous waste. This standard is defined by the EPA as passing the Toxicity Characteristic Leaching Procedure (TCLP).¹⁸ Testing was performed at LANL according to the EPA TCLP procedure.

NONACTINIDE EXPERIMENTATION

The nonactinide phase of this project was conducted according to an experimental plan in which the pH and cement/water/resin (C/W/R) wt % ratio were varied among 32 test samples.¹⁹ Each sample was prepared at the pH of either 9 or 12. A solution of approximately 9 molar NaOH was used for all pH adjustments. The specific C/W/R ratios were chosen to be in the vicinity of 60/30/10, a C/W/R ratio found in the literature survey to have experienced no problems.^{11,20} The boundary for the resin content was pre-established at 5 wt % and 15 wt %. The upper limit was chosen to prevent the TRUPACT-II drum wattage limit from being reached with a small number of containers. The work was conducted at full scale in 3-L containers to prevent problems associated with scaling up cementation data.

The expediency for the completion of the project necessitated that some concessions be made in experimental design. The number of resin types used in the development work was kept at the minimum considered adequate to investigate potential negative interactions between resin and cement. However, the two resins were chosen to accentuate these potential interactions as stated above in the section on resin selection. Work was restricted to separate tests on each resin; no blends were tested. In addition, performance evaluations of C/W/R ratios were not necessarily extended to failure. The performance of the nonactinide samples was judged against the performance criteria discussed above. The results of testing are listed in Tables 1, 2, 3, and 4. The results are also presented in tertiary diagrams for each resin in Figures 1 and 2. The assessment relative to each criterion is listed below.

Free Liquid: Failure of the waste form to completely reabsorb all bleed water by 24 hours was seen only in samples containing no resin. This failure occurred in samples prepared at both pH 9 and pH 12 with a C/W/R ratio of 60/40/0, which corresponded to a cement-to-liquid* (C/L) ratio of 1.5 kg/L. The no-resin sample at a C/L ratio of 2.0 (C/W/R ratio = 67/33/0) did not fail this performance standard. The presence of resin in the waste forms appeared to improve performance, as evidenced by waste forms prepared with both resins meeting this standard at C/L ratios of 1.4 and 1.5. These results are shown in Tables 1, 2, and 3. In the tertiary diagrams presented in Figures 1, 2, and 3, the boundary for free liquid is drawn at the C/L ratio of 1.5.

Compressive Strength: The compressive strength was monitored as a function of the C/W/R ratio, C/L ratio, and pH. The mix specifications and compressive-strength results for the 32 runs conducted are summarized in Table 1 for Dowex 50w-x8, Table 2 for Dowex 11, and Table 3 for

*The cement-to-liquid ratio is used in this report to express the relationship between the cement weight in kilograms and total liquid volume in liters. The liquid includes the water and the NaOH solution used for pH adjustment. This ratio is used instead of the dimensionless water-to-cement ratio commonly used in the cement industry in order to remain historically consistent with operations at LANL's Plutonium Facility (TA-55).

Table 1. Dowex 50w-x8 (Cation) Data

Sample	pH	C/W/R Ratio	Miscellaneous Data	Compressive Strength (psi)			C/L Ratio
				7 Days	14 Days	28 Days	
High Resin Samples							
11	9	65/22/13	Mix Limit ^a	4500	4812	6250	3.0
21	12	63/22/15		5100	4850	5550	2.86
8	9	57/29/14	Expansion ^b (S)	2188	2362	2562	2.0
6	9	58/29/13	Expansion (S)	2362	2600	2750	2.0
32	12	55/30/15	TCLP ^c	1688	1550	1875	1.8
19	12	53/32/15		1600	1350	1588	1.7
7	9	52/34/14	Expansion (F/S)	0	0	0	1.5
28A	9	52/34/14	Expansion (F/S)	0	0	0	1.5
28B	9	52/34/14	Expansion (F/S)	0	0	0	1.5
29	8	52/34/14	Expansion (F)	0	0	0	1.5
Low Resin Samples							
24	9	66/24/10		5600	5088	5250	2.8
25	12	66/24/10		5187	5750	5812	2.8
33	12	65/25/10	TCLP	4200	5012	5100	2.6
13	9	64/27/9		4438	4850	4025	2.4
9	9	59/31/10		2725	3062	3600	1.9
12	9	54/36/10	Expansion (S)	1437	1725	1550	1.5
20	12	53/37/10	Expansion (S)	1625	1375	1425	1.4

^aMix Limit: failed mixability criterion. ^bExpansion Failure, S = slow expansion, F = fast expansion; expansion failure also fails compressive-strength standard. ^cTCLP analysis run on these samples. These samples were not observed for expansion.

samples without resin. The C/W/R ratios were grouped in the tables into high (13 wt % to 15 wt %) and low (9 wt % to 10 wt %) resin-content categories. Compressive strength was shown to be increased by a higher C/L ratio and a lower resin content. Samples prepared at the same C/W/R ratio but different pHs did not display any consistent differences in compressive strength. No consistent difference in compressive strength was seen in samples prepared with different resins at similar C/W/R ratios except for a compressive-strength difference due to an expansion phenomenon in some Dowex 50w-x8 samples.

The Dowex 50w-x8 waste forms were found to be susceptible to an expansion phenomenon that allowed initial strength development but later caused complete strength failure of the 2-inch cube used for compressive-strength determinations. The failure was caused by the formation of closely spaced cracks that resulted in an expansion of up to 1/2 inch across each cube side. The cube became extremely fragile and easily crumbled into 1/16- to 1/8-inch fragments. This effect was observed 3 to 5 days after mixing and is specified in this report as fast expansion. This expansion phenomenon was seen on a delayed time frame and to a lesser degree in several 3-liter-container samples. This type of expansion was exhibited by varying degrees of bulging on the side and

bottom of the containers without appreciable degradation of structural integrity of the waste form. This delayed effect was evident only after the 28-day testing period was over and is specified in this report as slow expansion. Since no evidence of decline in compressive strength was seen in these samples during the 28-day period following cementation, the samples technically did not fail the performance standard addressing compressive-strength decline. Both the resin content and the C/L ratio were found to influence whether the sample would fast- or slow-expand or expand at all. In the samples with a resin content of 13 wt % to 15 wt %, fast expansion was observed in samples in the lowest C/L-ratio category of 1.5. On the other hand, slow expansion was observed in samples with a C/L ratio up to 2.0. In the 9 wt % to 10 wt % resin-content range, only slow expansion was seen, and it was seen only in samples with a C/L ratio of ≤ 1.5 .

Table 2. Dowex 11 (Anion) Data

Sample	pH	C/W/R Ratio	Misc. Data	Compressive Strength (psi)			C/L Ratio
				7 Days	14 Days	28 Days	
High Resin Samples							
10	9	62/24/14		3838	4575	4125	2.6
3	9	57/29/14		2200	2350	3200	2.0
5	9	58/29/13		2125	2125	1800	2.0
26	9	58/29/13		1550	1950	2350	2.0
30	12	55/30/15	TCLP [†]	1700	1938	2015	1.8
4	9	53/33/14		1350	1562	1862	1.6
27	9	52/34/14		925	1262	1325	1.5
Low Resin Samples							
31	12	65/25/10	TCLP	4062	4300	3825	2.6
16	9	63/27/10		3912	3937	5250	2.3
15	9	58/32/10		1975	2425	3500	1.8
17	9	53/37/10		1362	1500	1675	1.4
18	9	53/37/10		1300	1438	1625	1.4

[†]TCLP analysis run on these samples. These samples were not observed for expansion.

Table 3. No-Resin Sample Data

Sample	pH	C/W/R Ratio	Misc. Data	Compressive Strength (psi)			C/L Ratio
				7 Days	14 Days	28 Days	
14	9	67/33/0		4062	5075	5125	2.0
22	12	60/40/0	Liquid ⁺⁺	3087	3300	4312	1.5
23	9	60/40/0	Liquid	3612	3375	3950	1.5

⁺⁺Liquid: fails free-liquid criterion.

Mixability: In the high resin-content category, the Dowex 50w-x8 sample prepared at a 3.0 C/L ratio produced a viscosity that failed the mixability standard. The sample prepared at a C/L ratio of 2.86 encountered mixing difficulties, but was considered acceptable. In the low resin-content category, the viscosity of the Dowex 50w-x8 sample prepared at the highest C/L ratio of 2.80 was considerably less than the mixability limit. This viscosity being significantly lower than that of the high resin-content sample at the 2.86 C/L ratio indicates that the presence of resin does affect mixability. The Dowex 11 waste forms were not prepared to reach the mixability limit. In the tertiary diagrams presented in Figures 1 and 2, the failure boundary for mixability is drawn at the C/L ratio of 3.0.

Penetration Resistance: All samples passed the performance standard of achievement of ≥ 500 psi penetration resistance within 24 hours after cementation.

Tertiary Diagrams for Nonactinide Experimental Results: The tertiary diagrams in Figure 1 and Figure 2 show the C/W/R formulations tested with Dowex 50w-x8 and Dowex 11 resins, respectively. The solidly shaded regions define where all performance specifications combined for a successful matrix. The boundaries of this region in both figures include the 5 wt % and 15 wt % resin-content boundaries, the mixability limit established with Dowex 50w-x8 samples, and the free-liquid boundary originating from the lowest C/L ratio that met the free-liquid standard in samples not containing resin. The Dowex 50w-x8 tertiary diagram contains additional boundaries imposed by fast and slow expansion. The area in Figure 1 between the upper and lower expansion limits contains C/W/R formulations considered susceptible to slow expansion. The slow-expansion points technically are not failures because their structural problems occurred after 28 days. However, they are reported as failures to indicate their risk for eventual structural degradation such as that described above in the "Compressive Strength" section. The area below the lower expansion limit contains C/W/R formulations considered susceptible to fast expansion.

Based on the nonactinide results shown in the above tertiary diagrams, an optimum C/W/R ratio of 65/25/10 was chosen for both resins for further consideration in the actinide tests. This choice was dictated by the performance of the more restrictive Dowex 50w-x8 waste forms because the specific resin being cemented at RFETS will be unknown in most cases. The 65/25/10 ratio was selected because a formulation was desired that would maintain a significant distance from the failure boundaries of free liquid and compressive strength (expansion). This selection could also be described as a formulation with the highest C/L ratio without risking mixing problems. The resin content was chosen to be 10 wt % because of the much better resistance to the expansion phenomenon compared to the 15 wt % waste forms.

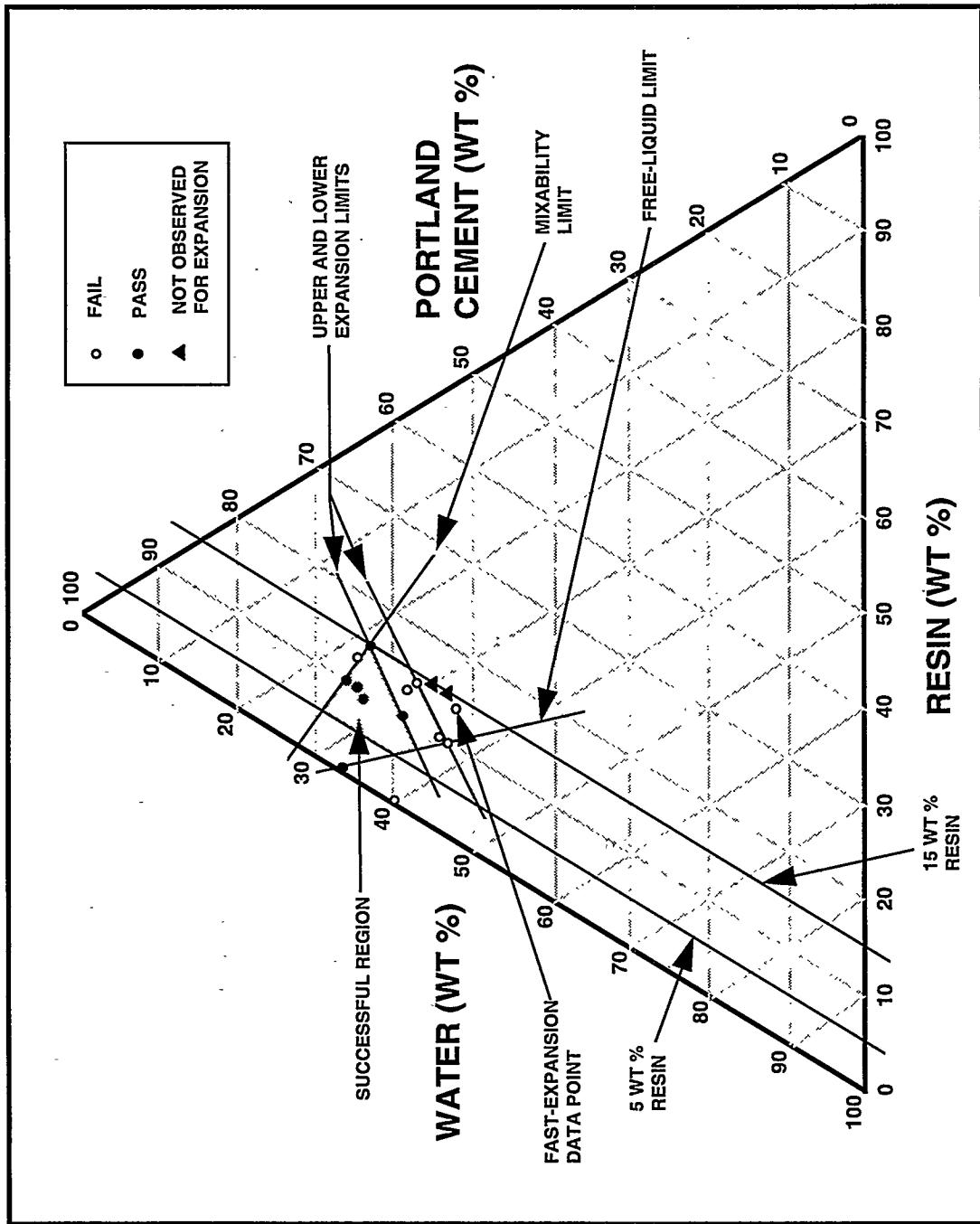


Fig. 1. Tertiary diagram of compositional ranges for Dowex 50w-x8 waste forms.

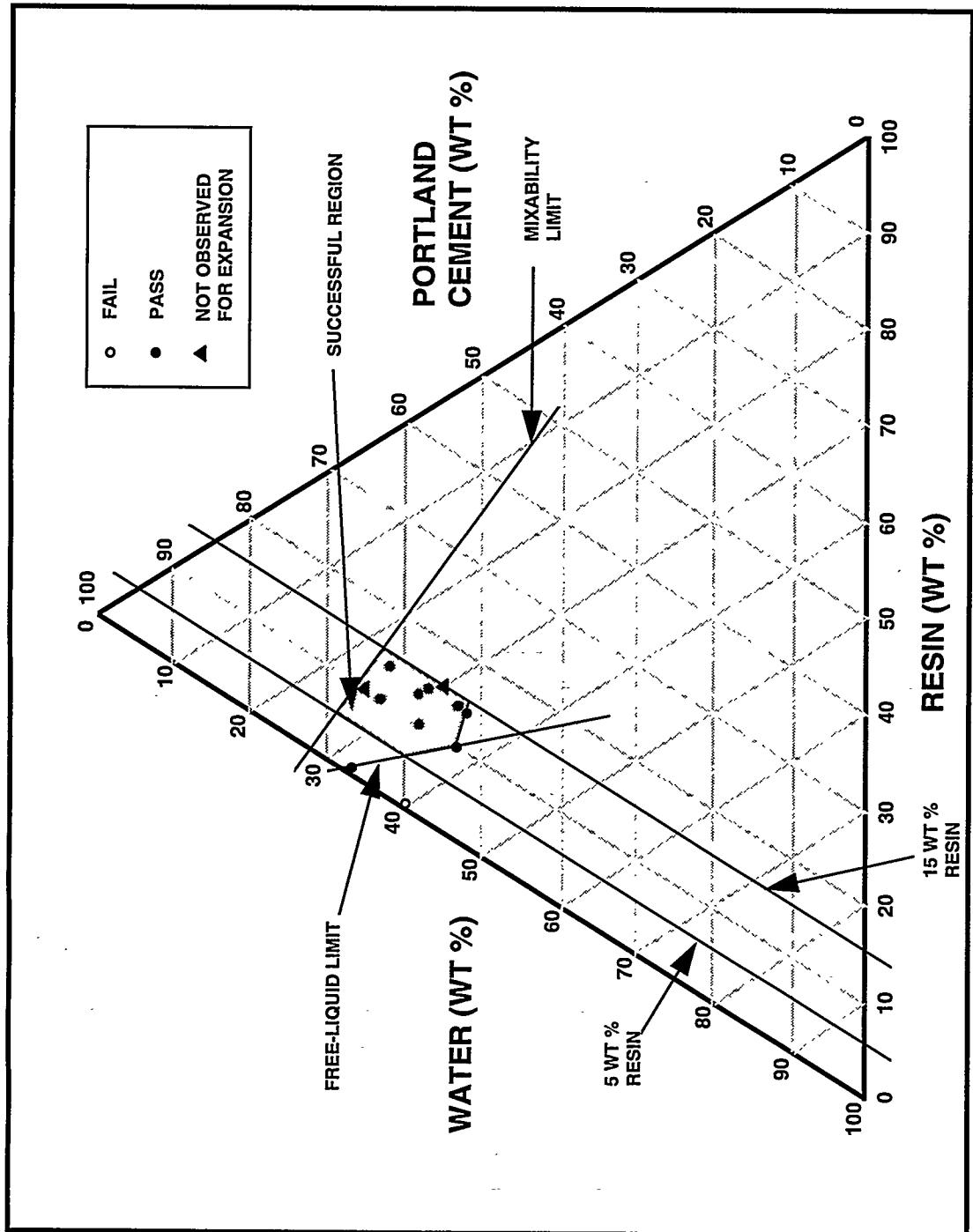


Fig. 2. Tertiary diagram of compositional ranges for Dowex 11 waste forms.

TCLP for RCRA Metals: The resins to be cemented were contacted with a solution containing RCRA metals at concentrations in excess of those reported to be in the RFETS feed stream.²¹ The resins were not rinsed before cementation (contrary to resins at RFETS) to accentuate the rigorousness of this evaluation. Two samples were prepared for each resin. These samples were considered to represent an optimum case (C/W/R ratio = 65/25/10) and a formulation with a significantly lower cement and higher resin content (C/W/R ratio = 55/30/15). All samples were prepared with resin slurries (resin + water) at pH 12. Both formulations easily passed TCLP standards for all metals, as shown in Table 4.

The relative performance is best shown in Table 4 by the leach resistance values. The leach resistance value indicates the ability of the cement to retain RCRA metals and can be defined as the percentage of the initial metal concentration that remains in the waste form after the TCLP. The leach resistance results show that almost no chromium, nickel, or lead was leached from the tested samples. Larger percentages of barium were leached, but the concentration was well below the RCRA limit of 100 ppm.

Table 4. TCLP Results

Sample #	Initial Conc. ^a (ppm)	TCLP Conc. ^b (ppm)	Leach Resistance ^c (%)
Chromium			
30	45	0.012	99.5
31	48	0.015	99.4
32	93	0.018	99.6
33	100	0.014	99.7
Lead			
30	79	<0.03	>99.2
31	67	<0.03	>99.2
32	170	<0.03	>99.6
33	150	<0.03	>99.6
Nickel			
30	75	0.01	99.7
31	65	<0.01	>99.7
32	240	<0.01	>99.9
33	230	<0.01	>99.9
Barium			
30	170	3.6	57.7
31	200	2.0	80.0
32	210	2.5	76.2
33	240	2.5	79.2

^aConcentration before TCLP relative to volume of waste form. ^bConcentration of TCLP extractant.

^cLeach Resistance (%) = $\frac{\text{Initial conc.} - (\text{TCLP conc.} \times 20)}{\text{Initial conc.}} \times 100$

ACTINIDE-BASED (HOT) EXPERIMENTATION

The hot experiments were conducted according to an experimental plan²² that was designed to confirm only specific portions of the nonactinide experiments. Primarily, the hot experiments were intended to determine if the optimum nonactinide formulation of 65/25/10 ratio was valid with actinide-containing resins. Accordingly, fewer formulations were tested, but more replicate testing was performed. The actinide samples were prepared at pH 9 and 10.5. A maximum of pH 10.5 was chosen to reduce the amount of NaOH needed. Lastly, samples in the high resin-content category were included for testing the upper boundaries of the resin content. No TCLP testing was conducted in the actinide testing because of the excellent performance of the nonactinide samples.

The nonactinide resins were converted to the actinide form by nitrating the Dowex 11 resin, then loading, eluting, and washing both resins. All hot cemented samples were prepared in full-scale, 3-L containers, and tests were conducted separately on each resin. Eight samples were run with Dowex 50w-x8. Only 5 samples were run with Dowex 11 resin since no problems were observed with this resin in the nonactinide testing. The performance of the 13 hot samples was judged against the same performance criteria used for the assessment of the nonactinide samples. The discussion on each criterion is found below.

Free Liquid: No free liquid was observed in any sample. No free liquid was expected since the C/L ratios of all hot samples were higher than the 1.5 ratio found to be the threshold for free-liquid generation in the nonactinide samples.

Compressive Strength: Table 5 (Dowex 50w-x8) and Table 6 (Dowex 11) summarize the formulation specifications and the compressive-strength data for the 13 samples. No expansion failure either in the 28-day cubes or in the 3-L can samples was observed. No expansion failure was expected because all hot samples had C/L ratios (2.1–2.6) higher than those that failed in the nonactinide samples (≤ 2.0). No consistent difference was observed between the compressive-strength developments of the pH 9 and 10.5 samples.

Mixability: The same C/W/R formulations were more viscous in the hot experiments than in the nonactinide experiments. The formulations that failed the mixability standard as hot samples showed acceptable mixability as nonactinide samples.* In the 10 wt % resin formulations of both resins, the 2.6 C/L ratio of the 65/25/10 formulation exceeded the mixability limit. The C/L ratio had to be reduced to 2.3 (C/W/R = 63/27/10) before efficient mixing was achieved. In the high resin-content Dowex 50w-x8 samples, the C/L ratio of 2.2 exceeded the mixability limit and had to be reduced to 2.1 to achieve adequate mixing. The Dowex 11 samples prepared at a 2.2 C/L ratio also exceeded the mixability limit. The reason for this lower limit in the hot samples is unknown.

*Although these samples exceeded the recommended maximum viscosity, their viscosity was low enough to permit preparation of samples from which all performance data could be collected.

Table 5. Hot Dowex 50w-x8 (Cation) Data

Sample	pH	C/W/R Ratio	Misc. Data	Compressive Strength (psi)			C/L Ratio
				7 Days	14 Days	28 Days	
High Resin Samples							
6	10.5	59/26/15	Mix Limit ⁺	2500	2825	3325	2.3
5	10.5	60/27/13	Mix Limit	2425	2925	3125	2.2
7	9	59/28/13		2500	2475	2825	2.1
8	9	59/28/13		2800	3200	4000	2.1
Low Resin Samples							
9	10.5	65/25/10	Mix Limit	3550	3625	4550	2.6
10	9	63/27/10		3575	3200	3175	2.3
11	9	63/27/10		3625	4050	4750	2.3
12	10.5	63/27/10		2975	3225	3475	2.3

⁺Mix Limit: failed mixability criterion.

Table 6. Hot Dowex 11 (Anion) Data

Sample	pH	C/W/R Ratio	Misc. Data	Compressive Strength (psi)			C/L Ratio
				7 Days	14 Days	28 Days	
High Resin Samples							
1A	10.5	60/27/13	Mix Limit ⁺	2450	3975	3325	2.2
2	10.5	60/27/13	Mix Limit	2800	1925	2250	2.2
3	9	60/27/13	Mix Limit	2250	1950	1975	2.2
4	9	60/27/13	Mix Limit	2300	3700	2525	2.2
Low Resin Samples							
1	9	65/25/10	Mix Limit	—	4250	2850	2.6

⁺Mix Limit: failed mixability criterion.

FINAL CONCLUSIONS/RECOMMENDATIONS

The above work has identified ranges for the C/W/R ratio and the pH of the pre cemented, resin-slurry that produced a cemented waste form meeting the performance standards identified in this report. The compositional ranges for the C/W/R ratios are found in the tertiary diagram presented in Figure 3. Other than the self-imposed limits for resin content of 5 wt % and 15 wt %, the boundaries of the tertiary diagram were defined by limitations in the areas of free-liquid presence, mixability, and compressive-strength development (expansion failure). The expansion, cold-mixability, and free-liquid failure boundaries in Figure 3 are taken from the nonactinide experiments presented in Figure 1. For Figure 3 the upper expansion limit from Figure 1 was

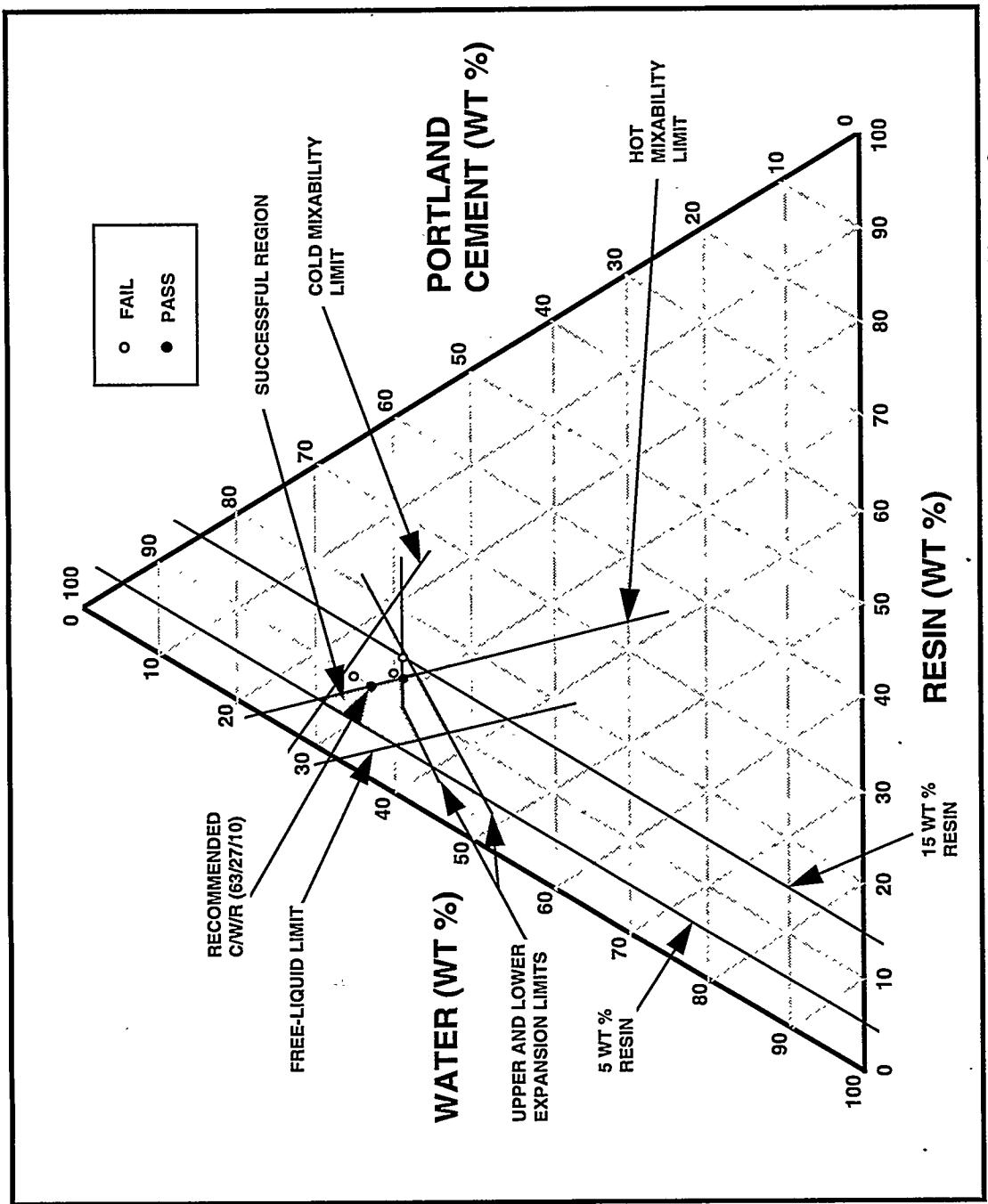


Fig. 3. Tertiary diagram of compositional ranges for hot Dowex 50w-x8 and Dowex 11 waste forms.

modified to include the successful data point of 59/28/13. No failures were encountered in the areas of penetration resistance or TCLP performance.

This tertiary diagram was constructed to address the most restrictive condition found, i.e., Dowex 50w-x8, and can therefore be used for all resins. Although acceptable waste forms can be produced within the indicated C/W/R ratio range, it is recommended that the operating conditions for the RFETS resins be targeted for a specific C/W/R ratio of 63/27/10.* This C/W/R formulation was chosen to be as close as possible to the mixability limit and as far as possible from the regions of free-liquid and expansion failure.[†] All pHs evaluated in this project (9, 10.5, and 12) successfully passed all performance standards. However, keeping the pH of the pre cemented resin slurry closer to the lower end of this range will reduce the addition of NaOH solution.

Expansion failure in Figure 3 was drawn using both fast- and slow-expansion data. Fast expansion constituted a failure to meet both the compressive-strength standards for ≥ 500 psi at 28 days and for no significant decline in compressive strength over the 28-day period. On the other hand, slow expansion did not fail either 28-day compressive-strength standard. However, slow expansion was considered undesirable because of problems that it could produce in container deformation and TCLP performance after the 28-day period. The area in Figure 1 between the upper and lower expansion limits contains C/W/R formulations considered susceptible to slow expansion. The area below the lower expansion limit contains C/W/R formulations considered susceptible to fast expansion. The experimenter may wish to restrict formulations to those above the upper expansion limit.[‡]

The flow diagram illustrating the implementation of the above recommendations at RFETS is found in Figure 4. A suggested procedure for this implementation is included in this report as Appendix B. During the course of this work, several observations were made and insights obtained that may be helpful for RFETS implementation of this procedure. These and other suggestions are contained in Appendix C. Appendix D contains a discussion of the statistical uncertainty in the above work and in the future implementation of this procedure. Denitration of the resin was initially considered necessary to stabilize the ignitability potential of the resins. This treatment was later abandoned as being unnecessary for stabilization. Appendix E describes the rationale and testing behind the decision to remove denitration from the flow diagram.

In summary, the information generated as a result of this project can be applied to other ion-exchange resin stabilization scenarios in the Department of Energy complex. However, as a result of the restrictions imposed by the project scope and schedule, additional investigations should be considered when this project's results are applied to other scenarios. Examples of

*Because of the more restrictive mixability limit found in the actinide experiments, the 65/25/10 ratio recommended in the nonactinide section was revised to 63/27/10.

[†]There is little danger in crowding the mixability limit because excessive viscosity is immediately observable and is rectified by dilution with water. Deliberately operating near the other regions of failure is much more risky because the occurrence of these other failures is delayed and incorrigible.

[‡]Because Revision 5 of the WIPP-WAC no longer contains a restriction on particulates, this project's compressive-strength standards are no longer needed to prevent particulate formation. Nevertheless, the decision was made to retain the compressive-strength standards for their benefit in preventing expansion of the waste form and container.

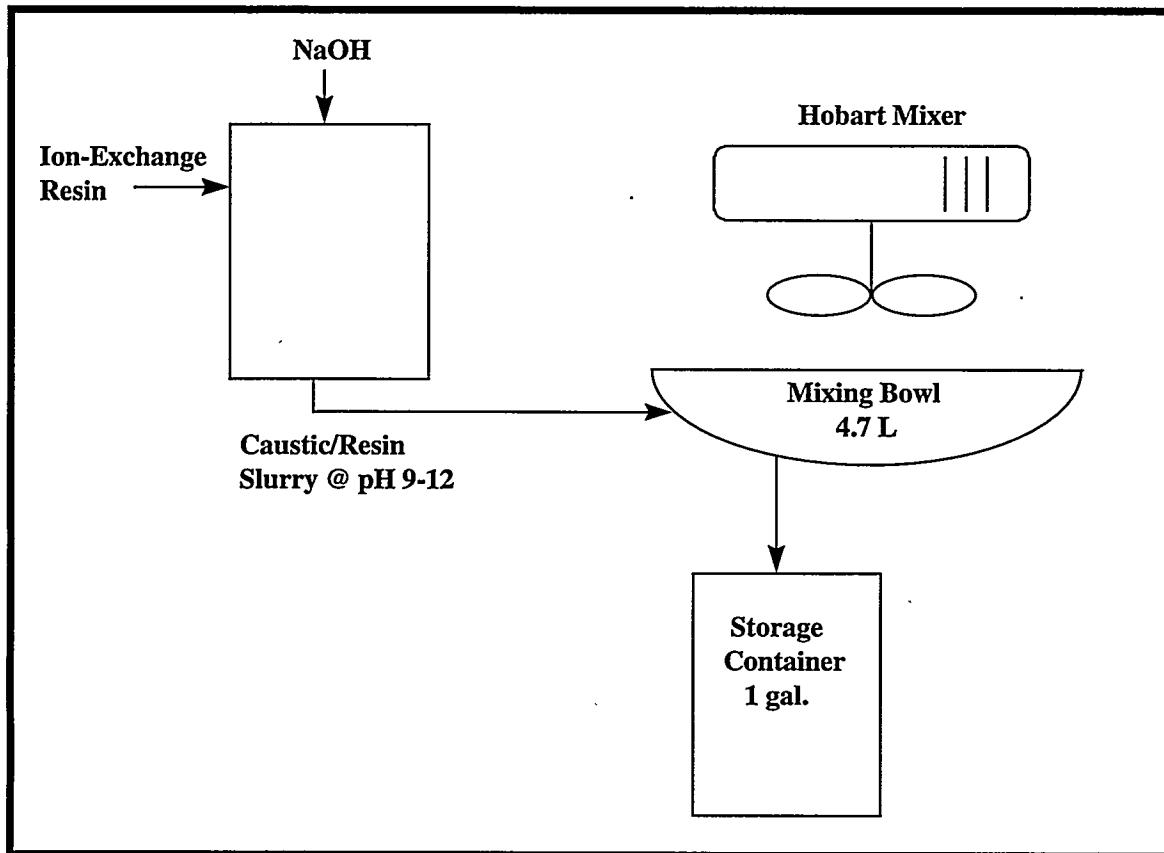


Fig. 4. Final ion-exchange resin cementation.

further work to augment the work presented in this report are to establish more fully the failure boundaries and evaluate potential stabilization problems when cementing mixtures of cation- and anion-exchange resins, as well as macroporous- and gel-type ion-exchange resins.

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APPENDIX A

Equipment for Sample Preparation and Data Acquisition

The equipment was assembled to match the equipment to be used at Rocky Flats Environmental Technology Site for the implementation of the recommendations in this report. Mixing was done using a Hobart mixer (model N50ASTM) with a whip agitator and a 4.7-liter mixing bowl. The compressive strength of all waste forms was determined using a model C, 12-ton hydraulic press from the Carver Laboratory Press Company. The compressive-strength data were taken on 2-inch cubes cast in Humboldt H-2810 cube molds. Penetration resistance was determined using a Humboldt model H-3143 hydraulic penetrometer for the nonactinide samples and a hand-held, spring-loaded penetrometer for the actinide samples.

APPENDIX B

Recommended Procedure for RFETS Resins

The following is the procedure used by NMT-2 in the Plutonium Facility (TA-55) at Los Alamos National Laboratory (LANL) to conduct this project's experiments. This procedure may be used as a foundation for the cementation of the actual resin at Rocky Flats Environmental Technology Site (RFETS).

1. Manually stir the resin inside its storage container to obtain homogeneity.
2. The density of the damp resin is needed to calculate the weight of the damp resin that is required to achieve the desired dry resin weight. Determine the density of the damp resin by doing the following:
 - a. Tare a 25 to 50 mL graduated cylinder on the balance.
 - b. Push the open end of the graduated cylinder into the resin.
 - c. Withdraw the cylinder, and then repeat step (b) if necessary to collect sufficient resin to reach the upper third of the cylinder volume scale.
 - d. Wipe all resin from the outside of the cylinder.
 - e. Tap the cylinder to move the resin to the bottom of the cylinder and remove the air pockets.
 - f. Record the volume of the resin in the cylinder.
 - g. Weigh the resin and cylinder to obtain the weight of the resin.
 - h. Divide the weight by the volume to obtain the damp resin density.

Data Required: Resin weight, resin volume, damp resin density.

3. Calculate the damp resin weight needed to obtain the desired dry resin weight by using the equations found in the "Optimum Formulation and Equations" section of this procedure.
4. Weigh the required amount of damp resin in an appropriately sized beaker and transfer the resin into a Hobart mixing bowl. Use a plastic kitchen-type spatula to clean out the resin from the beaker.
5. Calculate the amount of water in the damp resin using the equation in the "Optimum Formulation and Equations" section. Obtain the total amount of liquid (water + NaOH solution) required to match the optimum formulation, and subtract from this volume the water volume contained in the damp resin in order to obtain the remaining liquid to be added.

Data Required: Total liquid volume, water content of damp resin, and net liquid to be added to resin.

6. Add a volume of water approximately 60 to 80% of the total required liquid volume to the Hobart bowl with the resin. Use an appropriately sized graduated cylinder (approximately 2 L) for the volume measurement.

Note: The percentage of the total amount of liquid to be added in this step depends on whether cationic or anionic resin is being treated. Cationic resin will require much more caustic for pH adjustment, and therefore the percentage of the total added here should be much less in order not to exceed the total after pH adjustment.

7. Calibrate the pH electrode using buffers at pH 4 and 10.
8. Measure the initial pH of the resin slurry. Add NaOH solution to the resin slurry, and adjust the pH to within the target pH range. The pH electrode can be used to stir the resin slurry during the pH adjustment. If the pH is overshot, use dilute (0.35 M) nitric acid to readjust the pH to within the proper pH range. Add the nitric acid using a dropper.
9. Compare the volume of liquid now in the slurry (liquid in damp resin + water added + NaOH solution + HNO₃) with the total required. Add water or remove liquid to bring the total volume up to 100% of that listed in the “Optimum Formulation and Equations” section.
10. If water addition was required, readjust the pH if necessary. Use a dropper for reagent addition. Remove excess volume after pH adjustment if necessary.

Data Required: NaOH volume, HNO₃ volume, initial pH, final pH, additional volume added or removed to reach final volume.

11. Weigh the amount of cement powder called for in the “Optimum Formulation and Equations” section. Add all of the cement powder to the mixing bowl. Using the plastic spatula, hand-mix the cement with the liquid for 30 seconds to wet the cement. Record the time when the cement contacted the liquid.

Note: During the mixing that follows, observe the mixing in the bowl. To pass the mixability performance standard, the paste must not be too thick for the mixer to be able to blend the ingredients into homogeneity. If the mixture is too thick, terminate the test, and perform it again with a thinner mixture, or use the flat-beater agitator to increase agitation.

Data Required: time of cement/liquid contact (required for compressive-strength determinations).

12. Place the mixing bowl into mixer, install the agitator, and raise and lock the bowl into the mixing position.
13. Start mixing at rpm setting 1 (slowest) and mix for 30 seconds.

14. Stop mixing, lower the bowl, and scrap any paste from the sides of the bowl using the plastic spatula. Try to restrict the time the mixer is off to no more than 30 seconds.
15. Raise the bowl and restart mixing at rpm setting 2 for 1 minute.

Data Required: Mixability observations.

16. Stop the mixing, remove the bowl from the mixer, and pour the paste into the 3-L disposal can. Use the plastic spatula to remove all of the paste.

Note: If the compressive-strength testing is to be done to check performance against that of the hot samples prepared at LANL, samples will have to be prepared at this point. See ASTM C109/C 109M-95 for the method for determining the compressive strength of hydraulic cement mortars.¹⁵

17. Let the paste harden overnight.
18. Inspect the cement form the next day for free liquid and adequate penetration resistance. If the cement is satisfactory, place the lid on the can of cemented material, and prepare for its placement in the final overpack container.

Data Required: Pass or fail status for free liquid and penetration resistance.

Optimum Formulation and Equations for Procedure

Target C/W/R Ratio

C/W/R Ratio ^a	Cement Powder (g)	Water ^b (mL)	Dry Resin (g)
63/27/10	4725	2025	750

^aCement/water/resin wt % ratio. ^bAll liquids were assigned a density of 1 g/cm³ and measured out by volume instead of weight. All total water volumes include NaOH solution.

Dry density of Dowex 11: 0.701 g/cm³

Dry density of Dowex 50w-x8: 0.743 g/cm³

The equation for the determination of the damp resin weight needed to obtain desired dry resin weight is as follows:

$$\text{Damp resin weight needed} = \frac{\text{desired dry weight} \times \text{damp density}}{\text{dry density}}$$

The equation for the volume of water in the damp resin is as follows:

$$\text{Water volume in resin} = \frac{\text{damp density} - \text{dry density}}{\text{damp density}} \times \text{damp resin weight}$$

Equipment and Reagents for Procedure

Equipment:

1. pH meter and electrode
2. 3-L tin plated steel cans, 6-5/8" high x 6-1/2" in diameter, w/ lids (LANL stock LG-6466)
3. Hobart mixer with whip agitator (model N50ASTM)
4. 4.7-L Hobart mixing bowl
5. 25–50 mL graduated cylinder
6. Weighing scale
7. Beaker for weighing resin
8. Large (~2 L) graduated cylinder
9. Dropper for reagent addition
10. Container for weighing cement powder
11. Penetrometer
12. Plastic kitchen-type spatula

Reagents:

1. pH 4 and 10 buffers
2. Dilute (0.35 M) HNO₃
3. Industrial water
4. ~9 M NaOH solution
5. Portland cement (Type I/II)
6. Ion-exchange resin

APPENDIX C

Observations and Suggestions for Implementation

During this work, several points became evident that would be helpful in the implementation of this technology at Rocky Flats Environmental Technology Site (RFETS).

- The mixing was done with the whip agitator on the Hobart mixer. A higher cement content can be achieved by using the flat-beater agitator. However, using this agitator will reduce the amount of paste that can be mixed in the Hobart mixing bowl because the greater surface area of the flat-beater agitator causes significantly greater splashing. The reduction in volume to prevent splashing may result in insufficient product volume to fill the 3-liter container.
- The time it took for the preparation of a 3-L sample was approximately 1.5 hours. This preparation time included approximately 15 minutes for the pouring of the cube molds, which may not be part of the routine procedure at RFETS. This time can be reduced in actual operation by performing on larger batches such steps as the density determination for the damp resin (which took approximately 5 minutes) and the pH adjustment (which took approximately 20 minutes). See the "Recommended Procedure for RFETS Resins" (Appendix B) for a description of these steps as performed in this project.
- A convenient way to determine whether cationic or anionic resin is being encountered is by how much caustic is required for the pH adjustment. For a hot resin batch of approximately 500 grams, the cationic resin required close to 300 mL of 9M NaOH, whereas the anionic resin required less than 50 mL.
- In all experimental work, the liquids were assigned a density of 1 g/cm³. This assignment greatly simplified the operations by allowing the measurement of liquids by volume instead of weight. However, this action would introduce some error into the formulation makeup.
- The mixability limit is specific to the mixer used. If mixing equipment other than the Hobart N50ASTM with whip stirrer is used, the mixability limit will have to be redetermined.
- Before volumes greater than 3 liters are used, these recommendations should be verified with testing at the increased scale. There are several areas in which smaller-scale testing may fail to predict performance on a larger scale. Smaller-scale samples often do not show bleed water when the larger scale would.²³ In addition, larger-scale samples have a higher temperature rise during hydration. A higher temperature generally accelerates curing, but also can be so high that it cracks the monolith, which compromises performance in compressive-strength development and leaching resistance.²³

APPENDIX D

Operational Uncertainty

A procedural step that would introduce uncertainty into attaining the target formulation is the determination of the damp density of the resin. Since the formulations are designed in terms of the weight of the dry resin, the damp density is needed to calculate how much damp resin corresponds to the required amount of dry resin. This task requires determining the damp density by weighing a known amount of damp resin in a 25 to 50 mL graduated cylinder and then entering this damp resin density with the dry bulk density in the following calculation:

$$\text{Damp resin weight needed} = \frac{\text{desired dry weight} \times \text{damp density}}{\text{dry density}}$$

The precision of the weight value used in the damp density calculation was more than adequate with the 4-decimal-place balance used in this work. The precision of the volumes obtained with the graduated cylinder, though, was relatively poor because it was difficult to obtain a level top surface of resin in the cylinder. Furthermore, it was unknown how reproducible the tapping technique to remove air bubbles before the volume reading was. A study was done with nonactinide Dowex 50w-x8 resin to investigate these concerns. The authors' results showed an error of no more than 1 unit in the water/resin part of the cement/water/resin (C/W/R) formulation. For example, for the 63/27/10 ratio, the actual result could be from 63/28/9 to 63/26/11.

Another study was done to see what error would be introduced into the next density determination by the residual resin left in the cylinder after a reasonable attempt was made to remove the resin by shaking the cylinder. The weight of this resin could be tared out, but the volume discrepancy could not. It was determined that the average volume of residual resin was 0.63 mL. When inserted into the calculation, this volume proved to affect the formulation ratio by less than 0.2 units in the water/resin part of the C/W/R formulation. The option of rinsing out the residual resin is also viable, but would entail more work in this step and in recombining the wash solution with the next batch.

APPENDIX E

Denitration Studies

Denitration had originally been included in the scope of the cementation project. However, the need for denitration was questioned because the nonflammable cement matrix should easily stabilize the relatively small amount of nitrated resin contained within it. To confirm this point experimentally, a test was conducted in which a fragment of cemented (nonactinide), nitrated Dowex 11 was subjected to high temperature. The waste form was chosen to have a low C/L ratio and high resin content (nonactinide sample #4) to obtain a worst-case condition.

Anionic-exchange resin had been reported to ignite from approximately 165°C for resin in 7M HNO₃ to 265°C for water-damp resin.²⁴ In this experiment, the temperature was raised slowly to 260°C to cause the ignition of the resin. The waste form was observed at 100°C, 165°C, and 260°C. Between 165°C and 260°C, the resin beads turned black, indicating combustion. Upon examination after cool-down, the cement block was still rigid and could not be broken with firm manual compression. There was no evidence of any reduction in the structural integrity of the cemented waste form, much less of an explosive or burning event. The test thus validated the decision to remove denitration from the stabilization plan.