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SOLIDIFICATION OF RADIOACTIVE WASTE IN A CEMENT/LIME MIXTURE *

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ABSTRACT

The suitabilty of a cement/lime mixture for use as a solidification agent for different types of wastes was investigated. This work includes studies directed towards determining the waste/ binder compositional field over which successful solidification occurs with various wastes and the measurement of some of the waste form properties relevant to evaluating the potential for the release of radionuclides to the environment. In this study, four types of low-level radioactive wastes were simulated for incorporation into a cement/lime mixture. These were boric acid waste, sodium sulfate waste, ion exchange resins and incinerator ash.

INTRODUCTION

Cement/lime mixtures are commercially available as "masonry cement" and consist mainly of hydrated (slaked) lime ($Ca(OH)_2$) and 50 percent by weight of portland type I cement. The use of masonry cement was originally suggested to overcome the inhibiting properties of boric acid. However, it has also been recommended for solidifying sodium sulfate waste and ion exchange resins. The main objective of this study is to assess the suitability of masonry cement for the solidification of several types of wastes along with boric acid wastes.

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 waste forms.

Specimen formulations which were successfully solidified were further tested to evaluate the following waste form properties:

1) Effects of aqueous media, i.e. water immersion

2) Compressive strength[1]

3) Leachability[2]

BORIC ACID WASTE

Typical concentrations of boric acid waste from forced recirculation evaporators are about 12 wt%. The temperature of the waste as it is mixed with cement is approximately 77°C[3]. In this work the range of boric acid concentrations tested are between 12 and 25 wt%. This range reflects the maximum concentrations of boric acid which are commonly present in effluent from current technology evaporators. Based on the formulation development, the maximum waste to binder ratio (by weight) is 1.0 (wet boundary), whereas the recommended waste to binder ratio (by weight) is 0.8.

In pursuit of higher volume reduction factors, future waste streams will likely be further evaporated so that the final waste product contains as much as 100% dry solids. Therefore, simulated dry evaporator bottoms have been included for investigation. Figure 1 is the ternary compositional phase diagram for the production of acceptable dry boric acid waste forms with masonry cement. This diagram also indicates formulational 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. Envelopes of those formulations which cured within fourteen days after preparation and passed a two week water immersion test are indicated by the unshaded sections. Those formulations which didn't cure within fourteen days after preparation at room temperature are indicated by the lightly shaded area.

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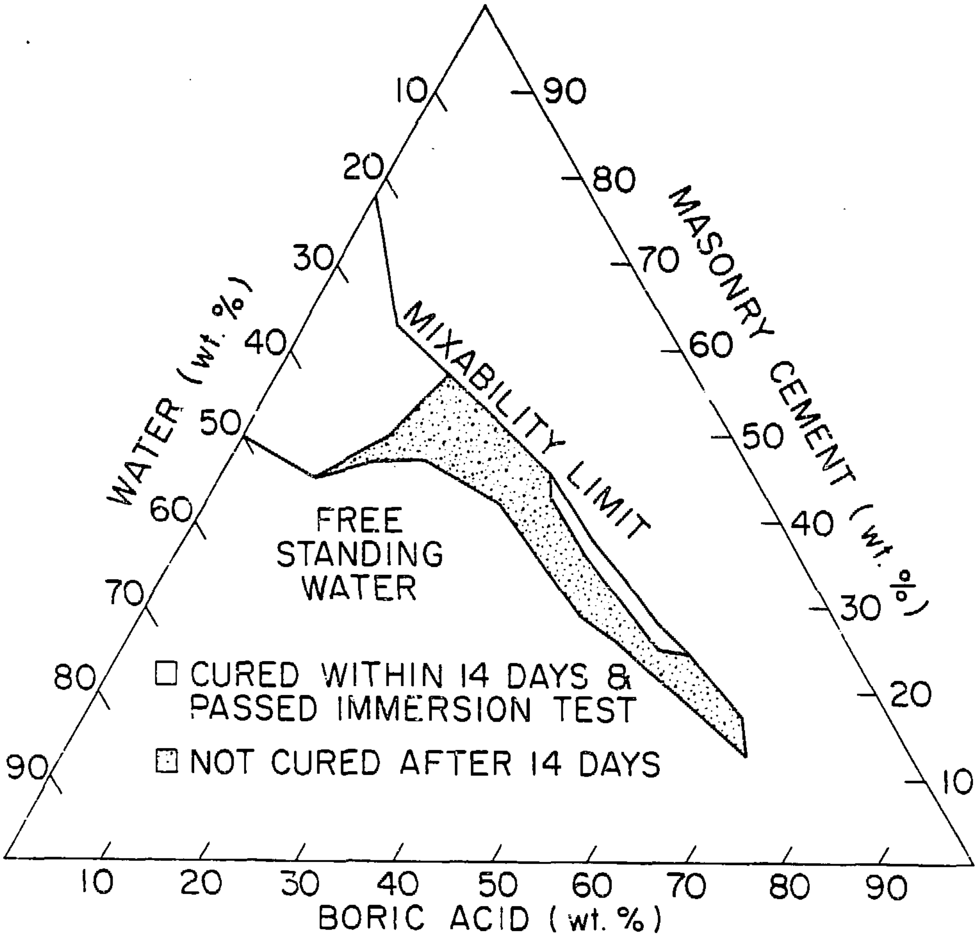

Fig. 1 Ternary compositional phase diagram for the solidification of boric acid waste (PWR dry evaporator bottoms) with masonry cement.

The larger unshaded area in Fig. 1 shows that approximately 15 wt% dry boric acid can be incorporated successfully into masonry cement. 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 eliminate any inhibiting effects using masonry cement the boric acid is added in molar concentrations equal to or less than the molar concentration of the alkali in the cement. Formulation specimens containing 15 wt% dry boric acid have a molar ratio of acid to base approximately equal to 1. The lightly shaded area in Fig. 1 represents the region in which the equal molar concentration law is broken. Here the inhibiting properties of boric acid dominate, and most of the formulation specimens failed to cure within fourteen days of preparation. The mechanisms of this failure are discussed in Reference 4.

It is interesting to note the smaller unshaded area in Fig. 1. Jumping across the "curing gap" (the lightly shaded area), formulation specimens in the smaller unshaded area appeared to be cured. This region includes dry boric acid loadings ranging from 35 wt% to as high as 60 wt%. 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 assurance.

Boron leachability was chosen as an indicator of masonry cement-boric acid waste form skeleton solubility. Leachability was measured using the proposed ANS 16.1 Standard Leach Test[2] extended to 56 days duration. Boron concentrations in the leachant were determined by means of a Perkin-Elmer 4000 Atomic Absorption Spectrophotometer. Results are shown in Table I for cumulative fraction releases of boron from waste forms fabricated under different conditions. Some were made using water at room temperature and others with water at 77°C to simulate actual temperatures of waste slurries. Cumulative fraction releases were slightly less for those samples made at room temperature. Analysis of these leachants for pH showed that pH values remained constant, approximately 12, over the course of the experiment for all samples. This indicates that in all cases an excess of alkali was present to overcome effects of the boric acid leaching out of the waste form.

The leachability of radionuclides from solidified boric acid waste forms was also measured according to the proposed ANS 16.1 Standard Leach Test[2]. The samples were spiked with ^{137}Cs, ^{85}Sr and ^{60}Co. Results are shown in Table I. Leachability of radionuclides was generally consistant for each isotope through the range of boric acid concentration from 5 to 15 wt%.

For masonry cement waste forms containing up to 15 wt% boric acid, the leachability index[2] for ^{85}Sr, ^{137}Cs and ^{60}Co was calculated to be 7.5, 6.2 and 9.0 respectively. In all cases these values exceed the minimum values for the leachability index given by the Nuclear Regulatory Commission[5].

Table II shows compressive strength values for masonry cement waste forms over a range of waste/binder ratios. Boric acid decreases the waste form's compressive strength more drastically as compared to incinerator ash and ion exchange resin. The compressive strength of a masonry cement-boric acid waste form containing 50 wt% masonry cement, 40 wt% water (77°C) and 10 wt% dry boric acid is 2.43 MPa, corresponding to 18% of the compressive strength obtained from waste forms consisting of plain masonry cement.

SODIUM SULFATE WASTE

Typical BWR regenerative waste from forced recirculation evaporators contain approximately 23 wt% sodium sulfate at a temperature of 77°C[3]. Simulated aqueous wastes containing 25-50 wt% sodium sulfate were utilized in this study. Although specimens containing as much as 40 wt% sodium sulfate can be prepared, waste forms containing more than 7 wt% sodium sulfate undergo catastrophic failure in an aqueous environment. Waste form volume increase is so severe that swelling, cracking, exfoliation and crumbling was observed during the first two weeks of water immersion. Figure 2 is a ternary compositional phase diagram showing the formulational boundaries within which waste forms can be prepared.

In comparison, under identical conditions waste forms made with 9 wt% sodium sulfate and portland type I cement survived water immersion with only little damage while a 7 wt% sodium sulfate and masonry cement sample failed catastrophically.

Temperature at which the waste was added to the cement also had a significant effect. Waste forms made with room temperature water and dry waste were much less likely to fail immersion tests than those samples fabricated with water at 77°C.

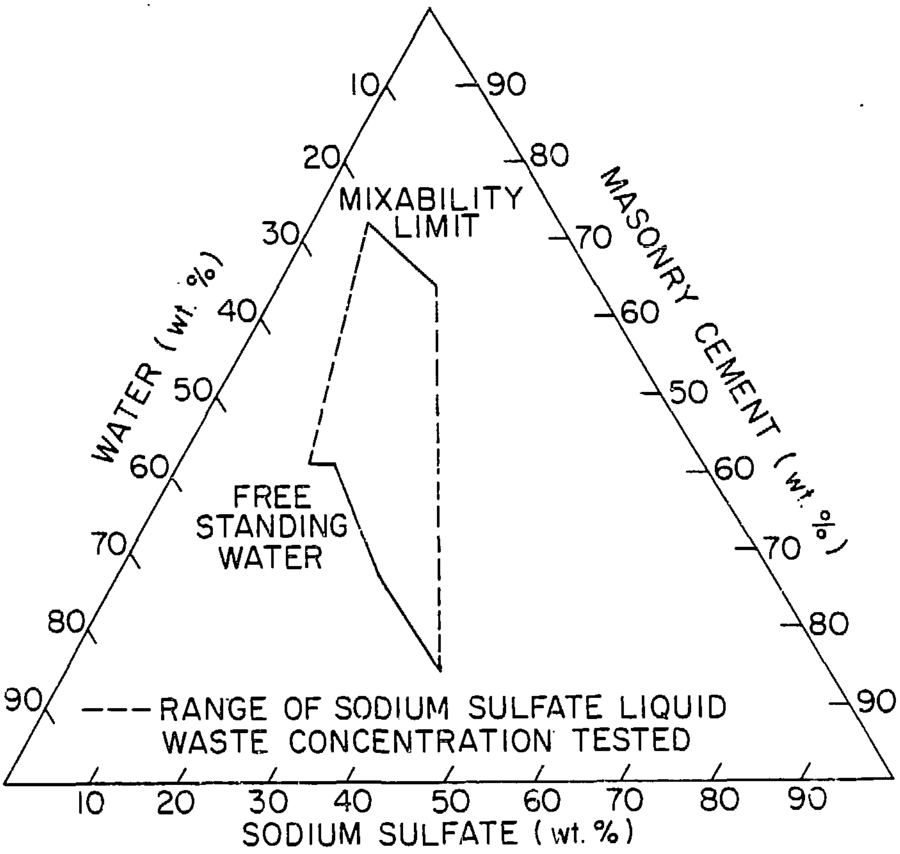

Fig. 2 Ternary compositional phase diagram for the solidification of sodium sulfate waste (BWR wet evaporator bottoms) with masonry cement.

TABLE 1

Cumulative Fraction Releases of Typical Masonry Cement Waste Forms

Waste Forms	Dry Waste Wt %	Sr	Co	Cs	B
Plain Masonry Cement	0	0.279	0.014	0.879	—
Masonry Cement and Boric Acid (at 22°C)	5	0.325	0.042	0.899	0.073
	10	0.253	0.044	0.891	0.137
	15	0.227	0.038	0.866	0.134
Masonry Cement and Boric Acid (at 77°C)	5	—	—	—	0.092
	10	—	—	—	0.185
Masonry Cement and Ion Exchange Resins	5	0.137	0.0002	0.624	—

TABLE II

Compressive Strength of Typical Masonry Cement Waste Forms

Waste Forms	Cement Wt %	Water Wt %	Dry Waste Wt %	Compressive Strength, MPa	Compressive Strength Ratio*
Plain Masonry Cement	65	35	0	20.6	—
	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°C)	5	3.74	0.43
	50	40	10	5.32	0.40
	50	40 (77°C)	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	0.80
	50	35	15	15.0	0.73
	60	35	5	19.7	0.96
	55	35	10	16.8	0.81

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

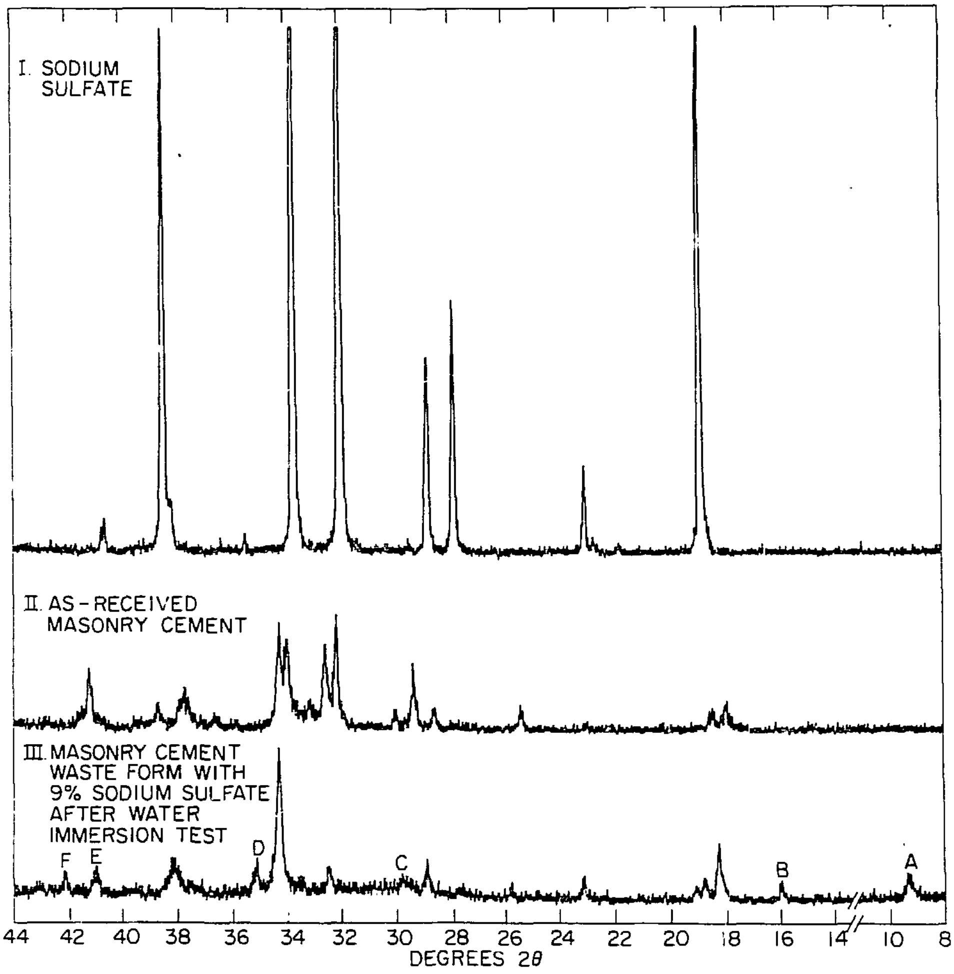

Fig. 3 X-ray diffractograms comparing different components of masonry cement-sodium sulfate waste form. Peak A, B, C, D, E, F of spectrum III are typical of calcium aluminum sulfate hydrate.

Figure 3 gives a series of x-ray diffractograms showing the possible reactions taking place among three components of masonry cement-sodium sulfate waste forms before and after water immersion testing.

It was determined by x-ray diffraction that in the presence of water the sulfates react 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)[6]. The major chemical reactions that take place between the masonry cement and sodium sulfate are as follows:

$$Ca(OH)_2 + Na_2SO_4 \cdot 10H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH + 8H_2O \quad (1)$$

$$4CaO \cdot Al_2O_3 \cdot 19H_2O + 3(CaSO_4 \cdot 2H_2O) + 16H_2O \rightarrow$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O + Ca(OH)_2 \quad (2)$$

The formation of calcium aluminum sulfate hydrate involves a volume increase because of its comparitively low density, i.e., 1.73 g/cm^3 as compared with an average of about 2.5 g/cm^3 for the other hydration products of cement[7], and thus causes cracking and damage in set cement. This phenomenon is known as sulfate attack on cement. Testing conducted for this study indicates that sodium sulfate present in sodium sulfate-masonry cement waste forms aggravates sulfate attack on cement. This is further aggravated when the waste stream is introduced to the concrete at elevated temperatures (77°C), as normally used at BWRs. Therefore, the use of masonry cement for solidification of BWR sodium sulfate waste is problematic.

ION EXCHANGE RESINS

Loaded mixed bed 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 for ordinary portland cements.

The samples were spiked with ^{137}Cs, ^{85}Sr and ^{60}Co. The leachability for ^{137}Cs was more than two orders of magnitude greater than that of ^{60}Co, which is typical for all types of portland cement waste forms. Comparison of the cumulative fraction releases of the three radionuclides from waste forms containing 5 wt% of ion exchange resin with releases from plain masonry cement (Table I) indicates that the former retain all radionuclides significantly better.

INCINERATOR ASH

Satisfactory formulations have also been developed which incorporate as much as 40 wt% incinerator ash in masonry cement. This loading is comparable to data found for portland cements.

Compressive strength values of masonry cement-incinerator ash waste forms are shown in Table II. This waste type had the smallest effect on compressive strength than any waste tested. Fifteen weight percent incinerator ash incorporated in masonry cement reduced compressive strength by 27%.

CONCLUSIONS

Several conclusions can be drawn from this study.

1) Boric acid waste can be incorporated into masonry cement with loadings up to 15 wt% of the samples. However, a small formulational envelope allows up to 60 wt% boric acid to be solidified under certain conditions.

2) Although 40 wt% Na_2SO_4 can be incorporated in masonry cement, only those samples with loadings less than 7 wt% survive immersion tests.

3) Leaching of ^{60}Co, ^{85}Sr and ^{137}Cs from waste forms containing 5 wt% mixed bed ion exchange resin was significantly less than leaching from plain masonry cement.

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