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PROPERTIES OF RADIOACTIVE WASTES
AND WASTE CONTAINERS

QUARTERLY PROGRESS REPORT

JANUARY - MARCH 1980

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NUCLEAR WASTE MANAGEMENT DIVISION

DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973



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ABSTRACT

Solidification experiments were performed with organic ion-exchange resins using Portland type II cement to investigate waste to binder ratios which result in monolithic waste forms. Test results are provided in tabular form showing formulations which result in considerable swelling, cracking, or splitting of the specimens upon solidification. The range of waste loadings which produce monolithic waste forms are given.

Experiments were conducted to establish appropriate waste/binder ratios within which simulated boric acid reactor waste may be incorporated into portland type III cement, to produce acceptable waste forms. Both pH-adjusted and pH-unadjusted boric acid solutions were used. Sodium hydroxide in solid pellet form was used to adjust the boric acid pH. Data are reported for 3, 6, and 12 weight percent boric acid wastes, with pH-adjusted values of 7, 10, and 12. Range of waste/binder ratios investigated are from 0.32 to 1.5. Results are summarized in the form of ternary compositional phase diagrams depicting envelope boundaries within which formulations exhibit no free standing liquids. The cure time is substantially reduced when NaOH pellets are used, rather than 10 M NaOH solution. This is attributed to the higher solid contents in the waste solution when NaOH in solid form is used.

A "two-part" urea-formaldehyde process was used to solidify four simulated LWR waste streams, viz. ion-exchange bead resins, diatomaceous earth, sodium sulfate, and boric acid wastes. The waste forms were evaluated on the basis of solid monolith, free standing liquid, corrosivity of the free liquids, and specimen shrinkage criteria. The results show that the two-part urea-formaldehyde process (a) is capable of solidifying LWR low-level wastes into solid free standing monoliths, (b) produces free standing water with pH approximately 2, and (c) produces specimen shrinkage of approximately 5 volume percent after four weeks in an enclosed environment.

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PROPERTIES OF RADIOACTIVE WASTES AND WASTE CONTAINERS
QUARTERLY PROGRESS REPORT, JANUARY-MARCH 1980

1. ION EXCHANGE RESINS
(J. W. Adams)

1.1 Solidification Experiments

1.1.1 Introduction

Organic ion exchange resins have been shown to swell when solidified in certain cement matrices, causing expansion and sometimes disintegration of the specimens during the curing process. It has been postulated that such reactions result either from competition for water by the unhydrated cement clinker and the unequilibrated ion exchange resin beads, or from the ion exchange resin beads alone exerting osmotic forces dependent on the ions within and surrounding the individual beads.⁽¹⁻³⁾

To examine the effects of water interaction in this process, samples covering a range of water to cement ratios, and waste (bead resins plus water) to cement ratios were chosen for examination. Water to cement ratios (by weight) were varied from 0.3 to 1.0, while waste to cement ratios ranged from 0.4 to 1.8. The resin beads used for the experiments were in the hydrated form containing 55% water by weight. The resultant matrix of test samples is shown in Table 1.1.

1.1.2 Specimen Preparation

Cation exchange resin beads used were nuclear grade IRN-77 (H^+) Amberlite resins, styrene with 8% divinyl benzene. Resin batches for individual samples were converted to the Na^+ form by washing three times in NaCl solutions, each containing approximately twice the number of Na^+ ions as the resin capacity. The resin beads were then washed in deionized water 7 to 10 times, and the pH adjusted to between 6.5 to 7.5 by dropwise addition of NaOH. The excess liquor was removed and amounts of portland type II cement were added to give a total weight of 220 gram per specimen. All specimens were prepared in 4.6 cm diameter by 9.7 cm high polyethylene vials which were capped after stirring.

1.1.3 Experimental Results and Conclusions

Final sample heights after solidification ranged from 6.4 cm to greater than 9.7 cm for those samples showing considerable swelling and cracking. Sample dimensions and physical appearances of the test specimens after a minimum of 28 days of curing are shown in Table 1.2. From these data, it is evident that expansion of the waste form is minimized by decreasing the water to cement ratio, while maintaining a low waste loading. Table 1.2 shows a line separating the sample formulations with little or no expansion from those that exhibited considerable swelling ("barreling effect"), cracking or splitting. Mechanical

Table 1.1

Formulation of Ion Exchange Resin Test Samples
(all weights given in grams)

Water Cement	Waste Cement								
		0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.3	15.7] ^a	41.2	61.1	77.0	90.0	100.8	110.0	117.9	
	47.1	41.2	36.7	33.0	30.0	27.5	25.4	23.6	
	157.1	137.6	122.2	110.0	100.0	91.7	84.6	78.6	
0.4	0.0	27.5	48.9	66.0	80.0	91.7	101.5	110.0	
	62.8	55.0	48.9	44.0	40.0	36.7	33.9	31.4	
	157.2	137.5	122.2	110.0	100.0	91.7	84.6	78.6	
0.5		13.8	36.7	55.0	70.0	82.5	93.1	102.1	
		68.7	61.1	55.0	50.0	45.8	42.3	39.3	
		137.5	122.2	110.0	100.0	91.7	84.6	78.6	
0.6		0.0	24.4	44.0	60.0	73.3	84.6	94.3	
		82.5	73.3	66.0	60.0	55.0	50.8	47.1	
		137.5	122.2	110.0	100.0	91.7	84.6	78.6	
0.7			12.2	33.0	50.0	64.2	76.2	86.4	
			85.6	77.0	70.0	64.2	59.2	55.0	
			122.2	110.0	100.0	91.7	84.6	78.6	
0.8			0.0	22.0	40.0	55.0	67.7	78.6	
			97.8	88.0	80.0	73.3	67.7	62.8	
			122.2	110.0	100.0	91.7	84.6	78.6	
0.9				110.0	30.0	45.8	59.2	70.7	
				99.0	90.0	82.5	76.2	70.7	
				110.0	100.0	91.7	84.6	78.6	
1.0				0.0	20.0	36.6	50.8	62.8	
				110.0	100.0	91.7	84.6	78.6	
				110.0	100.0	91.7	84.6	78.6	

^aEach entry is composed of three parts, viz., resin (15.7), water (47.1), and cement (157.1).

Table 1.2

Physical Characteristics of the Test Samples After Solidification
 Sample Heights (cms) After 28 Days of Curing Time
 (Diameter of all specimens = 4.5 cm)

Water Cement ↓ Waste Cement →	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.3	6.4	6.9	7.3	7.8	7.9	8.2	8.6	8.8
0.4	6.7	7.3	7.7	7.9	8.2	8.3	8.6	9.0
0.5	NE	7.6	7.9	8.2	8.3	8.7	8.8	8.9
0.6	NE	7.5	7.9	8.1	8.3	8.7	9.1	9.7
0.7	NE	NE	7.8	8.3	8.5	---	9.7	>9.7
0.8	NE	NE	7.8	8.2	8.6	>9.7	9.7	>9.7
0.9	NE	NE	NE	8.0	8.3	9.3	>9.7	>9.7
1.0	NE	NE	NE	6.9	7.6	8.8	9.0	>9.7

☐ = specimens with little or no swelling.

☒ = specimens with considerable swelling, cracking or splitting.

NE = not examined.

testing, as well as immersion testing ("mock leaching") of samples representative of various waste to binder ratios is planned.

1.2 References

1. P. Colombo and R. M. Neilson, Jr., Brookhaven National Laboratory, Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, January-March 1979, BNL-NUREG-51101, NUREG/CR-1126, October 1979.¹
2. M. Bon evie-Svendsen, K. Tailberg, P. Aittola, and H. Tollback, "Studies of the Incorporation of Spent Ion Exchange Resins From Nuclear Power Plants in Bitumen and Cement," in the Proc. of a Symposium on the Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vienna, March 22-26, 1976, IAEA-SM-207/78 (1976).¹
3. R. E. Lerch, Hanford Engineering Development Laboratory, Division of Waste Management, Production and Reprocessing Programs Progress Report, Jan-June 1977, HEDL-TME-77-74, July 1977.¹

¹Available for purchase from the National Technical Information Service, Springfield, VA 22161.

2. SOLIDIFICATION OF BORIC ACID WASTE USING PORTLAND TYPE III CEMENT (P. R. Hayde and H. K. Manaktala)

2.1 Introduction

The purpose of this investigation is to establish appropriate waste/binder ratios within which aqueous boric acid (simulated reactor waste) may be incorporated into the portland type III cement matrix to produce an acceptable waste form.

Portland type III cement was chosen as the matrix material to be evaluated because of its high early strength and rapid curing properties. Simulated waste solutions containing 3, 6, and 12 weight percent boric acid were employed to study the concentration parameter. (Typically, PWR waste contains 12 weight percent boric acid in aqueous solution.) Since it is well known that solidification of cement is inhibited by the inclusion of compounds with low pH value, it was decided to adjust the pH of the waste with sodium hydroxide (NaOH) before incorporating into the cement, in order to accelerate the curing process. Boric acid wastes were solidified in cement matrix without pH adjustment and at pH 7.0, 10.0, and 12.0.

Minimum and maximum waste/binder ratios were determined for each waste concentrate. The minimum waste/binder ratio represents a lower limit below which insufficient workability exists for mixing. Sufficient workability is dependent upon the mixing method employed; for this reason, the measurement is somewhat subjective. A maximum waste/binder weight ratio was also identified for each waste concentrate. This ratio refers to the potential presence of free standing water in a waste form. Any waste/binder ratio which exhibited either drainable liquids or appreciable surface dampness was deemed unacceptable. Waste/binder ratios ranging from 0.32 to 1.5 were examined.

2.2 Specimen Preparation

Waste form specimens were prepared in individual polymethylpentene containers with screw cap closures to prevent evaporative water loss. Formulations were developed for a 250-gram specimen mass, producing cylindrical waste forms 6.0 cm in diameter and 5.0 to 5.5 cm in height. Two specimens were initially prepared for each waste/cement ratio for a given boric acid concentration.

In order to maintain processing conditions most nearly similar to those encountered during commercial waste processing, each waste solution was heated to 170°F (76.7°C) and maintained at that temperature during the pH adjustment and until the waste was blended into the cement matrix. Solid pellets of NaOH¹ containing 98.9% NaOH by weight were used to increase the pH of the waste solution before solidification. The pH of the solutions were measured by both a pH meter and pH indicator solutions. Table 2.1 shows the pH solutions used.

¹Manufactured by Mallinckrodt Inc., Paris, KY 40361.

Table 2.1

Methods Used for Measuring pH of
Boric Acid Waste Before Solidification

pH Indicator	pH Adjusted Boric Acid (Simulated Waste)			
	pH 3 to 4	pH 7.0	pH 10.0	pH 12.0
Electronic pH meter ^a	*	*	*	*
Alizarin ^b		*		*
Alizarin Yellow G, GG ^b				*
Fisher Universal Indicator ^c		*	*	
Phenolphthalein ^c			*	

^aOrion Research (Model 601A/Digital IONALYZER), Cambridge, MA 02139.

^bManufactured by Chemical Service Incorporated, West Chester, PA 19380.

^cManufactured by Fisher Scientific Company, Fairlawn, NJ 07410.

2.3 Experimental Data

Table 2.2 shows the minimum/maximum workability limits for boric acid waste solidified in portland type III cement. Figure 2.1 presents graphically the ratios of sodium hydroxide to boric acid used in formulations which resulted in satisfactory solidification (no free standing water). Figures 2.2 to 2.4 are ternary compositional phase diagrams depicting envelope boundaries within which formulations exhibit no free standing liquid after solidification.

Table 2.2

Minimum/Maximum Workability Limits for
Boric Acid Waste Solidified in Portland Type III Cement
(pH-Adjusted With NaOH)

Boric Acid Waste Conc.	Waste (Boric Acid)/Binder (Cement) Ratio (by Weight)							
	pH 3.0		pH 7.0		pH 10.0		pH 12.0	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
3 wt. %	.32	.70	.32	.70	.34	.80	.34	.80
6 wt. %	.32	.70	.32	.70	.34	.80	.34	.80
12 wt. %	.35	---	.35	.50	.38	.70	.38	.90

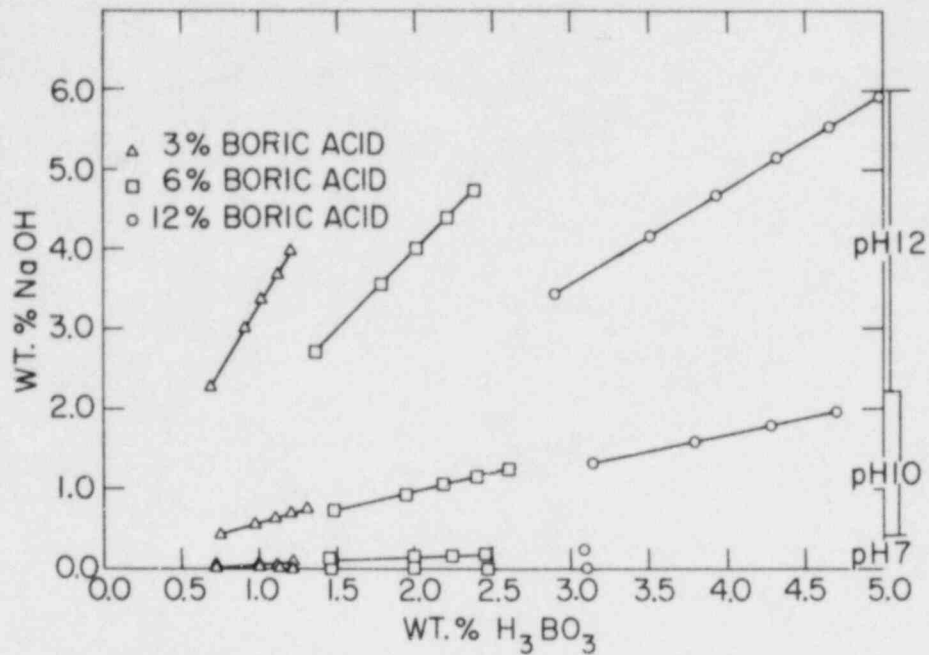


Figure 2.1. Ratio of sodium hydroxide to boric acid waste in successfully solidified formulations (No free standing water).

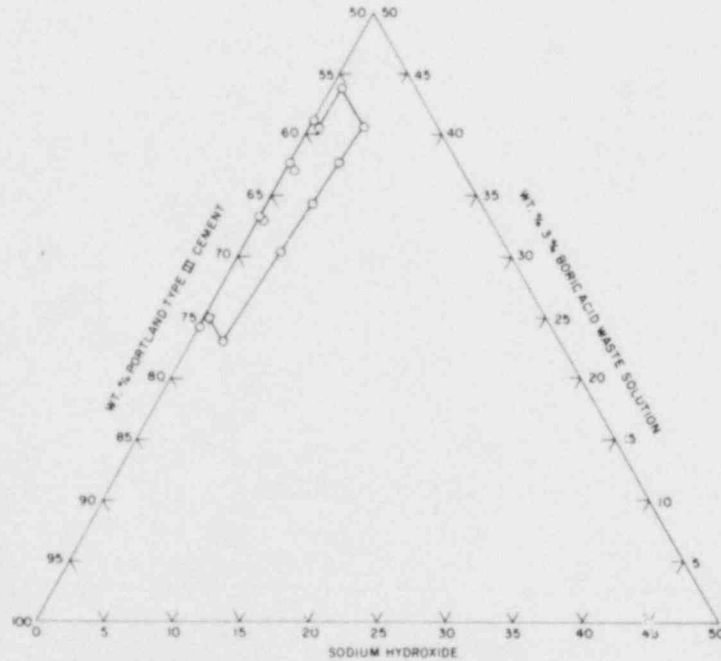


Figure 2.2. Compositional phase diagram for solidification of boric acid waste, after pH-adjustment with NaOH, in portland type III cement (waste conc.: 3 weight percent boric acid).

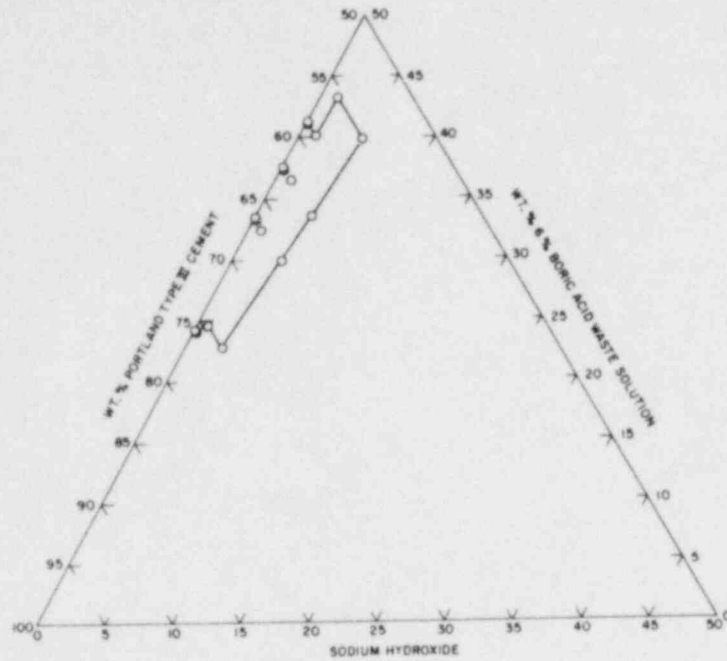


Figure 2.3. Compositional phase diagram for solidification of boric acid waste, after pH-adjustment with NaOH, in portland type III cement (waste conc.: 6 weight percent boric acid).

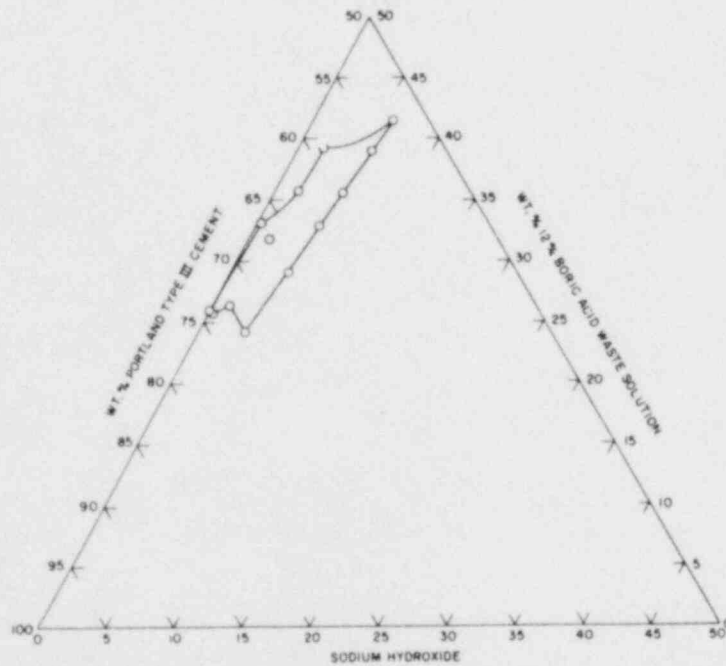


Figure 2.4. Compositional phase diagram for solidification of boric acid waste, after pH-adjustment with NaOH, in portland type III cement (waste conc.: 12 weight percent boric acid).

2.4 Results and Discussion

In comparing the results of the series of experiments described in this report, where NaOH pellets (98.9% NaOH by weight) were used to adjust the pH of boric acid waste prior to solidification, to the results obtained earlier, where 10 M NaOH solution was used instead,⁽¹⁾ we can conclude that:

While the process control boundaries for satisfactory solidification of boric acid waste in portland type III cement were not significantly altered by substituting 10 M NaOH solution with NaOH pellets for adjusting the waste pH, the cure time was substantially reduced. The cure times required to successfully solidify specimens containing no free standing liquid ranged from 2 to 10 days when NaOH pellets were used, whereas cure times ranging from 3 to 140 days were observed when 10 M NaOH solution was used. The reason for this significant reduction in the sample cure time is attributed to the higher concentration of dissolved solids in the waste forms that were pH adjusted with NaOH pellets.

Some difficulty in reproducibly establishing the amounts of NaOH needed for adjusting the pH value of the boric acid waste was experienced. The problem could be related to the fact that, (i) the boric acid has a high dissociation constant and does not react stoichiometrically with a strong base such as sodium hydroxide,⁽²⁾ and (ii) that during the process of pH adjustment, sodium hydroxide reacts with boric acid to form metaborates, tetraborates, and other complex compounds, many of which have buffering properties.⁽³⁾

2.5 Conclusions

- Process control envelopes for satisfactory solidification of boric acid waste in Portland type III cement are not significantly altered by using NaOH in the solid form (pellets) rather than 10 M NaOH solution.
- Cure time for waste form specimens is substantially reduced when NaOH pellets are used. This is attributed to higher solid content in the waste.

2.6 References

1. H. K. Manaktala, P. Colombo, R. M. Neilson, Jr., Brookhaven National Laboratory, Properties of Radioactive Waste and Waste Containers, Quarterly Progress Report, October-December 1979, BNL-NUREG-51148, NUREG/CR-1326, February 1980. Available for purchase from the National Technical Information Service, Springfield, VA 22161.
2. R. C. Weast and M. J. Astle, (eds.), CRC Handbook of Chemistry and Physics, CRC Press, Inc., Boca Raton, FL, 1979.
3. R. M. Adams, Boron, Metallo-Boron Compounds and Boranes, Interscience Publishers, Inc., New York, NY, 1964.

3. TWO-PART UREA-FORMALDEHYDE WASTE FORMS (L. W. Milian and H. K. Manaktala)

3.1 Introduction

New solidification processes and systems which utilize a particular type of matrix, e.g., cement, urea-formaldehyde, vinyl ester-styrene, and bitumen, are continually being developed. One such process, which is a modification of the presently used urea formaldehyde process has been recently developed⁽¹⁾ (called "two-part" urea-formaldehyde process here). The objective of this investigation is to evaluate the effectiveness of "two-part" urea-formaldehyde in incorporating various simulated LWR waste streams, and to characterize the materials condition of the waste forms.

3.2 Standard Urea-Formaldehyde Process Vs Two-Part Urea-Formaldehyde Process

A typical urea-formaldehyde process consists of chemically combining an aqueous emulsion of urea and formaldehyde with water or aqueous radwaste for polymerization. Addition of a weak acid, e.g., phosphoric acid, or an acid salt catalyst, such as a sodium bisulfate solution, is needed to trigger the polymerization reaction. Information on this standard urea-formaldehyde process was published in an earlier BNL report.⁽²⁾

The two part urea-formaldehyde process is different in the sense that it consists of two components, the urea-formaldehyde concentrate (part I) and a compound catalyst solution (part II). The urea-formaldehyde component consists of 100 parts by weight of commercially available urea-formaldehyde concentrate to which is added 4 parts of proprietary additive in powder form.⁽¹⁾ This additive has the dual function of aiding in specimen gelation and in reducing the water permeability of the polymerized radwaste product. The second component is a solution consisting of 50 parts tap water by weight, 50 parts technical grade prilled urea, 15 parts standard grade granular ammonium sulfate, and 1 part proprietary water soluble powder additive.⁽¹⁾ This compound additive acts as a polymer modifier, has the ability to be reactive with certain metal ions, and aids in the retention of radionuclides within the polymerized waste form. It, also, increases the capacity of the waste form to reabsorb the "weep" water that might appear in the form of moisture on the monolith soon after solidification.

3.3 Specimen Preparation

The specimen preparation process, including recommended waste loadings, was supplied by the vendor.⁽¹⁾ The key parameters that require proper monitoring and control include the mixing sequence, agitation mode, pH control of the aqueous waste prior to solidification, and the blending temperature. Four LWR simulated waste streams were used for this investigation. The chemical composition of these wastes is given in Table 3.1.⁽²⁾ The BWR precoat filter cake with diatomaceous earth (slurry) formulation used for specimen preparation represents wastes that are pumpable for short distances. At least five 350-gram specimens were prepared for each simulated waste stream. The average dimensions of the specimens were 6.2 cm in diameter and 9.5 cm in height. All specimens

Table 3.1
Waste Formulations

Bead Resin Waste (Dewatered)

Water	35.0 wt. %
Bead Resin (IRN-150) ^a	65.0 wt. %
Processing Temperature	70°F
pH	7

BWR Precoat Filter Cake With Diatomaceous Earth (Slurry)

Water	75.0 wt. %
Diatomaceous Earth	20.0 wt. %
Crud ^b	5.0 wt. %
Processing Temperature	70°F
pH	7

BWR Chemical Regenerative Waste of a Forced Recirculation Evaporator

Water	75.0 wt. %
Sodium Sulfate	22.9 wt. %
Sodium Chloride	2.0 wt. %
Crud ^c	0.1
Processing Temperature	170°F
pH	6

Boric Acid Waste of a Forced Recirculation Evaporator

Water	87.9 wt. %
Boric Acid	12.0 wt. %
Crud ^b	0.1 wt. %
Processing Temperature	170°F
pH	3.5

^aRohm and Haas Company, Philadelphia, PA 19105.

^bFine air cleaner test dust no. 1543094, AC Spark Plug Division, General Motors Corporation, Flint, MI 48556.

were prepared individually in polymethylpentene containers and were capped only after the exothermic reaction was completed. Table 3.2 lists the chemical formulation of the test specimens.

The temperature and pH value listed in Table 3.1 are typical values prior to solidification at reactor sites.⁽²⁾ Since two-part urea-formaldehyde process requires that all wastes be adjusted to an approximate pH of 6.0, and the temperature be kept below 49°C (120°F), the temperatures and pH values shown in Table 3.1 were modified for fabricating specimens for this investigation. A possible processing problem could arise in the case of the two higher temperature (77°C, 170°F) waste streams, viz. BWR Chemical Regenerative Waste and Boric Acid Waste (Table 3.1), if the waste solutions are cooled to the processing temperatures recommended for the two-part urea-formaldehyde process (< 49°C, 120°F). Lowering the waste temperature to below 49°C (120°F) will result in boric acid and sodium sulfate crystallite separating out of the solution. (The crystallite formation is less of a problem in the case of sodium sulfate waste than the boric acid waste). To minimize this problem, the waste solution was pH adjusted with 40% sodium hydroxide prior to lowering the temperature. The pH adjustment increases the solubility of boric acid at lower temperature, thus eliminating most of the crystallite formation problem. Waste temperature control is important for large scale waste forms. If the temperature of the waste solution is not lowered, the result could be a "doming" in the solidified product (50 cubic ft. liner size) due to the production of gases. Lowering the waste stream temperature will offset the temperature increase due to the polymerization reaction, thus preventing the "doming" effect.

3.4 Experimental Results

Table 3.2 lists the waste loadings, pH of the untreated waste, initial pH of the waste after mixing with the binder, temperature before solidification, gelation times, average peak exotherms, and free standing or drainable water for each of the waste forms. The free standing water given in grams, in Table 3.2, are averaged values for five samples. Test specimens weighed approximately 350 grams at the time of solidification.

Table 3.2
Formulations and Properties of Two-Part Urea-Formaldehyde Waste Forms

Waste Type	Waste/Binder (vol. ratio)	pH of Untreated Waste	Initial pH of Waste & Binder Combined	Waste Temp. (°C)	Gel Time (min)	Avg. Peak Exotherm (°C)	Free Standing Liquids (grams)
Bead Resin	1.50	---	4.7±0.1	21±0.5	99±4.0	13.5±1.0	2.50
BWR Precoat Filler Cake With Diatomaceous Earth	1.25	9.4±0.2	4.6±0.1	22±1.0	44±8.0	21.5±1.5	Negligible Surface Dampness
BWR Chemical Regenerative Waste	0.85	8.8±0.1	4.5±0.1	48±0.5	11±1.0	39.0±2.0	1.60
Boric Acid Waste of a Recirculation Evaporator	1.25	3.0±0.3	4.8±0.1	48±0.5	19±2.0	33.0±3.0	0.62

3.5 Discussion of Results

Apart from characterizing the macrostructure of the waste forms, the specimens were analyzed for free standing water criteria, corrosivity of free water to mild steel containers, and specimen shrinkage as a function of time. A brief discussion of each of these criteria follows:

3.5.1 Solid Monolith

All waste forms tested exhibited satisfactory solidification, which by definition is described as a product that is a free standing monolith.

Figures 3.1 through 3.4 show typical macrostructure of the cross-sectioned waste forms incorporating four different simulated wastes. A vertically sectioned BWR chemical regenerative waste form (Na_2SO_4) specimen shown in Figure 3.1 is homogeneous and exhibits no gross porosity or voids. Figure 3.2 shows ion-exchange bead resins in the waste form. The slight settling of the bead resins towards the bottom of the specimen is attributed to inadequate mixing of the waste and binder mixture prior to solidification, and the density difference between the bead resin and the matrix material. Figure 3.3 shows waste form containing diatomaceous earth waste. The waste is uniformly dispersed in the matrix. Darker spots in the macrograph are representative of the "crud" typically found in diatomaceous earth. Figure 3.4 shows the top view of the waste form containing boric acid waste. This specimen was photographed after letting the specimen stay in a capped capsule for four weeks after solidification. The picture shows crystallites of boric acid that separated out from the unbound aqueous waste that appeared as free standing liquid on top of the specimen.

3.5.2 Free Standing Liquid

The development of free standing water was examined. Free standing water by definition is the quantity of liquid that is not bound either chemically or mechanically with the solid matrix. A guideline for acceptable quantities of free water developed in any solidified waste is outlined in a preliminary draft report 10CFR Part 61 titled, "Disposition of Low-Level Radioactive Waste and Low-Activity Bulk Solid Waste."⁽³⁾ The proposed criteria states that the LLW monolith shall be in a dry solid form, and shall not have more than 0.5 volume percent or one gallon (whichever is less) of non-corrosive free liquid per container.

Tests conducted at BNL indicate that some free water was generated in all two-part urea-formaldehyde waste forms with the exception of BWR precoat filter cake with diatomaceous earth waste (Table 3.2). The waste forms containing bead resins and diatomaceous earth wastes exhibited a "slimy" coating on the surfaces in contact with the container in addition to free water. (In full scale operation, a water vapor venting system is employed in preventing the initial formation of condensate in the waste form during the polymerization reaction. This procedure was not used for our small scale laboratory specimens).

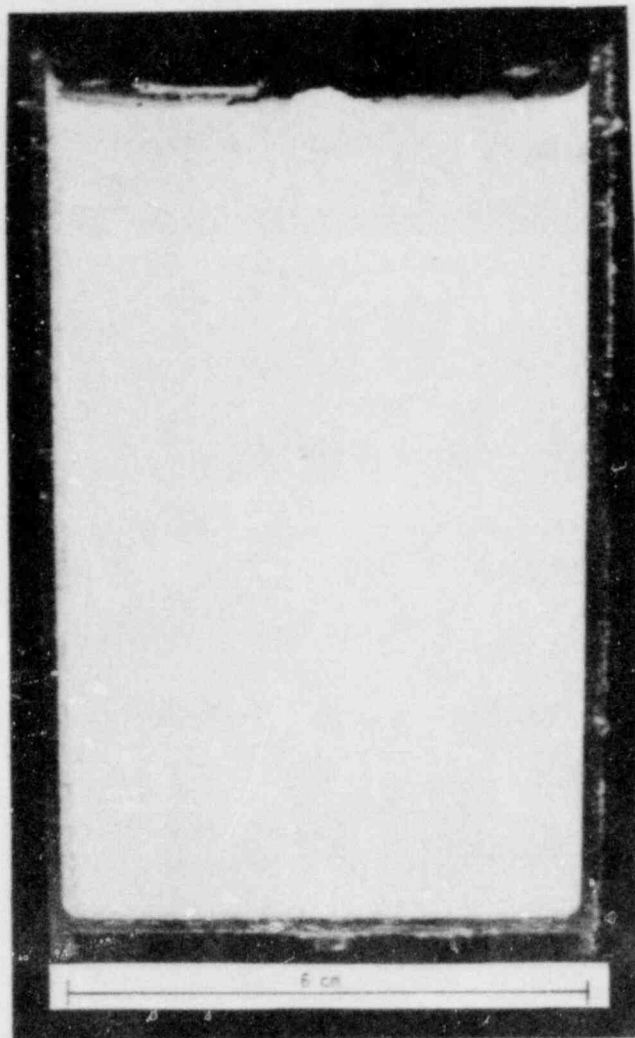


Figure 3.1. Two-part urea-formaldehyde BWR chemical regenerative waste (sodium sulfate). (specimen vertically sectioned).



Figure 3.2. Two-part urea-formaldehyde bead resins waste (dewatered formula). (specimen vertically sectioned).

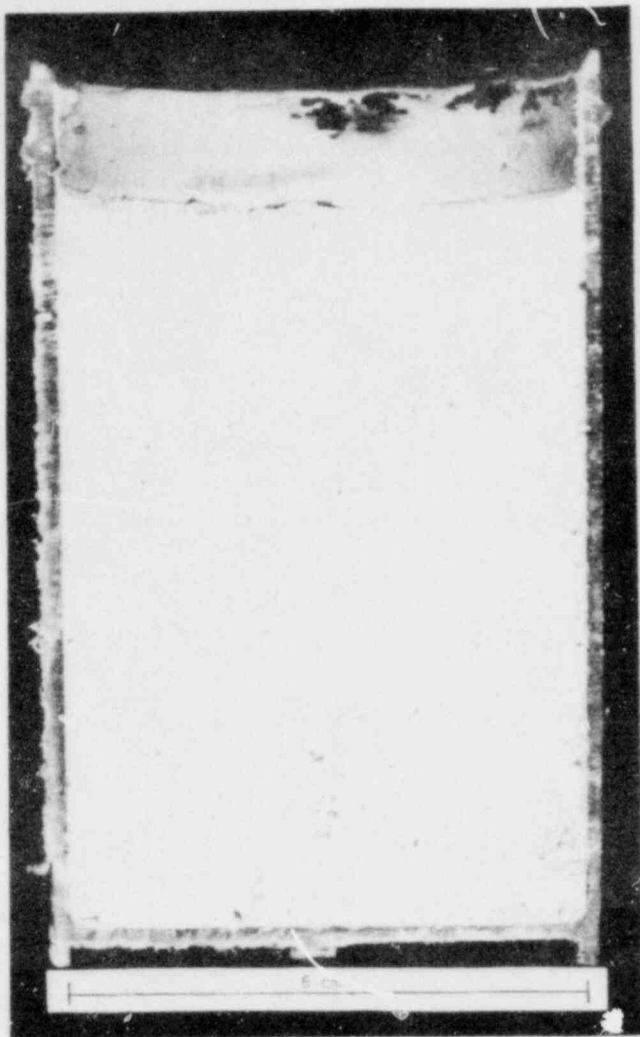


Figure 3.3. Two-part urea-formaldehyde BWR precoat filter cake with diatomaceous earth waste. (Slurry formula). (Specimen vertically sectioned.)

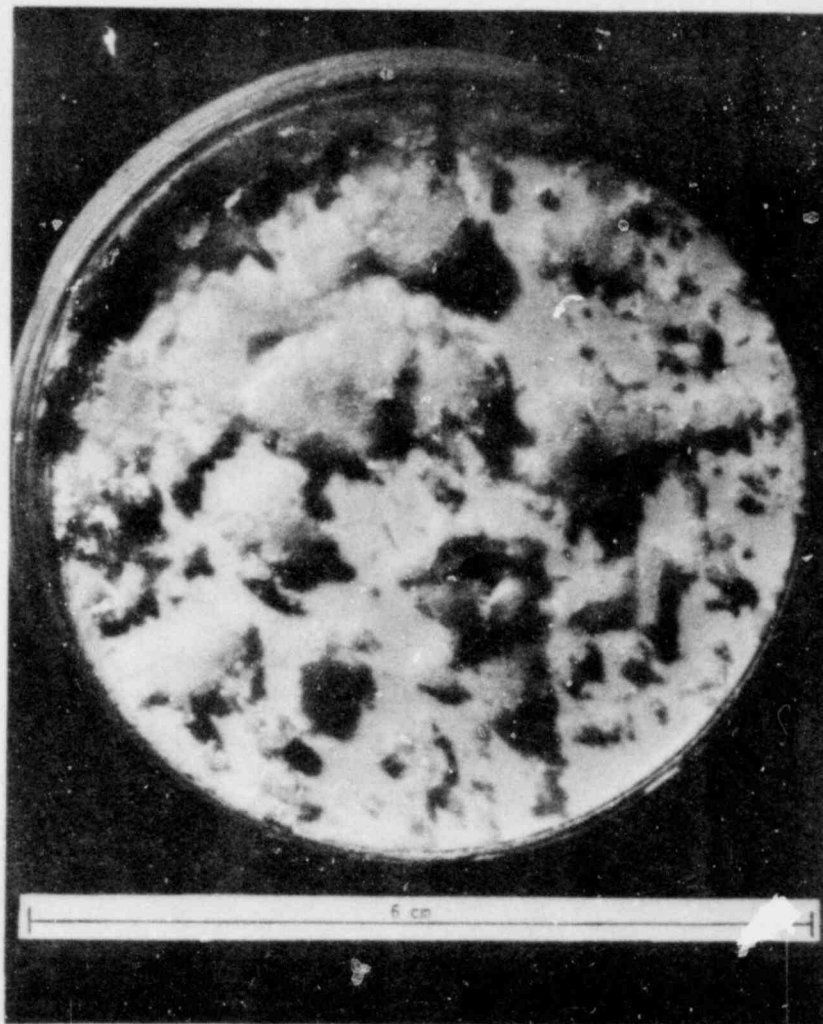


Figure 3.4. Two-part urea-formaldehyde boric acid waste. (Top view of the specimen).

Two weeks after solidification, the amounts of free water present in the capsules containing sodium sulfate, bead resin, and boric acid wastes were approximately 0.22, 0.21, and 0.31 volume percent respectively. After four weeks the free water in the bead resin waste form had increased to 0.83 volume percent, and that in sodium sulfate waste form to 0.53 volume percent.

No conclusions can be made on the basis of the lab scale tests as to whether the two-part urea-formaldehyde waste form will meet the free standing water criteria for large scale waste monoliths (55 gallon drum, or 50 cubic feet linear sizes).

3.5.3 Corrosivity of the Free Liquid

The corrosivity of the free standing liquid generated by the waste forms is of concern. In all two-part urea-formaldehyde waste forms tested, the pH values recorded for the free standing liquid were 2 or less. Free liquid of such corrosivity could pose a problem if the waste forms are solidified in mild steel containers.

3.5.4 Specimen Shrinkage

Specimen shrinkage was characteristic of the five BWR chemical regenerative waste forms prepared. The containers holding the specimens were capped and were allowed to remain undisturbed for two weeks at room temperature before being measured. Average volume reduction recorded was 4%. After four weeks, the decrease approached 4.5%. Part of this decrease in volume is attributable to the unbound aqueous liquids.

3.6 Conclusions

The following preliminary conclusions can be made about the two-part urea-formaldehyde process. These conclusions are based on the lab-scale experiments described in this report and have not been confirmed for large scale waste forms:

- two-part urea-formaldehyde process is capable of solidifying typical simulated LWR low-level waste into a solid free standing monolith.
- typical waste form produced by the two-part urea-formaldehyde process exhibits free standing water (unbound liquids).
- typical pH of the free liquid is approximately 2. The corrosivity of this solution could be a potential problem if present in a mild steel container.
- specimen shrinkage recorded after four weeks in a closed container, at ambient temperature, is approximately 5 volume percent.
- direct comparison of waste forms produced by the standard and two-part urea-formaldehyde processes is premature at the present time.

3.7 References

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2. P. Colombo and R. M. Neilson, Jr., Brookhaven National Laboratory, Properties of Radioactive Wastes and Waste Containers, First Topical Report, BNL-NUREG-50957, NUREG/CR-0619, August 1979. Available for purchase from the National Technical Information Service, Springfield, VA 22161.
3. Draft 10 CFR Part 61: Disposal of Low-Level Radioactive Waste and Low-Activity Bulk Solid Waste, November 5, 1979. Available from the U.S. Nuclear Regulatory Commission, Division of Waste Management, Washington, D.C. 20555.

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