

SOLIDIFICATION OF LOW-LEVEL RADIOACTIVE WASTES IN MASONRY CEMENT

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March 1987

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**Prepared for the
NATIONAL LOW-LEVEL WASTE MANAGEMENT PROGRAM
UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY**

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes:
Printed Copy: A04; Microfiche Copy: A01

ABSTRACT

Portland cements are widely used as solidification agents for low-level radioactive wastes. However, it is known that boric acid wastes, as generated at pressurized water reactors (PWR's) are difficult to solidify using ordinary portland cements. Waste containing as little as 5 wt% boric acid inhibits the curing of the cement. For this purpose, the suitability of masonry cement was investigated. Masonry cement, in the U.S. consists of 50 wt% slaked lime (CaOH_2) and 50 wt% of portland type I cement. Addition of boric acid in molar concentrations equal to or less than the molar concentration of the alkali in the cement, eliminates any inhibiting effects. Accordingly, 15 wt% boric acid can be satisfactorily incorporated into masonry cement. The suitability of masonry cement for the solidification of sodium sulfate wastes produced at boiling water reactors (BWR's) was also investigated. It was observed that although sodium sulfate - masonry cement waste forms containing as much as 40 wt% Na_2SO_4 can be prepared, waste forms with more than 7 wt% sodium sulfate undergo catastrophic failure when exposed to an aqueous environment. Waste form volume increase is so severe that swelling, cracking, exfoliation and crumbling occurs during the first several days of water immersion. It was determined by X-ray diffraction that in the presence of water, the sulfate reacts with hydrated calcium aluminate to form calcium aluminum sulfate hydrate (ettringite). This reaction involves a volume increase resulting in failure of the waste form. Formulation data was identified to maximize volumetric efficiency for the solidification of boric acid and sodium sulfate wastes. Measurement of some of the waste form properties relevant to evaluating the potential for the release of radionuclides to the environment included leachability, compression strengths and chemical interactions between the waste components and masonry cement.

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1. INTRODUCTION

Pressurized water reactors (PWRs) are controlled, in part, by the manipulation of the concentration of boric acid in the primary coolant. Boron has a very high neutron capture cross section, making it a convenient method for adjusting the reactivity, which in turn controls a reactor's power output. Thus, PWRs produce radioactive liquid waste that usually contains relatively high concentrations of boric acid. It is well known that boric acid waste is difficult to solidify using ordinary portland cements. The BO_3^- and $\text{B}_4\text{O}_7^{2-}$ ions in water strongly inhibit the curing of cement, and can, if present in sufficient quantities, prevent cement from adequately solidifying. Experiments conducted for this study show that wastes containing as little as 5 wt% boric acid inhibit the curing of the cement. However, ordinary portland cement can be used to solidify boric acid waste either by using a low waste/cement ratio or by incorporating additives. Lime has been chosen as the best additive for the application. It is relatively inexpensive and has strong alkalinity which is needed to neutralize the "buffer solution" of boric acid. Slaked lime is easier to handle in dry form than caustic soda and quick lime. The mixture of portland cement and lime is sold as masonry cement.

Although the use of masonry cement was originally suggested to overcome the inhibiting properties of boric acid, it is currently being suggested for solidification of radioactive wastes produced in boiling water reactors (BWRs), which usually contain high concentrations of sodium sulfate, and spent radioactive ion exchange resins.

In this work, four low-level waste types i.e., boric acid, sodium sulfate, spent ion exchange resins and incinerator ash are investigated to determine compability of masonry cement with the various types of wastes.

2. MASONRY CEMENT

2.1 Two Types of Masonry Cement

Mortars made with appropriate proportions of lime and cement, which combine the advantages of each, were introduced a long time ago in the construction field to improve plasticity and water-retention and to reduce shrinkage. These mortars are being sold as "masonry cement." Masonry cements now generally consist of a mixture of portland cement with a finely ground material (usually lime), and an air-entrainment agent. American and Canadian masonry cements generally contain about 50 percent of cement by weight. The lime, however, can be in the form of limestone, CaCO_3 , or hydrated lime (slaked lime), Ca(OH)_2 .

2.2 Type "M" Masonry Cement

Masonry cement tested in this work is manufactured by the Western Lime and Cement Company of West Bend, Wisconsin and is sold under the trademark as "Lime-Cement Type M." This product is a proprietary mixture of Type I portland cement and Miracle Type "S" Hydrated Lime. Hydrated lime or slaked lime, Ca(OH)_2 , is ground limestone which has been burned, driving off the carbon dioxide. The resultant oxide or quick lime, CaO , is then slaked by adding water. The determined constituents and calculated constituents of the Miracle Lime are given in Tables 2.1 and 2.2, respectively.

Table 2.1

Miracle Lime
Determined Constituents^{a,b}

Silica	(SiO ₂)	0.92%
Iron	(Fe ₂ O ₃)	0.26%
Aluminum	(Al ₂ O ₃)	2.02%
Calcium	(CaO)	42.97%
Magnesium	(MgO)	27.40%
Total Sulphur	(S)	0.01%
Sulphur Trioxide	(SO ₃)	< 0.01%
Phosphorus	(P ₂ O ₅)	< 0.002%
Carbon Dioxide	(CO ₂)	1.69%
Water at 12°		Trace
Water Total		24.36%
Insoluble Matter		0.05%
Loss on Ignition		26.05%
Available Lime Index	(Ca(OH) ₂)	44.78%
Strontium Oxide	(SrO)	0.26%
Manganese	(Mn)	0.015%
Ferrous Iron	(Fe)	0.04%

a) All determinations have been made according to methods prescribed by the American Society for Testing and Materials.

b) Adapted from Reference [1].

Table 2.2

Miracle Lime
Calculated Constituents^a

Calcium Carbonate	(CaCO ₃)	3.85%
Calcium Hydroxide	(Ca(OH) ₂)	54.00%
Magnesium Carbonate	(MgCO ₃)	--
Magnesium Hydroxide	(Mg(OH) ₂)	39.66%
Calcium Sulfate	(CaSO ₄)	2.21%

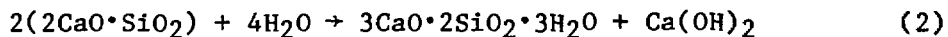
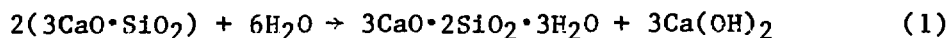
^a)Adapted from Reference [1]

3. INCORPORATION OF SIMULATED RADIOACTIVE WASTES IN MASONRY CEMENT

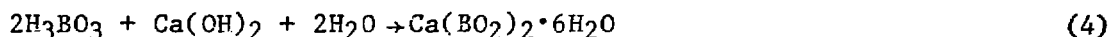
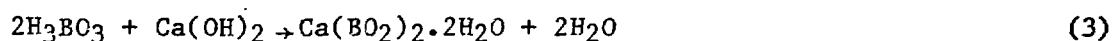
In this work four types of simulated low-level radioactive wastes are incorporated into masonry cement. These are boric acid waste, sodium sulfate waste, spent ion exchange resins and incinerator ash.

3.1 Boric Acid Waste

3.1.1 Chemical Interactions Between Boric Acid and Masonry Cement. It is known that boric acid waste, as generated at pressurized water reactors, is difficult to solidify using ordinary portland cement. Curing of portland cement is brought about by the hydration of the cement constituents, mainly tricalcium silicate, and dicalcium silicate, as shown in reactions (1) and (2).



The resulting calcium silicate hydrate is in the form of colloidal particles. As an electrolyte, BO_3^- may stabilize colloidal particles so that the cement-water paste does not coagulate [2]. The high concentration of slaked lime in masonry cement allows significantly higher amounts of boric acid waste to be incorporated into a waste form than ordinary portland cements. The more significant reactions occurring between slaked lime and boric acid are given below:



The end products of all these chemical reactions are calcium metaborate, calcium metaborate hexahydrate, and calcium tetraborate. These compounds are insoluble or slightly soluble in water and, therefore, do not ionize well. Consequently, the calcium borates do not inhibit cement from curing by stabilizing colloidal particles of $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, the main hydration product of portland cement.

3.1.2 Formulation Studies. The identification of formulation data to maximize volumetric efficiency for the solidification of radioactive waste in masonry cement is the focus of this study. For the purposes of this investigation the following criteria were applied to determine acceptable solidification formulations:

1) Workability - Sufficient workability (mixability) is required to provide a homogeneous mixture in a reasonable time utilizing conventional mixing techniques. For cement mixtures, a minimum volume of water is necessary to provide adequate workability. Insufficient water results in a dry, friable waste form upon curing. Mixability limits were determined by beginning with a mixture known to be unworkable and slowly adding water until an adequate consistency was achieved.

2) Monolithic Solid - All samples must cure to form a free-standing monolithic solid within a reasonable time (14 days).

3) Free Standing Water - No samples may contain any drainable free-standing water after a period of 24 hours. While free-standing water in cement systems may decrease with longer cure times due to continuing hydration, this conservative approach was adopted in order to develop reliable formulations for full-scale forms.

Specimen formulations which were successfully solidified were evaluated further to determine relevant waste form properties, as reported in Section 3.1.3.

Boric acid wastes, both aqueous and dry, are simulated in this study for incorporation into masonry cement. Aqueous boric acid waste refers to PWR wet evaporator bottoms. In pursuit of higher volume reduction factors, future waste streams will likely be further evaporated so that the final waste product can contain as much as 100% dry solids. Therefore, simulated dry boric acid waste has been included in this investigation.

3.1.2.1 Solidification of PWR Wet Evaporator Bottoms. The typical chemical formulation of boric acid waste from a forced recirculation evaporator is shown in Table 3.1.

Table 3.1

Composition of a Typical PWR Evaporator Concentrate Waste Stream^a

<u>Material</u>	<u>Weight Percent in Evaporator Bottoms</u>
Water	87.9
Boric Acid	12.0
Crud	0.1
Temperature	170°F (77°C)
pH	3.5

^a) Adapted from Reference [3].

Due to its relatively minor presence, crud was omitted from the chemical formulation of simulated PWR wet evaporator bottoms. A range in boric acid concentration from 12 to 25 wt% is covered in this work. This range reflects the maximum concentrations of boric acid which are commonly present in effluent from current evaporators.

The solubility of boric acid is rather low: 6.35 g/100 cc in 30°C water and 27.6 g/100 cc in 100°C water respectively. It is troublesome therefore, to prepare a simulated boric acid liquid waste solution for laboratory scale solidification. Instead, weighed quantities of dry boric acid reagent and masonry cement were put into a 1/6 horse power Hobart Model N-50 planetary action mortar mixer and a measured volume of 77°C water was added separately. Thus, simulated aqueous wastes, over the range of 12-25 wt% boric acid, could be covered in this study. After mixing for 2 minutes at low speed (approximately 120 rpm), formulation specimens were cast into 4.7 cm diameter by 10.0 cm height cylindrical polyethylene containers, to a sample height

of approximately 8.5 cm. The containers were capped to prevent evaporative water loss during the curing period. Samples were cured for 14 days prior to waste form testing and evaluation. All specimens were prepared and tested in duplicate.

A large number of samples were prepared and tested to determine satisfactory formulations. Fig. 3.1 shows the ternary compositional phase diagram for the production of acceptable aqueous boric acid waste forms with masonry cement. This diagram also indicates formulative regions which result in free standing water. Those formulations which contain the minimum water necessary to form a homogeneous mixable paste fall on the line labeled "mixability limit." Ternary compositional phase diagrams express formulations in terms of weight percentages of masonry cement, water and dry boric acid. The dashed lines in Fig. 3.1 represent the boundaries of formulations prepared. As discussed in this section these formulations simulate a range in boric acid concentration from 12-25 wt% in a PWR evaporator concentrate waste stream.

Based on Fig. 3.1, boric acid wet evaporator bottoms to masonry cement ratios are shown in Table 3.2.

Table 3.2

Boric Acid Wet Evaporator Bottoms to Masonry Cement Ratios

Boric Acid in Waste (wt%)	12	15	17.5	20	25
wet boundary	0.95	0.95	1.11	1.16	1.11
dry boundary	0.40	0.43	0.45	0.51	0.54

According to Table 3.2, a waste to binder ratio (by weight) of 0.8 is reasonable.

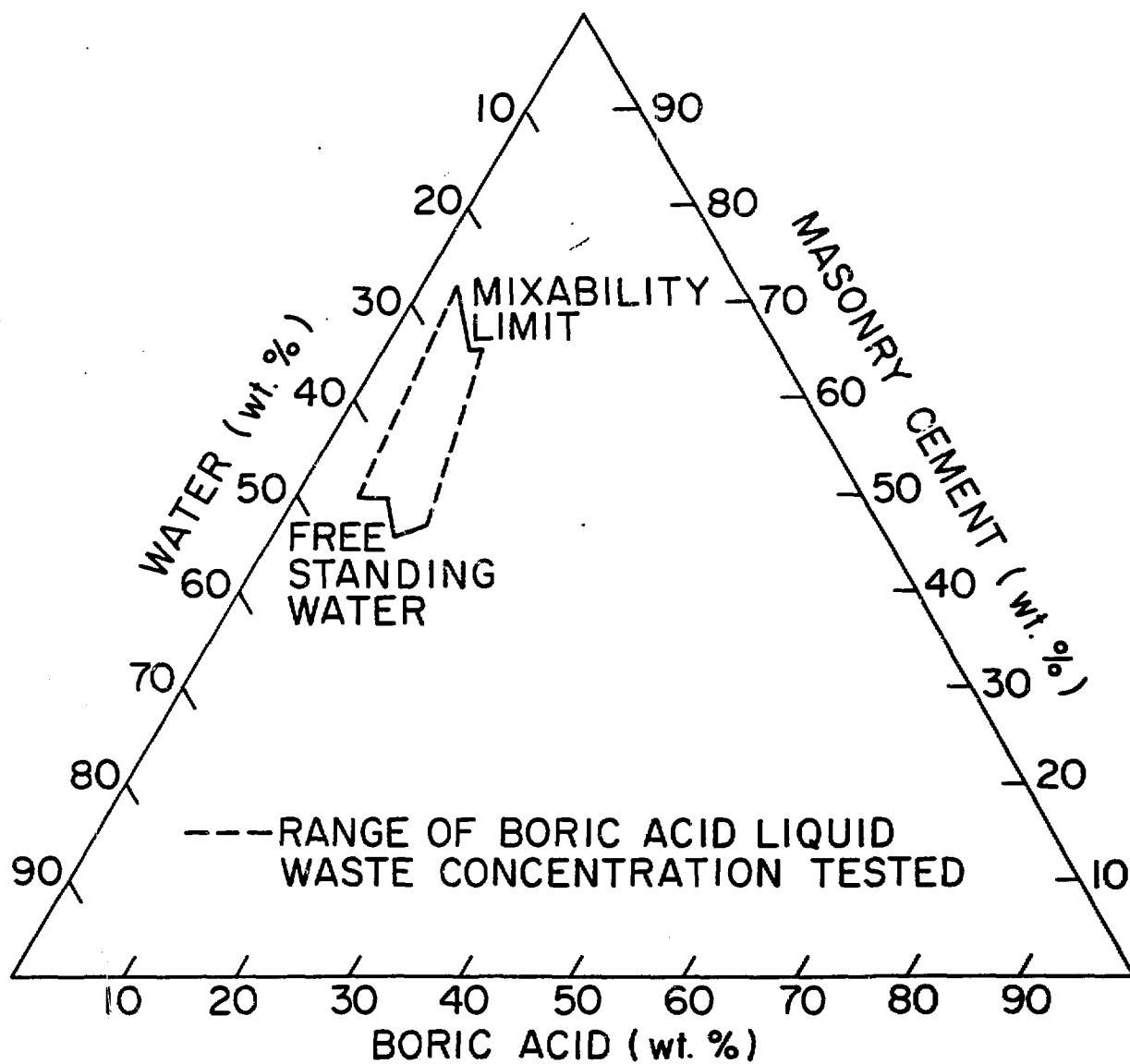


Figure 3.1 Ternary compositional phase diagram for the solidification of boric acid wet evaporator bottoms with masonry cement.

3.1.2.2 Solidification of Dry Boric Acid Waste. Formulation spec-

imens of boric acid dry waste were prepared and tested in the same way as described in Section 3.1.2.1 except that room temperature water was used instead of 77°C water.

Fig. 3.2 is the ternary compositional phase diagram defining compositional envelopes for acceptable dry boric acid evaporator concentrate waste forms with masonry cement. The envelopes of those formulations which cured within fourteen days after preparation and passed the two week water immersion test are indicated by the two unshaded sections. Those formulations which did not cure within fourteen days after preparation at room temperature are indicated by a lightly shaded area.

The larger unshaded area in Fig. 3.2 shows that approximately 15% dry boric acid can be incorporated successfully into masonry cement when water is added in a sufficient quantity. As a means of comparison, as little as 5 wt% dry boric acid waste will inhibit the curing of a portland type I cement waste form. The inhibiting properties of boric acid are overcome by the high concentration of alkali in the form of slaked lime in masonry cement. To completely overcome the cure inhibiting properties of boric acid, the molar concentrations of boric acid must be less than the molar concentration of the alkali in the masonry cement. Formulation specimens containing 15 wt% dry boric acid have a ratio M_a/M_b approximately equal to 1, where M_a represents molar concentration of acid and M_b is molar concentration of base. For this area, the recommended waste (dry boric acid plus water) to cement ratio (by wt.) is 0.8. The minimum water-to-cement ratio producing an adequately workable mixture with masonry cement alone (no boric acid) is 0.29 while the maximum water-to-cement ratio resulting in no drainable free standing water in a masonry cement-water mixture is 1.0.

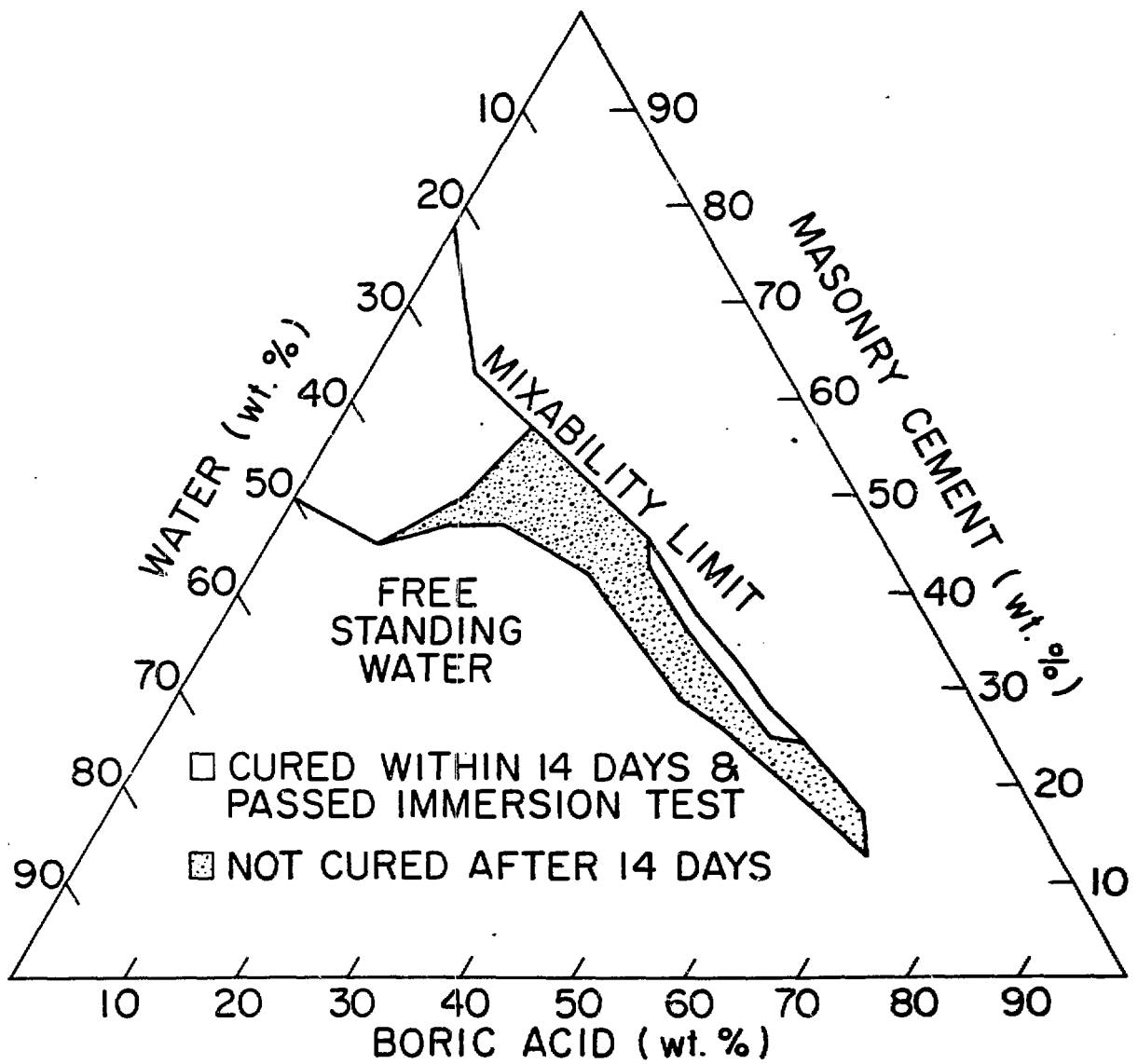


Figure 3.2 Ternary compositional phase diagram for the solidification of boric acid dry waste with masonry cement.

The lightly shaded area in Fig. 3.2 represents the region in which the equal molar concentration law is broken. In this case, the inhibiting properties of boric acid dominate, and most of the formulated specimens did not cure within the fourteen day period, at room temperature.

It is curious to see that there is another, smaller unshaded area located in Fig. 3.2. Jumping across the "curing gap" (the lightly shaded area) formulation specimens of the smaller unshaded area appeared to be cured. This region includes boric acid loadings ranging from 35 wt% to as high as 60 wt%. Based upon the known inhibiting effects of boric acid on the hydration of cement, the formation of a distinct mineral phase other than those normally associated with hydrated cement is postulated.

To explore possible reactions taking place among three formulational compositions and to identify possible resultant compounds formed, x-ray diffraction tests were performed by means of a Philips XRG 3100 X-ray Generator and a Type 15010000 Wide Range Goniometer. Qualitative x-ray diffraction was accomplished according to the method outlined by Griffin [4].

Figure 3.3 is a comparison of three separate x-ray diffractograms. Diffractogram I represents dry as-received masonry cement plus 62% dry boric acid. A successfully solidified specimen from the large unshaded area of Fig. 3.2 generated Diffractogram II. Finally, x-ray diffraction data from a sample taken from the smaller unshaded region of Fig. 3.2 is shown in Diffractogram III. Peaks A, B, C, D and E are unique to Diffractogram III. A search of published diffraction data [5] revealed that these peaks are associated with the mineral calcium-dravite, a member of the tourmaline group and described by the chemical formula $\text{CaMg}_3(\text{Al,Mg})_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$. It is concluded, therefore, that under certain conditions the formation of calcium-dravite may prevail over the hydration of masonry cement.

X-RAY DIFFRACTOGRAMS

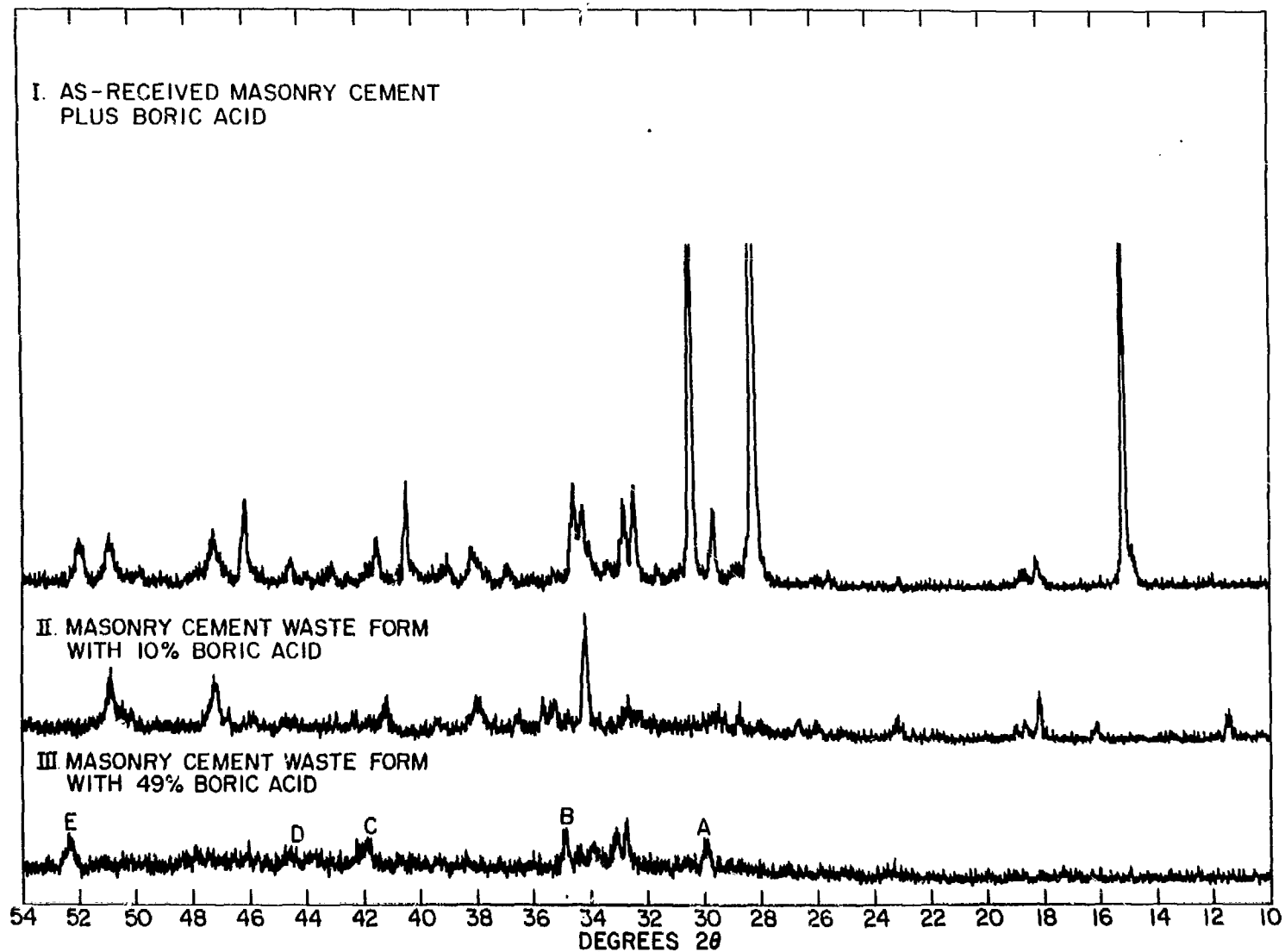


Figure 3.3 X-ray diffractograms comparing different components of masonry cement-boric acid waste forms. Peaks A, B, C, D, E of spectrum III are typical of calcium-dravite.

Preliminary observations imply that the formation of this mineral phase contributes toward the solidification of as much as 60 wt% dry boric acid waste with a mixture consisting of 25 wt% masonry cement and 15 wt% water. From a more practical standpoint, however, process control parameters would be extremely difficult to manipulate with sufficient precision within such a narrow compositional envelope, while still maintaining waste form quality control.

Granular boric acid reagent was used in this study. Formulations using powdered boric acid were also used to determine differences in processing parameters. Results indicate that 3 wt% - 8 wt% more water (depending on different waste/binder ratios) is needed to solidify powdered boric acid because of the larger grain surface to be moistened.

3.1.3 Waste Form Properties. Historically, little importance has been placed upon the performance of waste forms within the shallow land burial environment. However, experience gained in the operation of low-level waste disposal sites has led to the realization that waste form properties can play an important role in the isolation of radionuclides from the environment. In light of this information, BNL has developed a working set of preliminary waste form property evaluation criteria [6], in conjunction with the DOE-LLWMP Waste Form Development/Test Program. Relevant waste form properties which were investigated for this study include:

- evaluation of the effects of aqueous media, i.e., water immersion testing
- compressive strength
- leachability

Other waste form evaluation criteria including radiation stability and biological stability were not included as they were beyond the scope of this investigation.

3.1.3.1 Water Immersion. A low-level radioactive waste form must maintain its integrity under conditions encountered in land burial. One of the conditions is exposure to ground water which, depending on the type of waste, may cause swelling, dissolution, cracking and exfoliation of the waste form with time. These effects compromise the ability of the waste forms to adequately retain radionuclides. Swelling of the waste form may breach the container resulting in premature release of radionuclides. Disintegration of the waste form may reduce its integrity resulting in trench cap deterioration or trench subsidence. In addition, higher than normal leach rates would result due to the larger exposed waste form surface area.

To determine the effects of an aqueous environment on the mechanical integrity of waste forms, specimens were subjected to a two week water immersion test. Previous work demonstrated that gross changes in mechanical integrity can easily be observed for some waste form formulations well within a two week test period [7]. Although the continuous immersion of uncontained waste forms does not reflect actual burial site conditions, the immersion test is believed to be indicative of long-term waste form integrity in the presence of an aqueous environment.

The results of water immersion testing for dry boric acid-masonry cement waste forms are included in Fig. 3.2. Within the range of solidified aqueous boric acid evaporator concentrates which were formulated (see Fig. 3.1), no specimens failed in water immersion tests.

3.1.3.2 Compressive Strength. Mechanical integrity of waste forms is an important consideration in the safe handling and transportation of radioactive waste prior to disposal. Waste form failure under load may result in cracking or friability leading to possible dispersion of activity. Waste form failure creates a larger effective surface area from which activity can be leached. Therefore, mechanical properties of waste forms are of concern within the disposal environment.

Compressive strength testing was conducted as a measure of mechanical integrity. The compressive strengths of typical masonry cement waste forms were tested in accordance with the ASTM method C 39-72, "Test for the Compressive Strength of Cylindrical Concrete Specimens" [8]. Specimens were cast in 4.7 cm diameter cylindrical polyethylene vials and the length of specimens were 1.8 to 2.2 times the diameter. The vials were then capped to prevent evaporative water loss. Specimens were compression tested after curing for at least fourteen days. Compression test results of typical masonry cement waste forms are summarized in Table 3.3.

Data listed in Table 3.3 indicate that the compressive strength of a masonry cement waste form depends greatly on the amount of water in the formulation and on the amount and type of waste solidified. Some conclusions can be made based on Table 3.3.

1. The compressive strength of masonry cement waste forms is inversely proportional to the water content of the formulation.
2. All the waste types concerned have a negative effect on masonry cement waste form compressive strength; the more waste contained in the formulations, the lower the compressive strength will be, as long as the water content remains the same.

Table 3.3

Compressive Strength of Typical Masonry Cement Waste Forms

Waste Forms	Cement Wt %	Water Wt %	Dry Waste Wt %	Compressive Strength, Mpa	Compressive Strength Ratio*
Plain	65	35	0	20.6	--
Masonry Cement	60	40	0	13.5	--
	55	45	0	8.71	--
	50	50	0	3.40	--
	45	55	0	2.32	--
Masonry Cement and Boric Acid	50	45	5	4.51	0.52
	50	45 (77°F)	5	3.74	0.43
	50	40	10	5.32	0.40
	50	40 (77°F)	10	2.43	0.18
	50	35	15	6.19	0.30
Masonry Cement and Ion Exchange Resins	60	35	5	15.5	0.75
	55	35	10	11.3	0.55
	30	55	15	0.63	0.27
Masonry Cement and Incinerator Ash	50	45	5	7.35	0.84
	50	40	10	10.8	0.84
	50	35	15	15.0	0.73
	60	35	5	19.7	0.96
	55	35	10	16.8	0.81

*Compressive Strength Ratio = $\frac{\text{Waste Form Compressive Strength}}{\text{Plain Masonry Cement Compressive Strength}}$ (with same Water %)

3. Boric acid decreases the waste form compressive strength the most compared to incinerator ash and ion exchange resins, especially when boric acid evaporator bottom waste is used at 77°C.

3.1.3.3. Leachability. Leachability refers to the release of material from the waste or solidified waste form when in contact with liquids. To examine the retention capabilities of masonry cement for both boric acid concentrate and radionuclides, leach tests were conducted using the proposed ANS 16.1 Standard Leach Test [9]. Leach test specimens were right cylinders with diameters of 4.7 cm and heights of 6.8 cm. The leachates from some samples were analyzed for boron and for pH. Other leachates from identical waste forms (but containing the radioactive tracers Cs-137, Co-60 and Sr-85) were analyzed for radionuclides.

3.1.3.3.1 Boron Leaching. Masonry cement samples containing 5, 10 and 15 wt% boric acid were made in duplicate and cured for at least two weeks. The samples were leached with a modified ANS 16.1 leach test for 56 days. Boron concentrations of the leachant was determined by means of a Perkin-Elmer 4000 Atomic Absorption Spectrophotometer.

The results of these leach tests are shown in Figures 3.4 and 3.5. Cumulative fraction releases of boron are approximately 10% for samples containing 5% dry boric acid and 20% for samples containing 10 and 15% dry boric acid, at the end of 56 days of cumulative leach time. Figures 3.4 and 3.5 indicate that boron releases double if boric acid weight percentage increases from 5 to 10%, while cement weight percentages in the waste form formulations remain constant. Further increase of boric acid to 15 weight

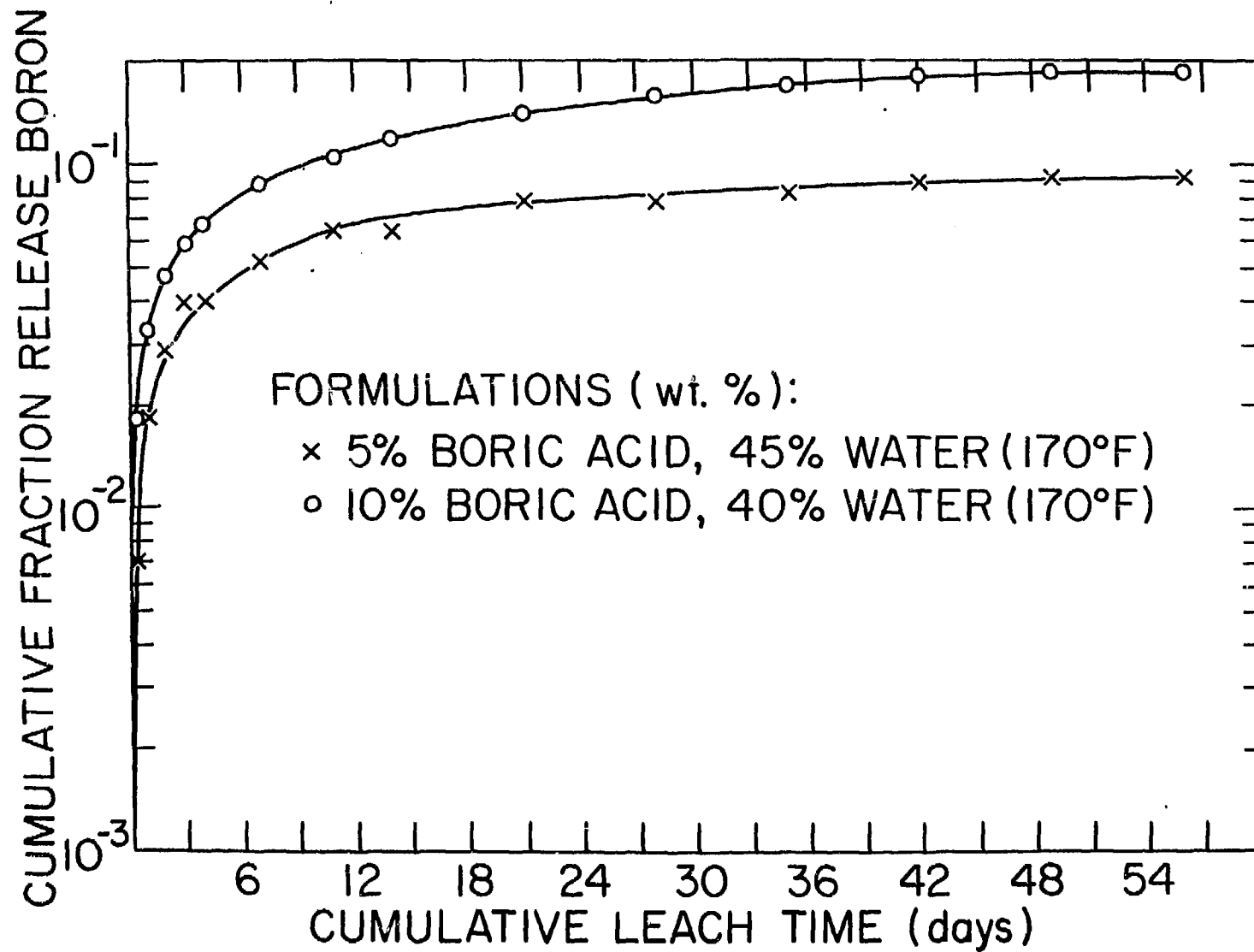


Figure 3.4 Leachability of boron from masonry cement waste forms containing 5 wt% and 10 wt% boric acid. Waste forms were made using aqueous boric acid at 77°C.

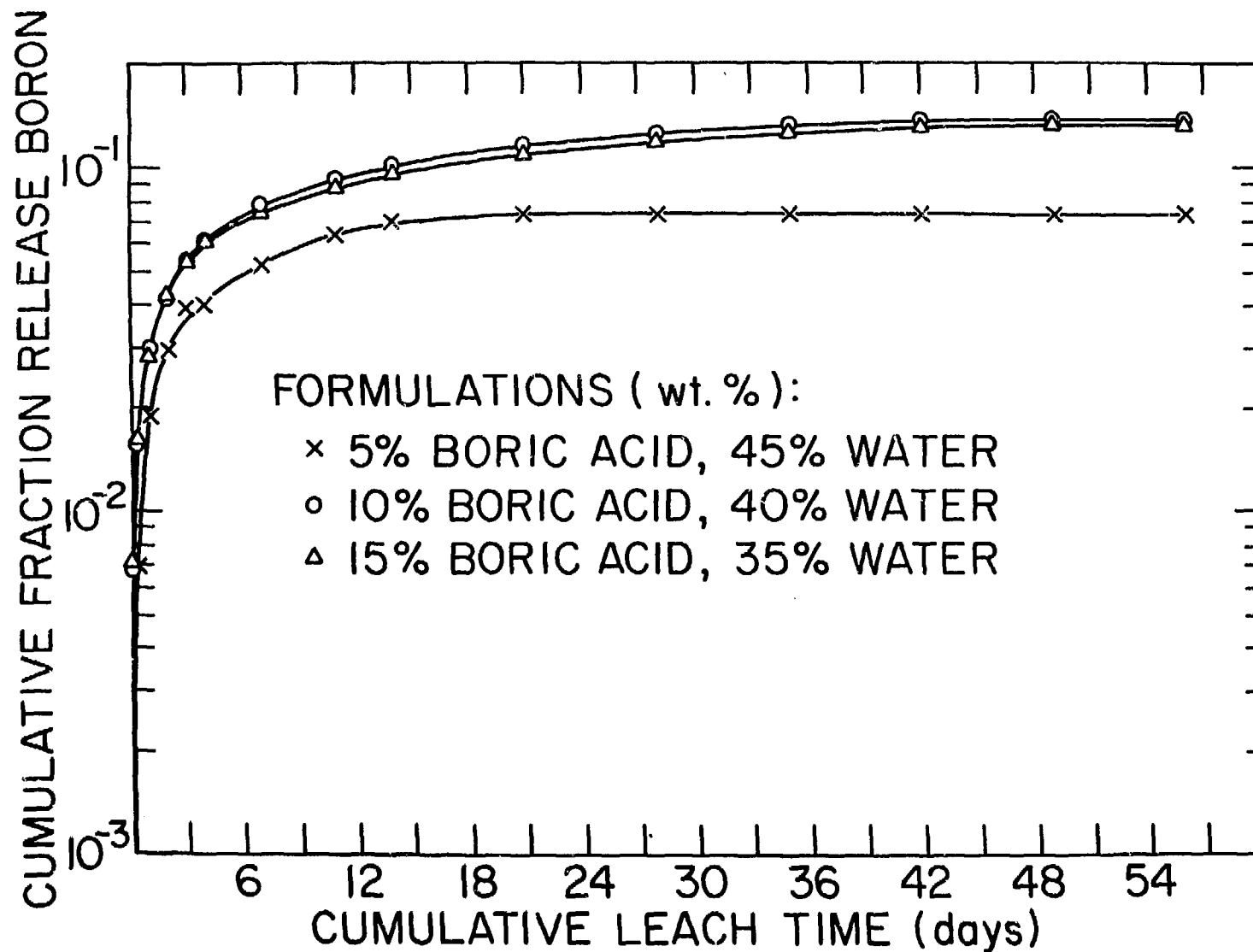


Figure 3.5 Leachability of boron from waste forms containing 5, 10 and 15 wt% boric acid. Waste forms were made using dry boric acid at room temperature.

percentage did not show a marked effect on waste leachability. Little difference in leachate boron concentrations from aqueous boric acid waste (77°C) forms and dry boric acid waste (room temperature) forms was detected.

3.1.3.3.2 Leachate pH. Leachant pH values were tested by means of a Beckman Model 3550 Digital pH Meter. Fifteen sets of different sampling time data show that leachant pH values remained essentially constant at pH \approx 12.0, for both waste forms fabricated with aqueous boric acid at 77°C and at room temperature using dry boric acid (including waste forms containing 5, 10 and 15 wt% dry boric acid). This data indicates that in all cases an excess of alkali was present to overcome effects of the boric acid leaching out of the waste form.

3.1.3.3.3 Radioactive Tracer Leaching. To examine the radionuclide retention capabilities of the waste forms, boric acid-masonry cement mixtures were spiked with Cs-137, Sr-85, Co-60. Considering that the radioactivity counting efficiencies are not the same for Cs, Sr and Co, and that the relative leachability of each isotope from the waste forms vary, the concentrations of Cs-137, Sr-85 and Co-60 used were in the proportion of one to three to ten. Therefore, 4.52 μ Ci of Cs-137, 13.41 μ Ci of Sr-85 and 41.34 μ Ci of Co-60 were incorporated into each boric acid-masonry cement waste form to be leach tested. Leachability of duplicate solidified boric acid-masonry cement waste forms was measured according to the proposed ANS 16.1 Standard Leach Test [9].

Fig. 3.6 indicates that leachability of each isotope was generally not effected by different boric acid loadings. Cumulative fraction releases of Cs-137 for masonry cement samples containing 0, 5, 10 and 15 wt% boric acid were all approximately 90%. Releases of Sr-85 averaged 46% with no observed effect of waste loading. Leachability of Co-60 was almost 20 times lower than that of Cs-137 with an average 4% cumulative fraction release. These differences in leaching of various radionuclides are typical of cement waste forms. While Co-60 leaching was identical for samples containing 5, 10 and 15 wt% boric acid other samples containing no waste leached this radionuclide 3 times slower.

For masonry cement waste forms containing up to 15 wt% boric acid, the leachability index [9] for Sr-85, Cs-137 and Co-60 were calculated to be 7.5, 6.2 and 9.0 respectively. In all cases these values exceed the minimum values for the leachability index required by the Nuclear Regulatory Commission [10].

3.2 Sodium Sulfate Waste

In this study sodium sulfate waste refers to wet evaporator bottoms from a boiling water reactor (BWR).

The typical chemical formulation of BWR chemical regenerative waste from a forced recirculation evaporator is shown in Table 3.4. Sodium chloride and crud were omitted from the chemical formulation of simulated wet evaporator bottoms because of their minor percentages.

3.2.1 Formulation Studies. The same criteria as outlined in Section 3.1.2 were applied to determine the range of acceptable formulations for the solidification of sodium sulfate waste in masonry cement.

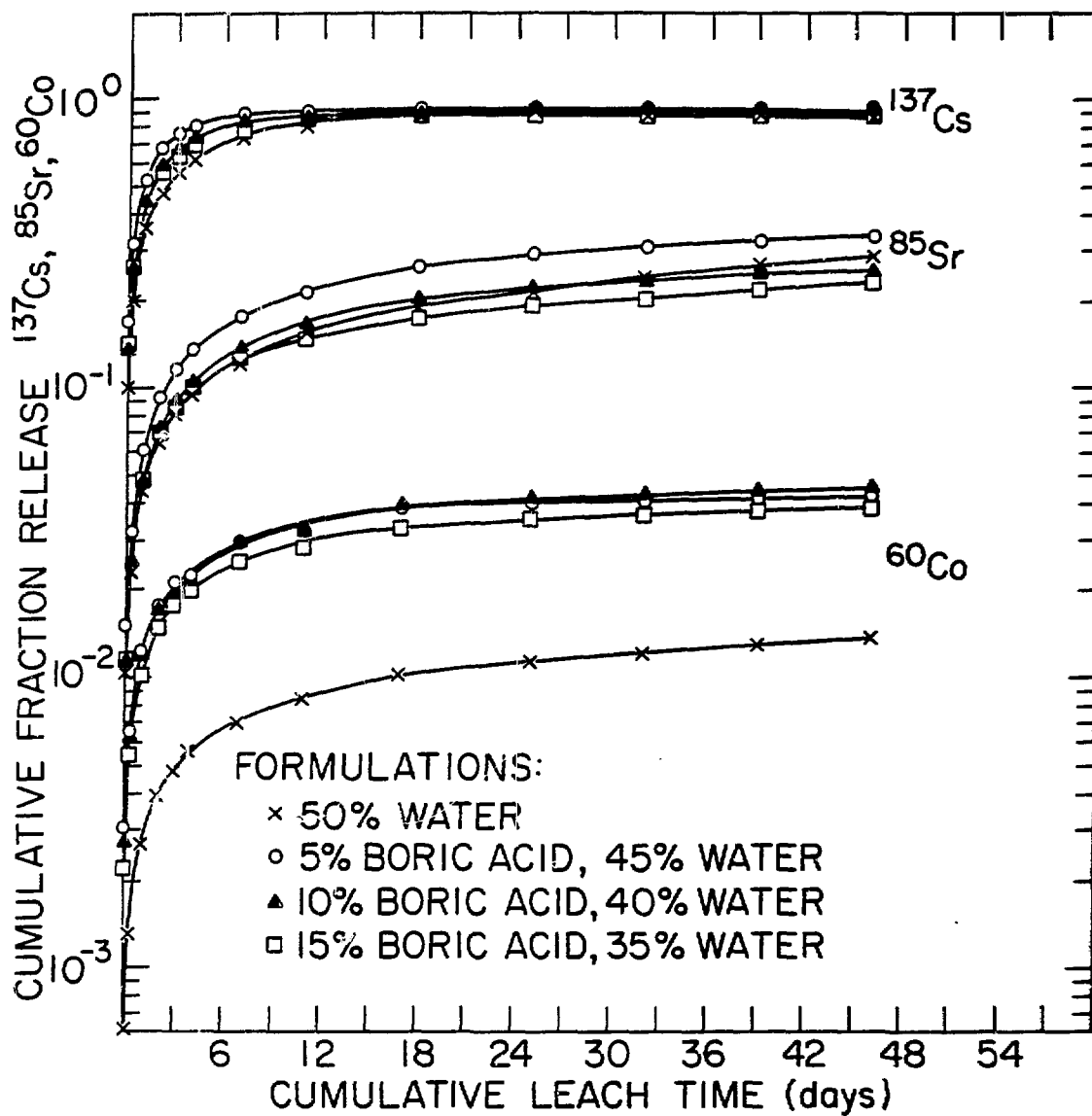


Figure 3.6 Leachability of ^{137}Cs , ^{85}Sr and ^{60}Co from masonry cement waste forms with and without simulated boric acid waste.

Table 3.4

Composition of a Typical BWR Evaporator Concentrate Waste Stream^a

<u>Material</u>	<u>Weight Percent in Evarporator Bottoms</u>
Water	75
Sodium Sulfate	22.9
Sodium Chloride	2.0
Crud	0.1
Temperature	170°F (77°C)
pH	6

a) Adapted from Reference [2].

Sodium sulfate-masonry cement waste form specimens were formulated in the same way as described in Section 3.1.2.1. The simulated aqueous sodium sulfate waste covered in this study ranges from 25-50 wt%.

Fig. 3.7 is the ternary compositional diagram for the solidification of this waste in masonry cement. The dashed lines in Fig. 3.7 represent the range of formulations tested and do not necessarily indicate compositional limits. The wet and dry boundaries are also given in Table 3.5.

3.2.2 Waste Form Properties. All the formulation specimens which were successfully solidified and met the waste form criteria, as discussed in Section 3.1.2, were evaluated to determine relevant waste form properties, as described in Section 3.1.3.

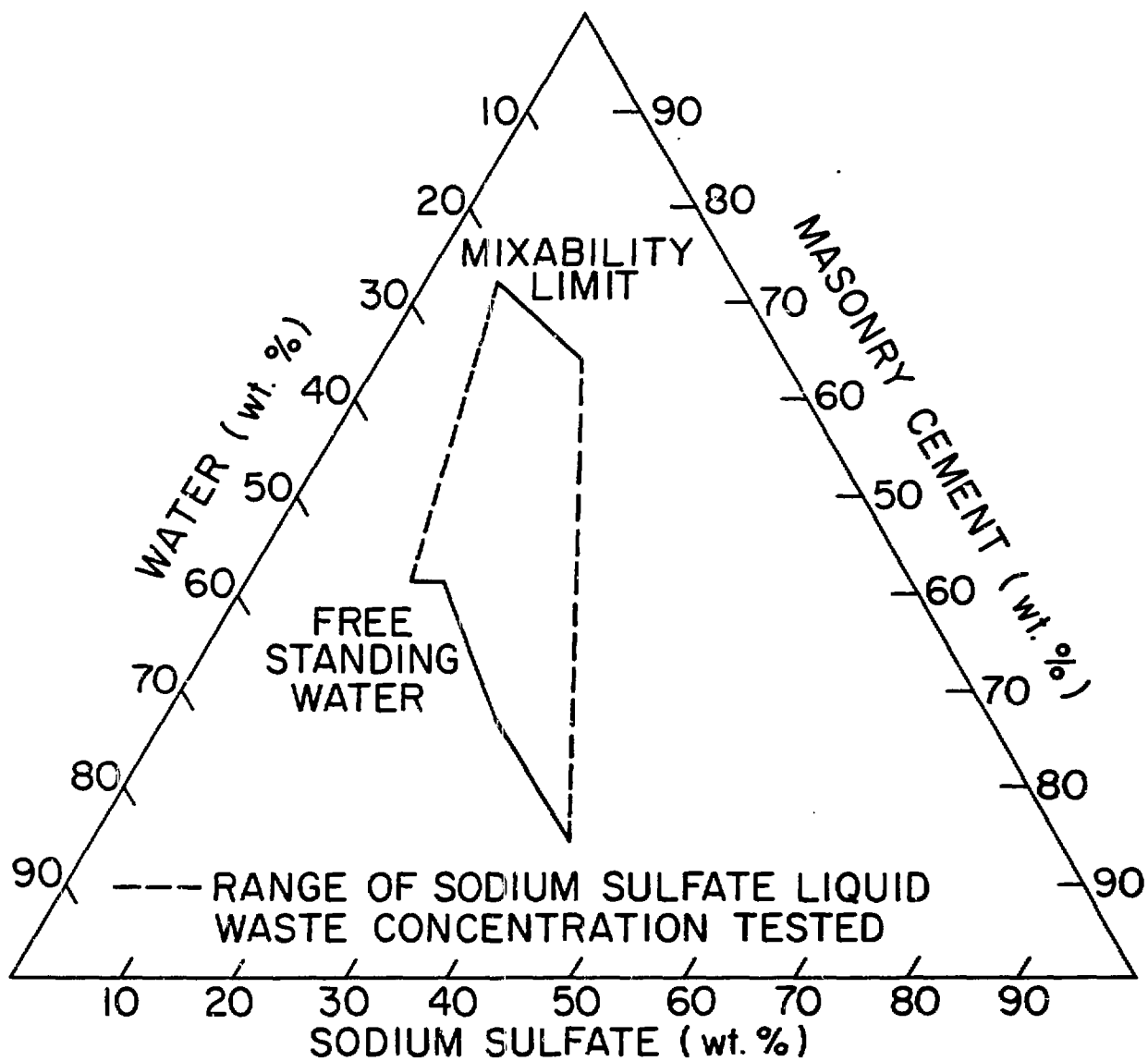


Figure 3.7 Ternary compositional phase diagram for the solidification of sodium sulfate wet evaporator bottoms with masonry cement.

Table 3.5

Sodium Sulfate Wet Evaporator Bottoms to Masonry Cement Ratios

Sodium Sulfate in Waste (Wt%)		25	30	40	50
waste/cement ratio (wt)	wet boundary	1.41	1.41	2.68	6.00
	dry boundary	0.40	0.40	0.49	0.56

3.2.2.1 Water Immersion. During the water immersion testing of solidified aqueous sodium sulfate evaporator concentrates, all of the specimens formulated within the compositional range depicted in Fig. 3.7 either cracked severely or totally collapsed within two weeks in water immersion. Examples of this dramatic effect are shown in Figs. 3.8-3.10.

The results of this test indicate that although specimens containing as much as 40 wt% sodium sulfate in masonry cement can be prepared, waste forms containing more than 7 wt% sodium sulfate undergo catastrophic failure in an aqueous environment. Waste form swelling is so severe that cracking, exfoliation and crumbling is observed during the first two weeks of water immersion. By comparison, waste forms consisting of 9 wt% sodium sulfate and ordinary portland type I cement remained essentially intact in water immersion while a 7 wt% sodium sulfate and masonry cement sample made under identical conditions failed catastrophically. It was also observed that the temperature at which the waste is added to the cement has a significant effect on its waste form stability. The samples fabricated at elevated waste stream temperatures (77°C) failed in a shorter time than those fabricated at room

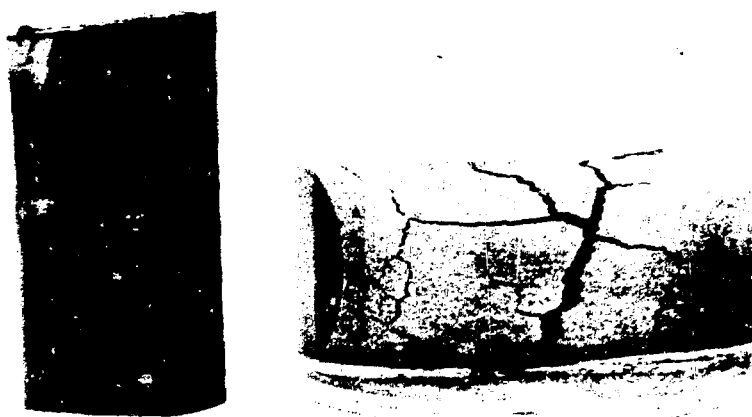


Figure 3.8 Masonry cement waste forms containing 15 wt% sodium sulfate before and after the water immersion test.

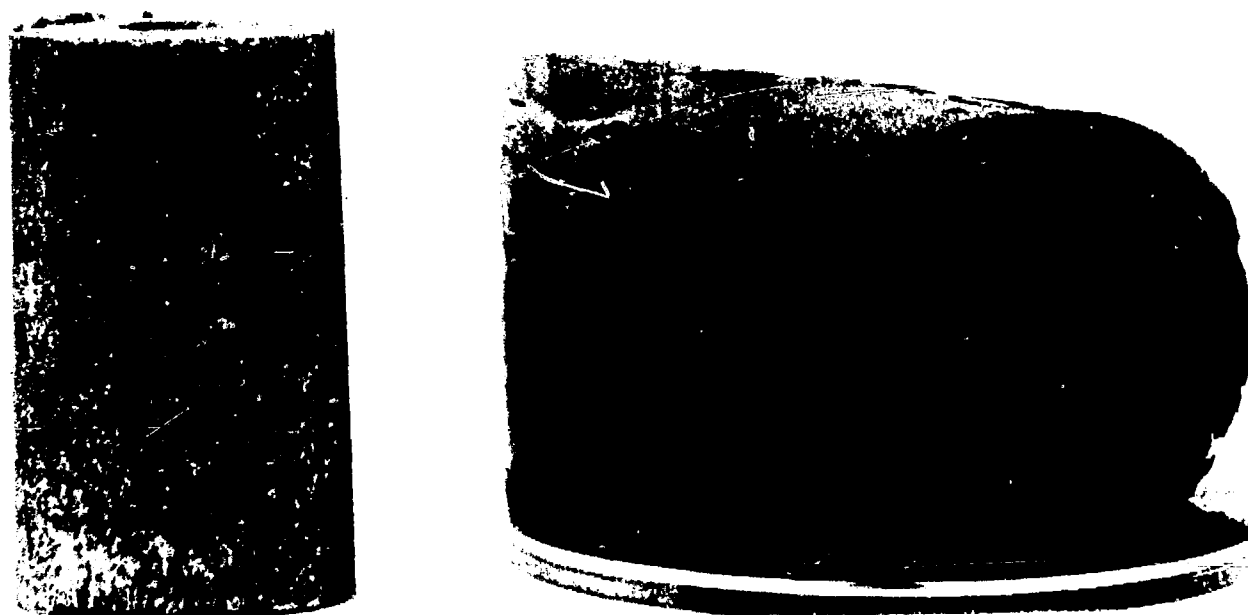


Figure 3.9 Masonry cement waste forms containing 18 wt% sodium sulfate before and after the water immersion test.



Figure 3.10 Masonry cement waste forms containing 43 wt% sodium sulfate before and after the water immersion test.

temperature, when immersed in water. Fig. 3.11 shows the effect of waste stream temperature on the stability of the masonry cement waste forms containing 13 wt% sodium sulfate immersed in water.

Waste stream temperature also affects the stability of sodium sulfate-portland type I cement waste forms during water immersion testing. Fig. 3.12 is a comparison of the effect of waste stream temperature on the stability of portland type I cement waste forms containing 9 wt% sodium sulfate during a two week water immersion testing.

To compare the possible reactions taking place among three formulations of sodium sulfate-masonry cement waste forms before and after water immersion testing and to identify possible resultant compounds formed in the waste form during water immersion, x-ray diffraction techniques were used.

The same x-ray diffraction apparatus as described in Section 3.1.2.2 was used in this study, and the same procedure for x-ray peak identification [4] was followed. Fig. 3.13 gives a series of x-ray diffractograms showing the possible reactions taking place among three components of sodium sulfate-masonry cement waste forms before and after water immersion testing. Comparison of diffractograms I, II and III in Fig. 3.13, indicates that typical peaks A, B, C, D, E, F of diffractogram III may be identified as calcium aluminum sulfate hydrate (ettringite), $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ [11].

It was determined by x-ray diffraction that in the presence of water the sulfate reacts with the free calcium hydroxide in masonry cement to form calcium sulfate, and with the hydrated calcium aluminate to form calcium aluminum sulfate hydrate (ettringite) [11]. The major chemical reactions that take place between the masonry cement and sodium sulfate are as follows:



Figure 3.11 A comparison of the effect of waste stream temperature on the stability of masonry cement samples containing 13 wt% NaSO_4 after water immersion for 14 days. The sample on the left was prepared with waste at 20°C, while the sample on the right was prepared at 77°C.



Figure 3.12 A comparison of the effect of waste stream temperature on the stability of portland type I cement samples containing 9 wt% NaSO_4 after water immersion for 14 days. The sample on the left was prepared with waste at 20°C , while the sample on the right was prepared at 77°C .

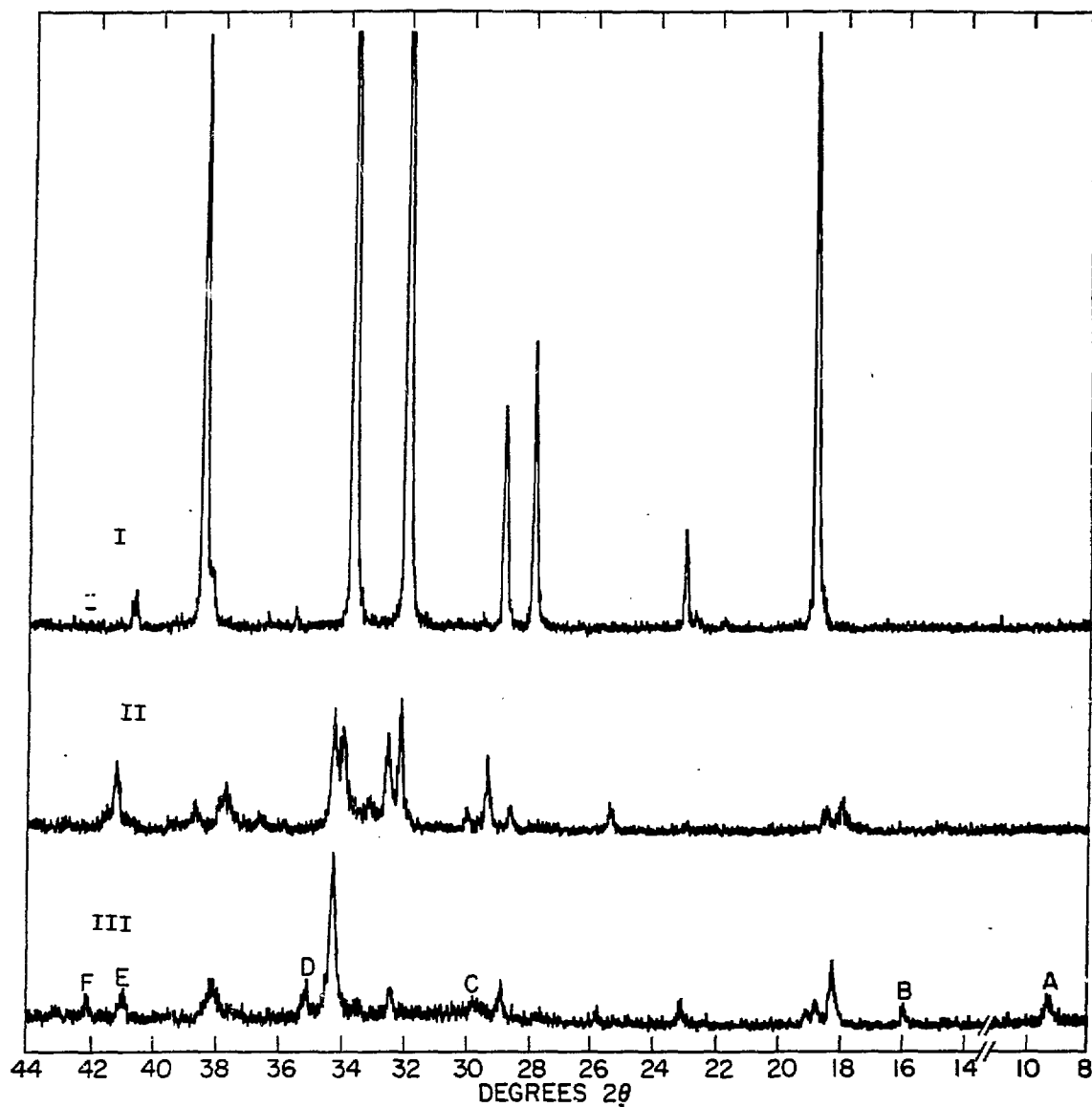
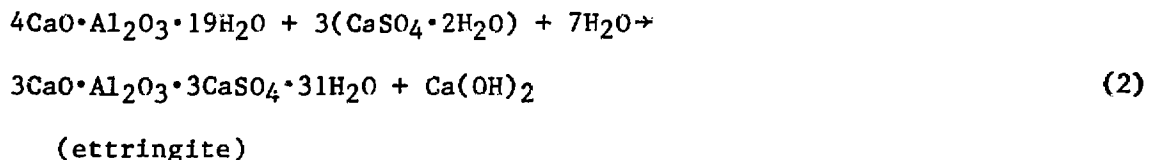


Figure 3.13 X-ray spectra comparing different components of a masonry cement-sodium sulfate waste form.

Spectrum I: sodium sulfate

Spectrum II: dry masonry cement

Spectrum III: masonry cement waste form (containing 9 wt% sodium sulfate) after water immersion tests.



The formation of calcium aluminum sulfate hydrate involves a volume increase because of its comparatively low density i.e., 1.73 g/cm³ as compared with an average of about 2.5 g/cm³ for the other hydration products of cement [12, 13] and thus, causes cracking and damage in set cement. Testing conducted for this study indicates that the presence of slaked lime in masonry cement intensifies degradation of sodium sulfate-masonry cement waste forms when immersed in water. An example is shown in Fig. 3.14. Fig. 3.11 has already shown that this phenomenon is further aggravated when the waste stream is mixed with masonry cement at elevated temperatures (77°C), as normally used at boiling water reactors. From this, it can be concluded that the use of masonry cement for the solidification of BWR sodium sulfate waste is problematic, particularly in view of waste form requirements, as set forth in the NRC Branch Technical Position Paper [10].

Since all the aqueous sodium sulfate-masonry cement formulation specimens containing more than 9 wt% sodium sulfate failed during the two week immersion test, further studies involving this system were abandoned. As a result of this failure, no attempt was made to test and evaluate other waste form properties.

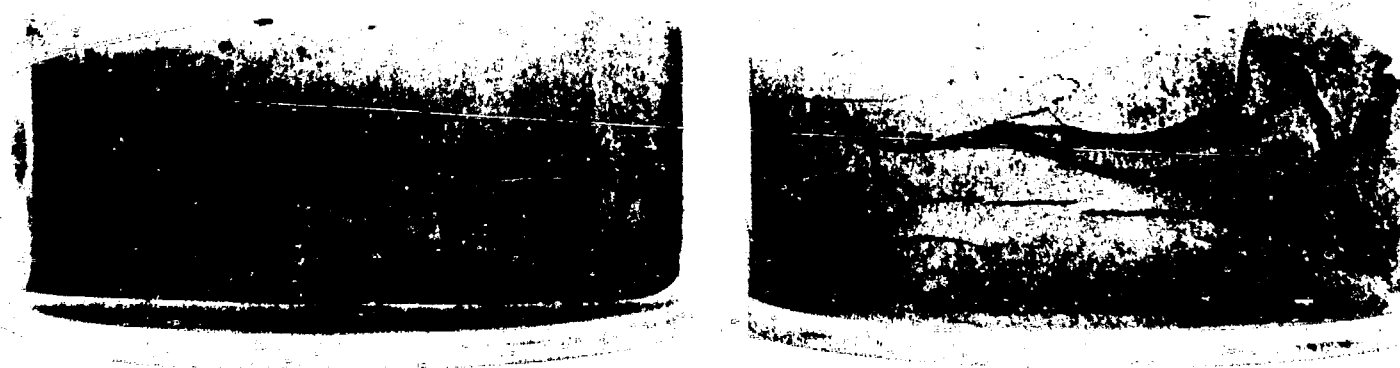
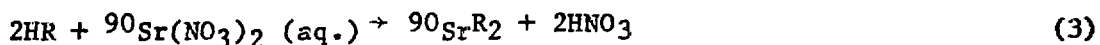


Figure 3.14 A comparison of the effect of cement type on the stability of samples containing 9 wt% NaSO_4 after water immersion for 14 days. The sample on the left is made with portland type I cement, while the sample on the right is made with masonry cement.

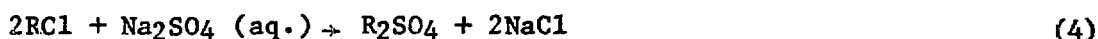
3.3 Spent Ion Exchange Resins

Ion exchange is a process in which cations and anions, dissolved in an electrolytic solution, are interchanged with ions in a solid phase. Ions exchange on a stoichiometrically equivalent basis with dissolved ions of the same charge. The structure of the solid phase ion exchanger is not permanently altered and the process is reversible (through regeneration), as demonstrated by the following typical exchange reactions:

Cation Exchange:



Anion Exchange:



where R represents the insoluble matrix of the exchanger. Equation (1) describes the removal of strontium-90 from a waste stream by cation exchange. Equation (2) describes the removal of sulfate by anion exchange.

Ion exchange resins are used extensively in light water reactors to remove impurities in the primary coolant. Dissolved ionic species in the coolant can lead to increased corrosion, higher radiation doses due to activation products and reduced neutron efficiency. Typically, reactor resin beds are replaced when either: 1) their exchange capacity can no longer be restored through chemical regeneration or 2) they present a significant radiation dosage hazard to plant personnel.

3.3.1 Simulation of Spent Reactor Ion Exchange Resins. Previous studies [14] indicated that both resin type and loading affect the solidification of ion exchange resin with cement. Loaded mixed bed (cation:anion=2:1 by weight) bead type the ion exchange resins were utilized in this study so as to simulate the reactor waste without using "hot" (radioactive) resins.

As-received Nuclear Grade Amberlite cation (IRN-77) and anion (IRN-78) ion exchange resins, manufactured by Rohm and Haas Co., Philadelphia, PA, were rinsed by demineralized water. The cation resin was batch loaded in a solution containing sodium chloride, calcium chloride and aluminum nitrate to provide a mixture of single and multivalent ions. The quantity of each loading compound in solution was equal to the resin's total theoretical exchange capacity. Therefore, the quantity of ions present in the loading solution was three times in excess of what was theoretically needed to satisfy the resin's exchange capacity. After soaking in this aqueous solution for at least 24 hours with occasional stirring, the resins were drained and rinsed five times with deionized water. Radioactive tracer studies show that by loading the cation resin in this manner, the loading efficiency is as high as 98% of the resin's theoretical exchange capacity. Anion resins were batch loaded in the same way using a loading solution consisting of sodium sulfate, sodium chloride and sodium nitrate. The interstitial water remaining in both cation and anion resins were removed using low pressure air [14]. After the interstitial water was removed, the resins were ready for formulation studies.

3.3.2 Formulation Studies. The same criteria as described in Section 3.1.2 were applied in this study. A large number of specimens were prepared and tested to determine the range of acceptable formulations for the solidification of ion exchange resin waste in masonry cement. The ternary

compositional phase diagram developed for the solidification of loaded mixed bed bead resin with masonry cement is shown in Fig. 3.15. This diagram expresses formulations in terms of weight percentages of cement, dry resin and total water. Typical resin waste, however, is either dewatered and contains up to 70 wt% water, or is in the form of a resin slurry which contains as much as 80 wt% water. A procedure which enables the adaptation of information contained in Fig. 3.15 to any given bead resin waste stream is described in Reference [14].

Formulation studies indicated that loaded mixed bed bead ion exchange resins can be solidified in masonry cement to approximately 10 dry wt% (equivalent to 22% of wetted resin) without failure when immersed in water for periods of several weeks. This is approximately the same loading as that can be obtained with ordinary portland cements [14].

3.3.3 Waste Form Properties. As discussed in Section 3.1.2, all the formulation specimens which were successfully solidified, i.e. which were workable, free standing monolithic solids with no drainable free standing water, were evaluated further to determine relevant waste form properties, as reported in Section 3.1.3.

3.3.3.1 Water Immersion. The results of water immersion testing for loaded mixed bed bead ion exchange resins-masonry cement waste forms are included in Fig. 3.15. The slightly shaded area in Fig. 3.15 shows that not all the specimens which were formulated successfully passed the two week water immersion test. Waste forms containing more than 10 dry wt% resin waste in masonry cement lost their integrity during water immersion testing. Figure

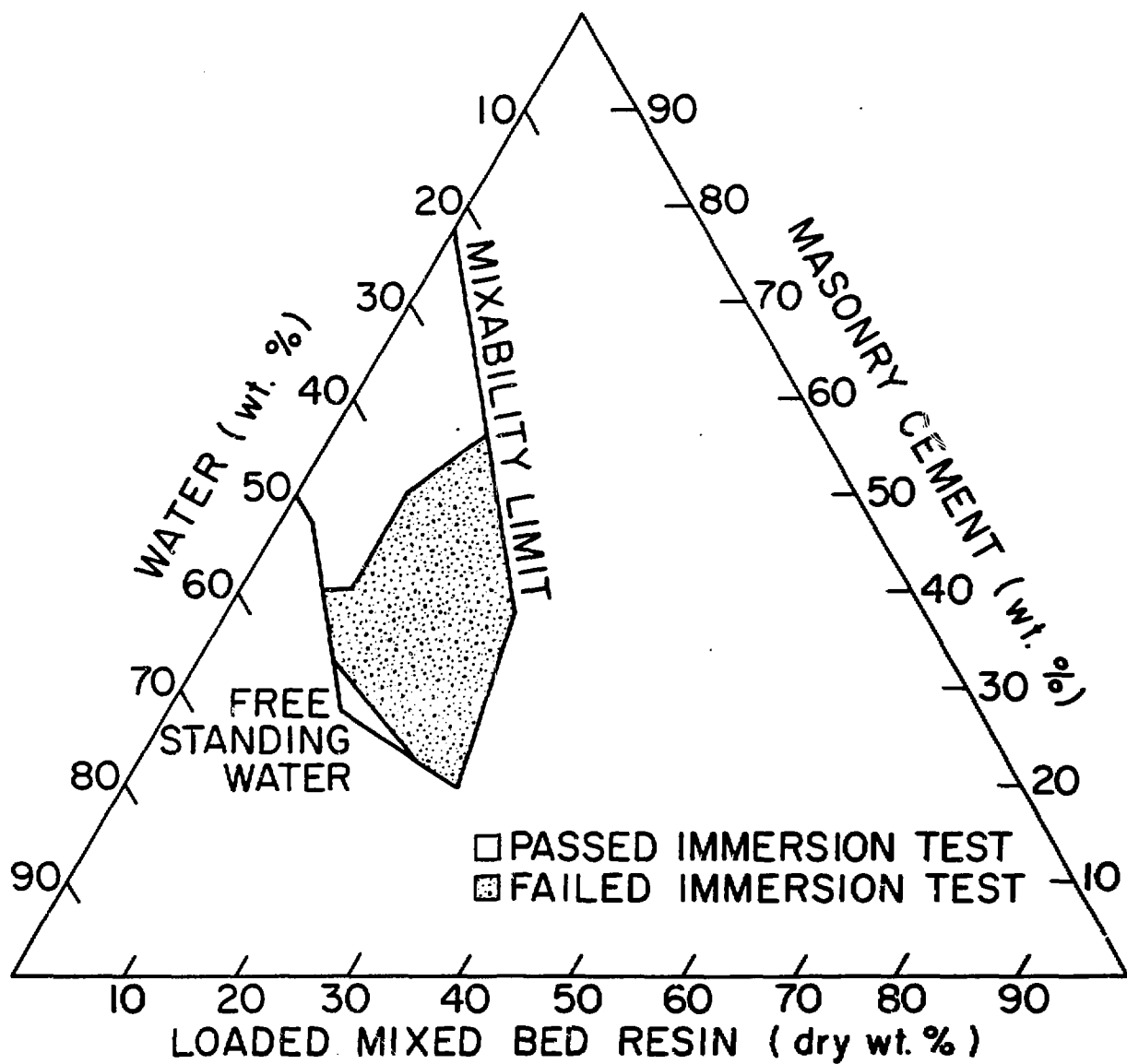


Figure 3.15 Ternary compositional phase diagram for the solidification of loaded mixed bed bead ion exchange resins with masonry cement.

3.16 shows the results of a two week water immersion test for masonry cement waste forms containing 3 and 25 dry wt% resin waste. The waste form containing 25 dry wt% resin displayed excessive swelling and cracking while the 3 dry wt% waste form remained intact.

The loss of waste form integrity can be attributed to resin shrinking/swelling due to competition between the cement and resin for water and/or to the adsorption of soluble cement species by the resin during the setting and hardening of the cement waste form [14].

3.3.3.2 Compressive Strength. The compressive strength of loaded mixed bed, bead type ion exchange resin-masonry cement waste forms was tested in accordance with the ASTM method C 39-72, "Test for the Compressive Strengths of Cylindrical Concrete Specimens" [8].

Compression test results of spent ion exchange resins-masonry cement waste forms are also summarized in Table 3.3.

As described in Section 3.1.3.2, all the waste types tested in this investigation have a negative effect on the compressive strength of masonry cement. Compressive strength of spent ion exchange resin-masonry cement waste forms is inversely proportional to resin loading through the range of dry resin weight percentage from 0 to 15 dry wt%.

3.3.3.3 Leachability. For the purpose of leachability studies, loaded mix bed, bead type ion exchange resin (in the weight proportion of: cation:anion = 2:1) were used for ion exchange resin waste forms, but only cation resin was spiked with radioactive isotopes. Cation exchange resin was chemically and radiochemically loaded simultaneously. Stable cesium chloride,



Figure 3.16 Results of a 14 day water immersion test on masonry cement samples containing loaded bead type ion exchange resin. The sample on the left contains 25 dry wt% resin, while the sample on the right contains 3 dry wt%.

strontium chloride and cobalt chloride solutions were prepared at concentrations such that each single aliquot offered the same milliequivalence of cations as 20% of the resin's theoretical exchange capacity. Stable loading solutions were mixed with radioactive tracers, then a measured amount of "as received" cation resin IRN-77 was added. The resultant resin slurry was stirred occasionally and put aside for at least 24 hours. The cation resin was chemically loaded to approximately 60% of its theoretical exchange capacity. Radionuclide uptake was 98%. As described in Section 3.1.3.3.2, Cs-137, Sr-85 and Co-60 were used in the proportion of one to three to ten i.e., 4.52 μ Ci of Cs-137, 13.41 μ Ci of Sr-85 and 41.34 μ Ci of Co-60. Duplicate samples were leach tested in accordance with the proposed ANS 16.1 test [9] extended to 53 days duration. Leach test specimens were right cylinders with a diameter of 4.7 cm, and a height of 6.8 cm.

Figure 3.17 shows the cumulative fraction releases of Cs-137 and Sr-85 from a masonry cement waste form containing 5 wt% dry ion exchange resin. A comparison of the radionuclide cumulative fraction releases for masonry cement-ion exchange resin waste forms with those obtained using plain masonry cement (Figure 3.6) clearly indicates the improved retention capabilities attributed to the ion exchange resin. This is illustrated in Figure 3.18 which compares leaching of Co-60 from masonry cement waste forms with and without ion exchange resin. Increasing the ion exchange resin wt% from 0 to 5 results in 0.7, 2 and 100 fold decrease of cumulative fraction release for Cs-137, Sr-85 and Co-60 respectively, at the end of 53 days. The data in Figures 3.17 and 3.18 also show that the leachability of Cs-137 is more than two orders of magnitude greater than that of Co-60 from a masonry cement waste form containing 5 wt% dry ion exchange resins, which is typical of cement waste forms.

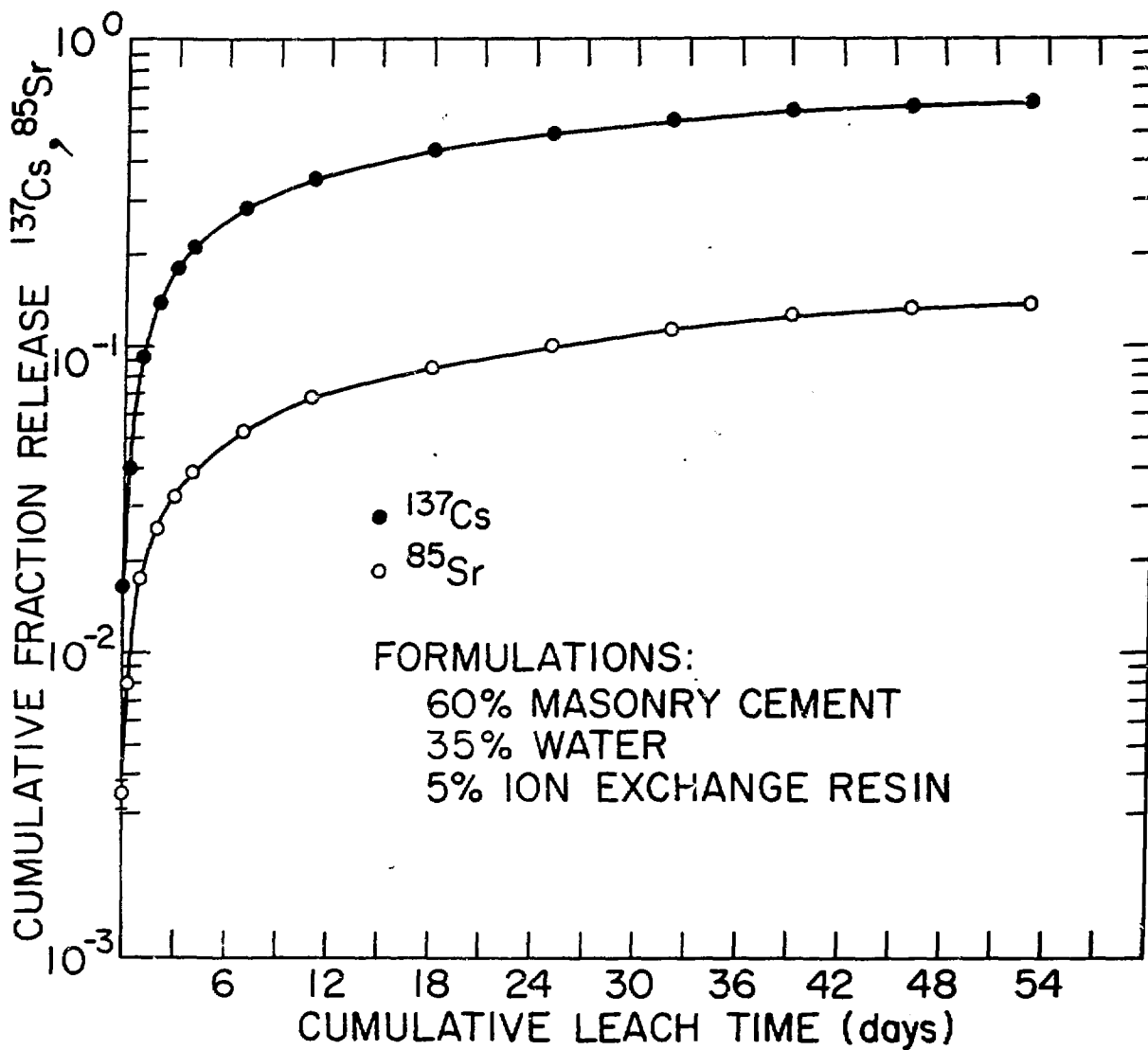


Figure 3.17 Cumulative fraction release of ^{137}Cs and ^{85}Sr from masonry cement waste form containing 5 wt% dry ion exchange resin.

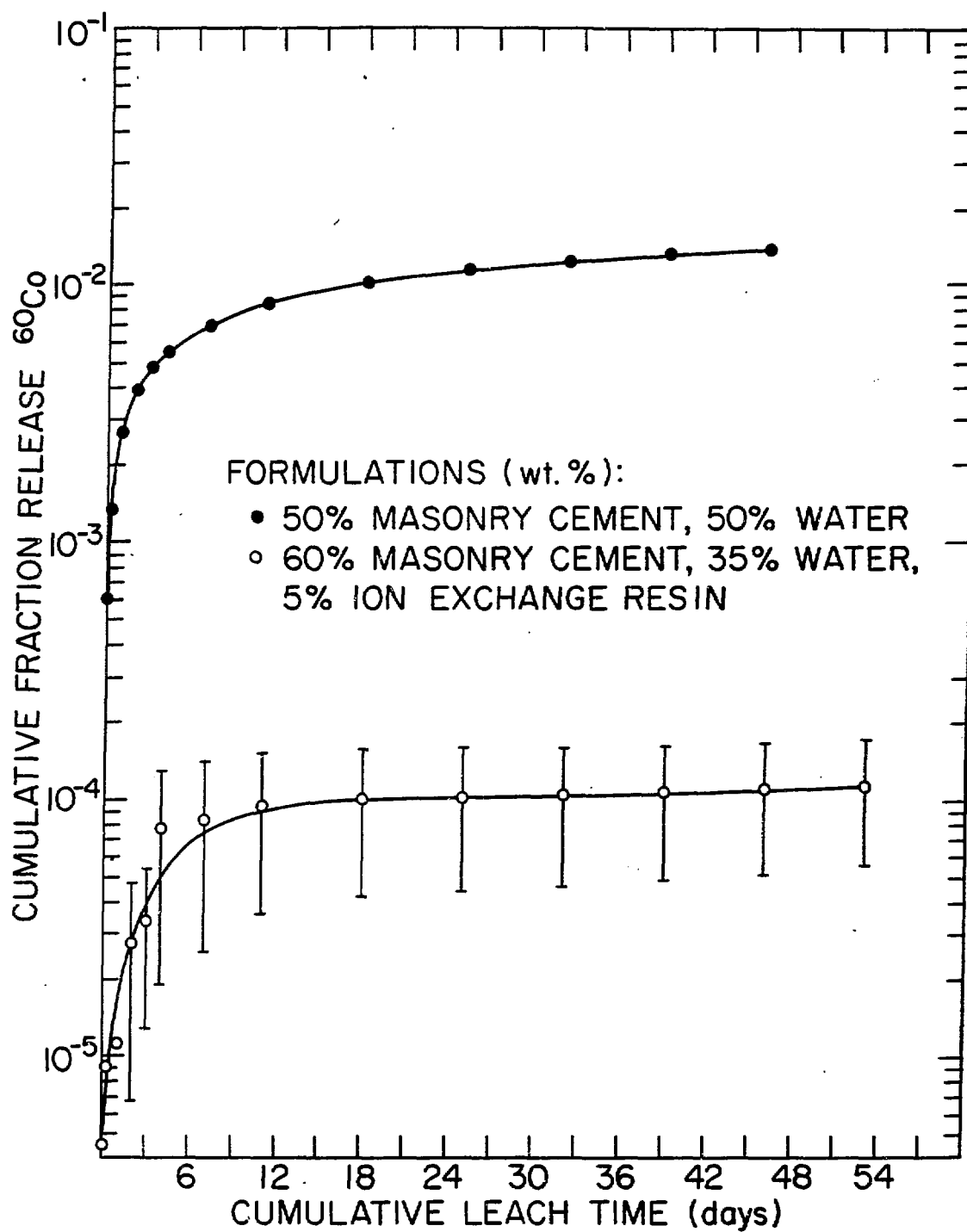


Figure 3.18 Cumulative fraction release of ^{60}Co from masonry cement waste forms with and without ion exchange resin.

Figures 3.17 and 3.18 show that the leachability of an ion exchange resin-masonry cement waste form containing 5 wt% dry waste is different than that of a boric acid waste form with the same dry waste percentage (see Fig. 3.6). At the end of the test, leachability of Cs-137, Sr-85 and Co-60 from an ion exchange waste form was 0.7, 2 and 400 times lower, respectively, than that from a boric acid waste form.

3.4. Incinerator Ash

As a large fraction of solid low-level radioactive waste consists of combustible materials, incineration is regarded as an attractive option to attain high volume reduction. Typically, combustible wastes are of very low activity. However, when volume reduction factors as high as 100:1 are achieved, the ash residue which remains can contain considerable activity. From the standpoint of handling, transportation and disposal, the solidification of ash to reduce the potential for dispersion is prudent.

3.4.1 Rotary Kiln Incinerator Ash. Incinerator ash produced by the rotary kiln incinerator developed at the Rockwell International Rocky Flats plant was utilized for this investigation. This incinerator was used to burn a non-radioactive waste feed whose composition is representative of the combustible low-level wastes generated at the plant. A typical waste feed composition is listed in Table 3.6.

The feed rate to the incinerator for waste solids was 6.8 kg/hr; waste liquids were fed at a rate of 0.45 liter/hr. The incinerator was operated at a temperature of $1000^{\circ}\text{C} \pm 100^{\circ}\text{C}$ with an after-burner temperature of $1400^{\circ}\text{C} \pm 100^{\circ}\text{C}$. The chemical composition of the resultant ash, as measured by DC arc emission spectroscopy, is shown in Table 3.7. Confidence

Table 3.6

Rotary Kiln Feed Composition

<u>Constituent</u>	<u>Weight %</u>
Paper	40.0
Polyethylene	22.8
Neoprene	18.8
Kerosene	9.5
Polyvinyl Chloride	7.9
Tributyl Phosphate	1.0

limits for this analysis are approximately +10% for concentrations above one weight percent and +50% for lower concentrations. While the silicon content of the ash is listed as >10 wt%, an analysis at the Rocky Flats plant gave a silicon content of 15 wt%. The elements listed, with the exception of carbon, are largely present as oxides. The ash contained no significant radioactivity content above background levels. The rotary kiln ash has a bulk density of approximately 0.23 g/cm³. It has a visual appearance similar to cigarette ash (gray-white in color), but exhibits color gradations and has carbon present as a distinct particulate. In the presence of water the ash exhibits a pH of approximately 6.

3.4.2 Formulation Studies. The same criteria as described in Section 3.1.2 were applied in this study to determine the range of acceptable formulations for the solidification of incinerator ash in masonry cement.

Formulation specimens of incinerator ash were prepared and tested in the same way as described in Section 3.1.2.1 except that weighed quantities of

Table 3.7

Rotary Kiln Incinerator Ash Compositional Analysis

<u>Element</u>	<u>Weight %</u>
Al	18
C	13.1
Si	>10
Ca	5
Ti	4.8
Zn	2.6
Mg	1
Na	0.5
Fe	0.3
K	0.1
Ni	0.1
Cu	0.08
Cr	0.05
Sr	0.05
Mn	0.03
Pb	0.03

room temperature water was added separately instead of 77°C water. After mixing for 2 minutes at a speed of approximately 120 rpm, formulation specimens were cast into 3.1 cm diameter cylindrical polyethylene containers with a sample height of approximately 6.3 cm. These smaller sample sizes were necessary because of the limited amount of rotary kiln incinerator ash available.

Fig. 3.19 is a ternary compositional phase diagram developed for the solidification of the rotary kiln incinerator ash with masonry cement. Formulations which successfully met the criteria outlined in Section 3.1.2. were obtained which incorporate as much as approximately 40 wt% incinerator

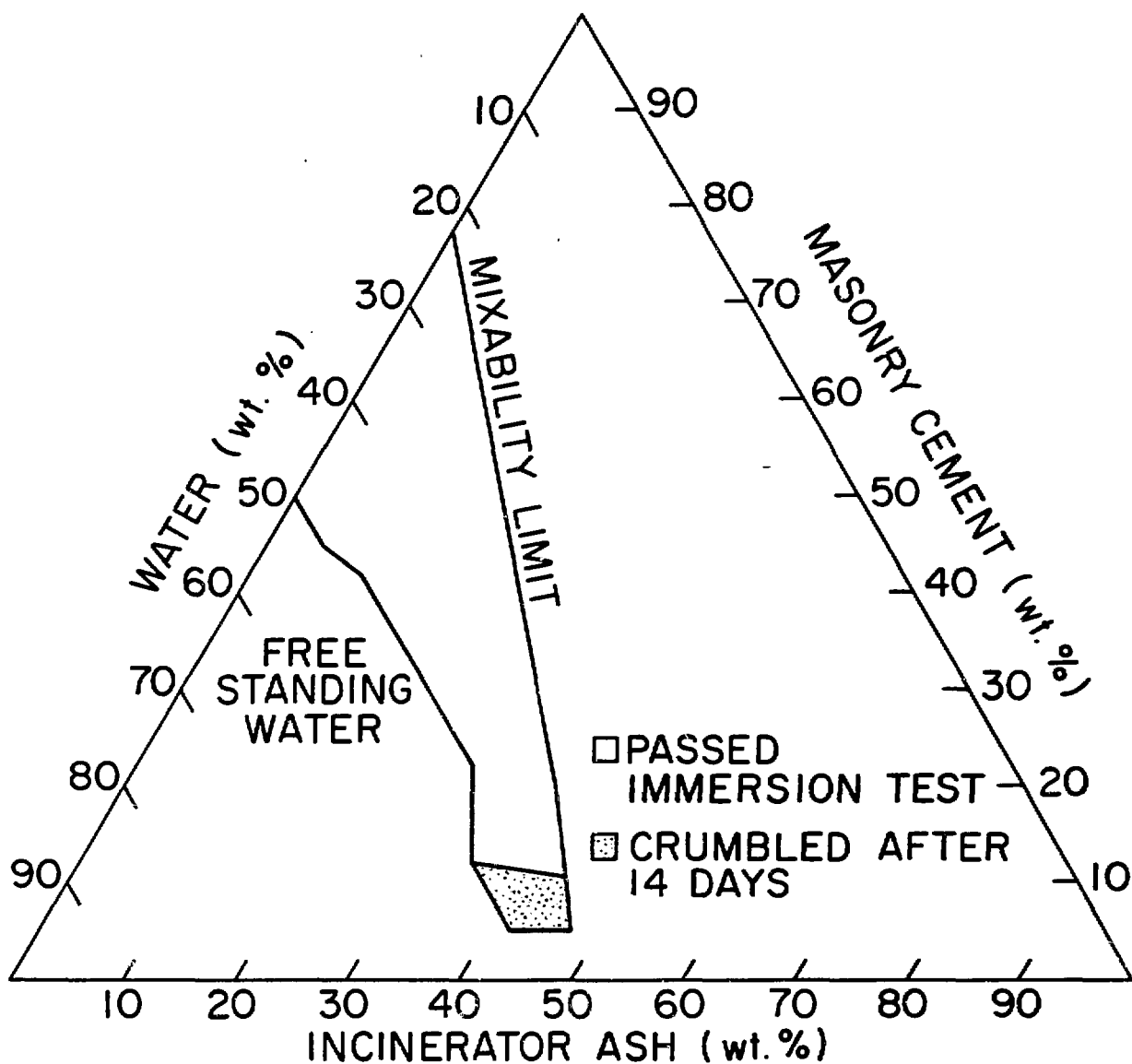


Figure 3.19 Ternary compositional phase diagram for the solidification of as-received rotary kiln incinerator ash with masonry cement.

ash using approximately 10 wt% masonry cement. The unshaded envelope in Fig. 3.19 represents this formulational region. Some specimens were solidified using as little as 10 wt% masonry cement but these samples were extremely friable and tended to crack upon removal from their preparation containers. These formulations fall in the slightly shaded envelope in Fig. 3.19.

3.4.3 Waste Form Properties. As discussed in Section 3.1.2, all the formulation specimens which were successfully solidified i.e, which were workable free standing monolithic solids with no drainable free standing water, were evaluated further to determine relevant waste form properties, as reported in Section 3.1.3.

3.4.3.1 Water Immersion. The results of water immersion testing for the rotary kiln incinerator ash-masonry cement waste forms are included in Fig. 3.19. The unshaded envelope in Fig. 3.19 shows that all the specimens which successfully met the solidification formulation criteria outlined in Section 3.1.2 passed two week water immersion test.

3.4.3.2 Compressive Strength. The compressive strengths of incinerator ash-masonry cement waste forms were tested in accordance with the ASTM method C 39-72, "Test for the Compressive Strength of Cylindrical Concrete Specimens" [8]. Specimens were cast in 4.7 cm diameter cylindrical polyethylene vials and the length of specimens were within 1.8 to 2.2 times their diameter.

Compressive strength values of incinerator ash-masonry cement waste forms are shown in Table 3.3. Compressive strength of plain masonry cement is also listed in Table 3.3 for comparison. Table 3.3 shows that incinerator ash had

the smallest effect on the waste form's compressive strength than any of the other wastes tested in this study. For 10 wt% dry waste loading, incinerator ash, ion exchange resin and boric acid decrease the compressive strength of plain masonry cement (with the same water wt%) by 20%, 45% and 60% respectively.

4. CONCLUSIONS

Based on the formulation development and waste form property evaluation conducted for this investigation, several conclusions can be drawn.

1). Masonry cement can successfully incorporate up to approximately 15 wt% dry boric acid (PWR evaporator concentrate) waste. As a means of comparison, as little as 5 wt% dry boric acid waste will inhibit the curing of a portland type I waste form. A small formulational envelope (shown in Fig. 3.2) allows up to 60 wt% dry boric acid to be solidified into masonry cement under certain conditions.

2). Incorporation of sodium sulfate (BWR evaporator concentrate) waste in masonry cement is less straightforward. Although successful formulations containing as much as 40 wt% Na_2SO_4 can be prepared, these specimens undergo catastrophic failure in the presence of an aqueous environment. Only those samples with loadings less than 7 wt% dry sodium sulfate survive water immersion testing.

Testing conducted for this study indicates that slaked lime present in masonry cement aggravates degradation of sodium sulfate-masonry cement waste forms when immersed in water. This phenomenon is further aggravated when the sodium sulfate waste stream is mixed with masonry cement at elevated temperature (77°C), as normally used at boiling water reactors. Therefore, the use of masonry cement for the solidification of BWR sodium sulfate waste

is problematic, particularly in view of waste form requirements as set forth in the NRC Branch Technical Position Paper [10].

3). Loaded mixed bed bead type ion exchange resins can be solidified in masonry cement in moderate quantities i.e., approximately 10 dry wt% (equivalent to 22 wt% of wetted resin) without failure when immersed in water for a period of two weeks. This is roughly equivalent to the behavior of ordinary portland cement, as reported in earlier work [14].

4). Satisfactory formulations can be developed which incorporate as much as 40 wt% incinerator ash using approximately 10 wt% masonry cement. This loading is comparable to data found for ordinary portland cements [15].

5). Leachability of radionuclides (Co-60, Sr-85 and Cs-137) is generally consistent for each isotope through the range of boric acid concentration from 5 to 15 wt%.

6). Leaching of Co-60, Sr-85 and Cs-137 from waste forms containing 5 wt% dry resins is significantly less than leaching from plain masonry cement.

7). Leachability of Cs-137 is approximately two orders of magnitude greater than that of Co-60 from both boric acid-masonry cement waste forms and ion exchange resin-masonry cement waste forms, which is typical of ordinary portland cement waste forms.

8). Among all the waste types tested, boric acid decreases waste form compressive strength the most, while incinerator ash has the smallest effect on compressive strength of masonry cement waste forms.

In conclusion, masonry cement appears to be a useful solidification agent for several types of low-level radioactive waste. It should be noted that no solidification material, either among those currently in use or those proposed for future use, has been demonstrated to be applicable for all types of low-level radioactive waste.

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