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PHYSICAL PROPERTIES OF SALTSTONE:
A SAVANNAH RIVER PLANT WASTE FORM

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A SAVANNAH RIVER PLANT WASTE FORM

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ABSTRACT

A cement-based waste form, "saltstone," has been designed for disposal of Savannah River Plant low-level radioactive salt waste. Laboratory and field tests indicate that this stabilization process greatly reduces the mobility of all of the waste constituents in the surface and near-surface environment. Bulk properties of this material have been tailored with respect to salt leach rate, permeability, and compressive strength. Microstructure and mineralogy were characterized by SEM and x-ray diffraction analyses.

Compressive strength was found to increase as the water to cement ratio decreased. Porosity and mean pore size increased with increasing water to cement ratios. Bulk diffusivities of the various ions dissolved in the pore solutions were also found to increase as water to cement ratios increased.

INTRODUCTION

Experiments to develop a cement-based waste form, saltstone, for Savannah River Plant (SRP) low-level salt waste are in progress. Data for two formulations are presented in this paper to illustrate the range in properties of formulations being tested. A discussion of leaching data and mechanisms for these two materials is presented by Barnes, et al. [1].

The saltstone material must be designed to meet requirements for processing, emplacement, and performance. Acceptable slurry and cured material properties are listed by Langton, et al. [2]. The waste form must also be durable under the conditions of the disposal environment.

In the current SRP reference process, saltstone will be processed using conventional high-volume grout mixing equipment. It will be pumped through a pipeline and emplaced in trenches excavated above the water table and below grade [3].

EXPERIMENTAL PROCEDURE

Simulated SRP waste was used in this study. The composition of the solution is shown in Table I. Properties of the current SRP reference formulation, designated here as mix 84-40, and test mix 84-41 were measured. Ingredients in these waste forms are shown in Table II. Slurries were mixed in a Hobart mixer with whip attachment. ASTM mixing procedures were followed except that the slurries were stirred for an additional 20 minutes to simulate field practices. Mixing was done at room temperature and samples were cured at 38°C and 100% relative humidity.

TABLE I

Composition of Simulated
SRP Waste Solution

Component	Wt %
H ₂ O (deionized)	69.00
NaNO ₃	17.05
NaNO ₂	4.26
NaOH	4.60
NaAlO ₂	2.74
Na ₂ SO ₄	2.08
NaCl	0.13
Na ₃ PO ₄	0.14

TABLE II

Composition of
Formulations Tested

Mix Number	Component	Wt %
84-40	Cement (Class H)	12
	Fly ash (Class C)	48
	Salt solution	40
84-41	Cement (Class H)	12
	Fly ash (Class F)	38
	Salt solution	50

SLURRY PROPERTIES

Slurry properties for mixes 84-40 and 84-41 are shown in Table III. Flow table, flow cone, and vicat setting time tests were used to characterize these slurries. Both mixes have acceptable properties; however, mix 84-40 has better processing properties than mix 84-41.

TABLE III

Slurry Properties

Test (ASTM)	84-40	84-41	Acceptable Values
Flow table	>150%	>150%	>150%
Flow cone (average)	26 seconds	83 seconds	15-90 seconds.
Vicat setting time	48 hours	90 hours	4-120 hours
Slurry density	1.72 g/cc	1.65 g/cc	-

CURED PROPERTIES

Physical properties of saltstone formulations were measured as a function of time. Data for compressive strength, static modulus, bulk density, and porosity are shown in Tables IV and V for mixes 84-40 and 84-41, respectively. The compressive strength of mix 84-40 is about 20 times higher than that of mix 84-41. Also mix 84-40 gains about 70% of the 180-day strength within the first 28 days of curing. However, strength gain was not observed during this time for mix 84-41. Figure 1 illustrates the effect of curing time on compressive strength for the two materials tested.

TABLE IV

Physical Properties of Mix 84-40

	Compressive Strength (MPa) (σ)*	Static Modulus (MPa)	Bulk Dry Density (g/cc)	Hg Intrusion Porosity (Pore Fraction)	Total Porosity (%)
7d	17.00 (0.5)	3146.0	1.54	0.39	40.0
28d	26.60 (1.1)	3574.0		0.22	40.0
56d	32.99 (0.3)	4511.0	1.48	0.46	40.0
90d	33.60 (0.5)	4195.0	1.50	0.41	37.2
180d	38.80 (0.6)	4649.0	1.59	0.33	38.6

* σ = standard deviation measured on 3 samples.

TABLE V

Physical Properties of Mix 84-41

	Compressive Strength (MPa) (σ)*	Static Modulus (MPa)	Bulk Dry Density (g/cc)	Hg Intrusion Porosity (Pore Fraction)	Total Porosity (%)
7d	1.18 (0.1)	359.0	1.06	0.45	54.8
28d	1.91 (0.1)	724.0	1.05	0.45	64.6
56d	2.08 (0.1)	532.0	1.05	0.45	54.2
90d	1.82 (0.1)	399.0	1.03	0.48	59.5
180d	1.91 (0.1)	206.0	1.03	0.47	60.2

* σ = standard deviation measured on 3 samples.

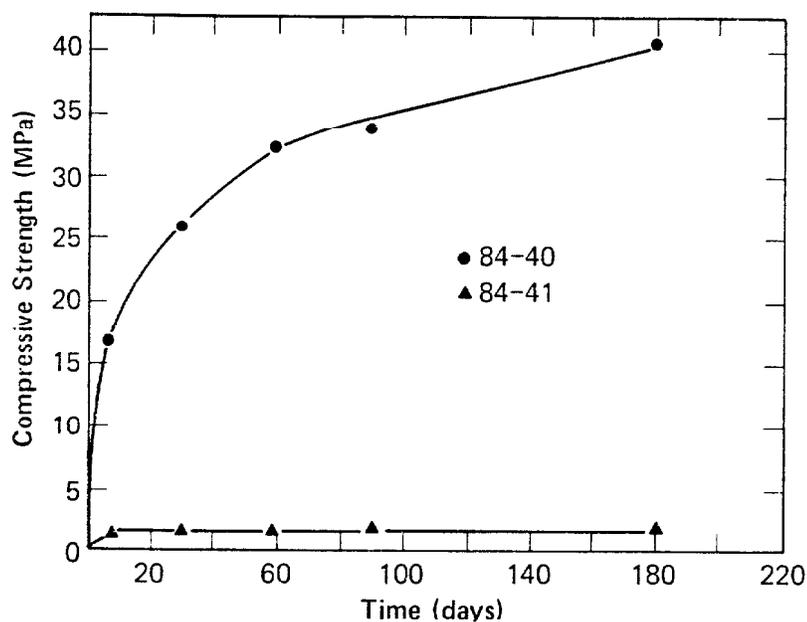


FIGURE 1. Compressive Strength Versus Time for Mixes 84-40 and 84-41

Porosity data were determined by two techniques, mercury intrusion porosimetry and the water saturation method. The water saturation technique gives higher values for cement-containing materials since mercury does not access closed pores. In addition, pore size distributions for mixes 84-40 and 84-41 were measured as a function of time. Results are shown in Figure 2. Mix 84-40 has a greater proportion of pores less than 1 μm in radius compared to mix 84-41 in which a large fraction of the pore volume is made up of voids greater than 10 μm in radius.

Scanning electron microscope images of mixes 84-40 and 84-41 are shown in Figures 3 and 4. These photographs were taken after samples were cured for 6 months. The microstructure of mix 84-40 appears more massive and less porous than that of mix 84-41. This visual evaluation correlates with measured differences in porosities and permeabilities.

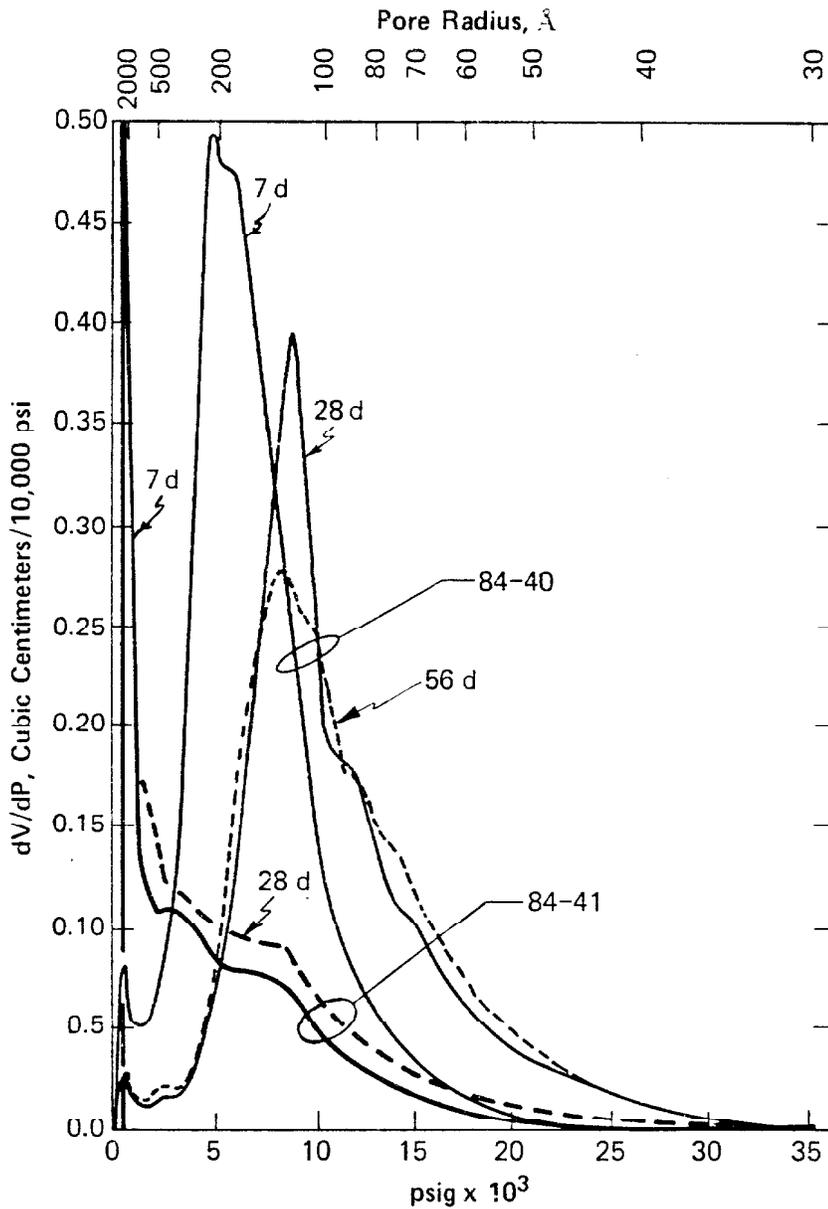


FIGURE 2. Pore Size Distributions of Mixes 84-40 and 84-41 at Different Curing Times

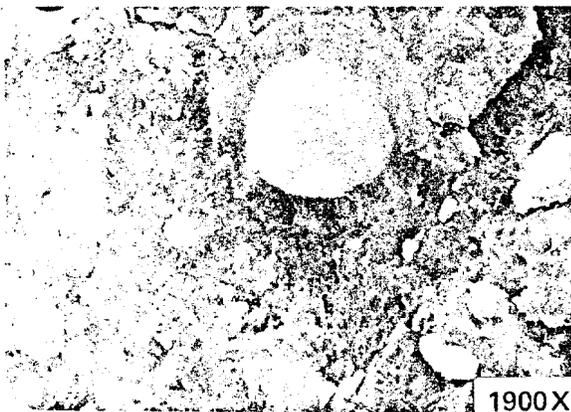


FIGURE 3. SEM of the SRP Reference Saltstone, Mix 84-40 After Curing Six Months at 38°C, 100% RH



FIGURE 4. SEM of Test Mix 84-41 After Curing Six Months at 38°C, 100% RH

X-ray diffraction analyses of both of these materials indicated that they contain some unhydrated cement and fly ash in addition to hydrated calcium silicate gel (CSH). Mix 84-40 also contains hexagonal tetracalcium aluminate monosulfate, cubic tricalcium aluminate hexahydrate (hydrogarnet), and a compound with a basal spacing of 10.18 Å (probably sodium-substituted CSH gel). At 28 days, sodium salts were not observed in x-ray patterns. After 6 months, NaNO₃ was detected in x-ray patterns indicating that some NaNO₃ crystallized from the pore solution.

Diffusivities have been measured for waste ions in the saltstone pore solution by two different methods. In one study, ³⁶Cl⁻ was used as a radioactive tracer with mix 84-40 [V. Quisenberry, Clemson University, unpublished results, 1984]. In the other, Cs⁺ diffusivity of mix 84-41 was measured by a method developed by A. Kumar [Pennsylvania State University, personal communication, 1983]. Ion diffusivities in the bulk saltstone were found to be 5 x 10⁻⁷ cm²/sec for mix 84-40 and 1.7 x 10⁻⁷ cm²/sec for mix 84-41.

DISCUSSION

Sulfate resistant API Class H cement was used in both formulations described in this paper. The low tricalcium aluminate content and coarse particle size (surface area of about 2000 Blaine) of this cement were found to reduce apparent slurry viscosities and the rate of heat generation due to exothermic hydration reactions. Mix 84-40 was found to be superior to mix 84-41 in terms of both processing and performance. Differences in physical properties were attributed to differences in fly ash. Class C ash hydrates in water, whereas Class F ash is not cementitious in itself. Higher compressive strengths and lower porosities in mix 84-40 can therefore be correlated with a greater amount of hydrated material. Improved leaching properties (reduced contaminant mobility) can also be correlated with higher cement contents in the formulation. [1]

Higher cement content results in more CSH gel matrix material which adds strength and fills pores. This can be represented as an effective water to cement ratio, W/C_{eff} in which reactive fly ash and cement are added together. For mix 84-40 the W/C_{eff} is 0.4; for mix 84-41 it is about 2.8. SEM micrographs of 6-month-old samples support including Class C ash as cementitious material. After 6 months, extensive reaction of the ash was observed. This is not the case for Class F fly ash. This Class F fly ash was considered noncementitious during the first 6 months of curing.

Measurement of physical properties as a function of time is necessary since cement hydration reactions continue long after the waste form has set. Mix 84-40 showed increasing strength up through 180 days of curing. The strength of mix 84-41 leveled off after about 30 days of curing. This is additional evidence for long-term hydration of the Class C fly ash.

Both mixes showed good durability based on property measurements as a function of curing time. Strength loss was not observed. However, testing will be extended for curing times up to at least 1.5 years to confirm durability.

CONCLUSIONS

Most physical properties of saltstone can be related to the water to cement ratios for the various formulations tested. Compressive strength increases as W/C decreases; porosity and mean pore size decrease as W/C in the potential formulations decrease. This is also the general case for conventional cement-containing construction materials.

Bulk diffusivities for ions dissolved in the saltstone pore solution were in the range of 1-5 x 10⁻⁷ cm²/sec. This same range for soluble ion diffusivities has been measured in ordinary portland cements and mortars by other investigators [6,7]. The lower bulk diffusivity for the reference mix is related to a lesser degree of saturation (about 50%) and lower porosity

(about 40%) compared to the test mix (80% and 60%, respectively). This reflects an initially lower proportion of waste solution and use of reactive fly ash in the reference mix.

The current SRP reference mix is preferred over the test mix because of superior processing properties, improved physical properties, and leaching characteristics.

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