

IMMOBILIZATION OF IFR SALT WASTES IN MORTAR*

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INTRODUCTION

Portland cement-base mortars are being considered for immobilizing chloride salt wastes produced by the fuel cycles of Integral Fast Reactors (IFR). The IFR is a sodium-cooled fast reactor with metal alloy fuels. It has a close-coupled fuel cycle in which fission products are separated from the actinides in an electrochemical cell operating at 500°C [1]. This cell has a liquid cadmium anode in which the fuels are dissolved and a liquid salt electrolyte. The salt will be a mixture of either lithium, potassium, and sodium chlorides or lithium, calcium, barium, and sodium chlorides.

Portions of the cadmium anode and salt electrolyte are removed as waste after each electrorefining cycle. The cadmium alloy contains noble metal fission products, such as zirconium, ruthenium and molybdenum, and the salt contains alkali metal, alkaline earth, rare earth, and halide fission products. Both phases contain small amounts of actinides. Various methods are being explored for converting the metal and salt wastes into forms acceptable for ultimate disposal. The metal wastes may be incorporated into a matrix of a corrosion-resistant metal such as copper.

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The salt wastes will be contacted with a Cd-Li alloy at 500°C to remove the last traces of actinides and most of the rare earth fission products. Essentially all of the alkali metal, alkaline earth, and halide fission products remain in the treated salt.

One method being considered for immobilizing the treated nontransuranic salt waste is to disperse the salt in a portland cement-base mortar that will be sealed in corrosion-resistant containers. For this application, the grout must be sufficiently fluid that it can be pumped into canister-molds where it will solidify into a strong, leach-resistant material. The set times must be longer than a few hours to allow sufficient time for processing, and the mortar must reach a reasonable compressive strength (~7 MPa) within three days to permit handling. Because fission product heating will be high, about 0.6 W/kg for a mortar containing 10% waste salt, the effects of elevated temperatures during curing and storage on mortar properties must be considered.

MORTAR DEVELOPMENT

Initial screening tests to identify mortar formulations suitable for immobilizing treated salt waste have been completed. Two salts, CaCl_2 -33 wt % NaCl and KCl- 33 wt % LiCl which simulate possible electrolytes, were used in these studies. Mixes with Types I or II portland cement, several fly ashes, sands and silicas with a range of particle sizes, clays and various admixtures have been evaluated by measuring their fluidity, set times, compressive strengths, and the leach rates of chloride ions. Fluidities, set times, and strengths were determined using modified ASTM procedures. The amounts of chloride leached

from cured specimens were measured using the ANS 16.1 procedure [2]. From these data, a normalized fraction leached, defined as the fraction of chloride ions leached multiplied by the volume to surface ratio of the specimen, was calculated. The normalized fraction leached is proportional to the square root of exposure time during the initial leaching period, and the proportionality constant is the effective diffusivity, D , with units of cm^2/s . The leachability index, L , is then defined as $L = \log(1/D)$.

From these tests, a baseline mortar mix of about 45% Type I portland cement, 27% Class F fly ash, and 28% water containing up to 10% waste salt appears to meet IFR requirements. Formulations around this composition range resulted in pumpable grouts having initial set times of several hours. Compressive strengths after three days curing at room temperature are 10 to 20 MPa and 50 to 70 MPa after 56 days. Leachability indexes for chloride ions were generally in the range of 7 to 8. The NRC recommends an index of 6 for low level wastes, but a higher leachability index (lower leach rate) is likely to be required for the IFR waste form, because it will be a Greater-than-Class C waste for about 200 y.

The addition of chloride salts to mortars caused a general degradation of grout and mortar properties. The salts weakened the mortar, especially the early strength, but salt-mortar matrices with adequate strengths could be prepared as shown in Table I. Each group listed represents the average properties for several individual mixes within a narrow composition range. The salt containing CaCl_2 , which is commonly used to accelerate concrete setting, caused some mixes to reach an initial

TABLE I. Effect of Chloride Salts on Compressive Strength of Mortars
Curing: Humid Air at 30°C

Group No.	Water Ratio ^a	Fly Ash Ratio ^b	Salt (%)	Sand Ratio ^c	Compressive Strength (MPA)				Initial Set Times (h)
					Curing Time (days)				
					3	7	28	56	
1.	0.50	—	0	2.0	22.1	26.9	32.3	29.5	4.2
2.	0.50	—	4 ^d	2.0	6.8	23.4	28.3	33.3	1.7
3.	0.50	—	8 ^d	2.0	11.0	12.4	18.1	17.1	<2.3
4.	0.50	0.60	0 ^d	2.0	11.6	16.3	19.7	23.2	>7.0
5.	0.50	0.60	4 ^d	2.0	4.4	14.2	19.8	25.2	~4.6
6.	0.50	0.60	8 ^d	2.0	5.4	6.4	16.8	24.5	4.5
7.	0.50	0.60	18 ^d	2.0	1.8	3.2	6.0	14.6	1.6
8.	0.30	0.30	0	—	49.8	71.9	65.1	93.5	<4.3
9.	0.30	0.30	7 ^e	—	27.0	27.3	39.3	69.4	>5.7

^aWater/(cement + fly ash).

^bFly ash/cement.

^cSand/(cement + fly ash).

^dCaCl₂-33% NaCl.

^eKCl-44% LiCl.

set in less than an hour. The other salt resulted in longer set times and slightly more fluid grouts. Producing more fluid grouts enabled the water ratio to be lowered for mortars with the KCl-LiCl salt which resulted in relatively strong mortars as typified by Group #10 in Table I.

Although fly ashes weakened the mortars, they tended to delay setting, as shown in Table II. These effects were somewhat dependent on the silica to calcia ratio of the fly ash. The set retarding property was particularly important for salts containing CaCl₂.

Table II. Effects of Fly Ash on Compressive Strength of Mortars
 Curing: Humid air at 25°C
 Salt Content: 9% of CaCl₂-33% NaCl

Group No.	Water Ratio ^a	Fly Ash Ratio ^b	SiO ₂ ^c / CaO	Compressive Strength (MPA)				Initial Set Times (h)
				Curing Times (days)				
				3	7	28	56	
1.	0.50	—	—	—	33.6	38.6	70.1	1.7
2.	0.50	0.30	9.7	22.9	25.5	39.6	46.7	2.6
3.	0.50	0.61	9.7	23.5	35.7	40.0	50.7	>5.7
4.	0.50	0.30	12.6	21.7	32.6	45.3	55.9	0.7
5.	0.50	0.60	12.6	19.4	27.6	45.0	56.3	1.7
6.	0.50	0.30	3.5	20.8	34.3	38.9	52.7	<2.3
7.	0.50	0.60	3.5	19.5	29.0	43.5	50.3	2.0
8.	0.50	0.30	1.8	28.3	41.8	42.1	44.0	<3.2
9.	0.50	0.60	1.8	37.2	40.4	51.8	63.9	4.9

^aWater/(cement + fly ash).

^bFly ash/cement.

^cWeight ratio in fly ash.

Much of the work has been directed toward optimizing the mortar composition to minimize chloride leach rate and to identify additives that result in more impermeable mortars. It is important to minimize the amount of water used since higher water/cement ratios will decrease strength and leach resistance. The minimum ratio of water to cement plus fly ash that produced a workable grout was about 0.3. The effects of some other components on leachability index are illustrated in Table III. Results are shown for specimens cured at room temperature for 56 days. Leach rates from specimens cured for 112 days were lower by a factor of about 2.

Table III. Effects of Some Additives on Leachability
of Mortar-Salt Matrices
Curing: 56 d in humid air at 30°C

Group No.	Water Ratio ^a	Ash Ratio ^b	SiO ₂ ^c CaO	Salt in Mortar (wt %)	Other Additive (wt %)	Leach Index.
1.	0.5	0	-	9.d	-	6.8
2.	0.5	0.6	9.7	10.d	-	7.1
3.	0.5	0.6	12.6	9.d	-	7.1
4.	0.5	0.6	2.6	9.d	-	7.2
5.	0.4	0.6	12.6	3.d	-	8.0
6.	0.4	0.6	2.6	3.-6.d	-	7.8
7.	0.9-1.0	1.0	9.7	9.d	10 ^f	6.3
8.	0.9-1.0	0.3-0.4	9.7	9.d	10 ^f	6.2
9.	0.35	0.3	9.7	3.-6.e	20 ^g	7.2
10.	0.35	0.45	9.7	6.e	20 ^g	7.6
11.	0.4-0.8	0-.45	9.7	3.e	20-30 ^h	8.4
12.	0.45	0.50	9.7	10.e	20 ^h	8.0

^aWater/(cement + fly ash + slag).

^bFly ash/(cement + slag).

^cWeight ratio in ash.

^dCaCl₂ - 33% NaCl.

^eKCl - 44% LiCl.

^fAttapulgate - 25% Indiana red pottery clay.

^gWeldon sand.

^hBlast furnace slag + 5% pottery clay.

The leachability index was only slightly effected by salt contents up to about 7%, but the index decreased as the salt content was increased above 8% (compare Groups #5 and 6 with #2, 3, and 4, and #11 with #12). Mortars having leachability indexes well above 7 could be prepared with 10% salt. The CaCl₂-NaCl and KCl-LiCl salts leached at about the same rate from comparable mortars, but workable grouts with lower water ratios could be produced with the KCl-LiCl salt.

Mortars made without fly ash (Group #1) had lower leachability indexes (higher leach rates) than mixes containing various types of fly ash (#2, 3, and 4). The type of ash, as characterized by the SiO_2/CaO ratio, had no significant effect on leachability. Replacement of a large fraction of the cement with blast furnace slag produced mortars with the highest leachability indexes we have measured to date (see #11 and 12). Because slag acts a pozzolan in this mix, it was included with the cement in calculating the water and fly ash ratios.

Two clay materials, attapulgite and indian red pottery clay that reportedly adsorb cations such as cesium and strontium [3], were investigated, but they resulted in weak mortars having higher chloride leach rates (#7 and 8). These materials required a high water ratio to produce workable grouts and the grouts tended to separate. To prepare the Group #7 and 8 mixes, it was necessary to add about 0.05% trisodium phosphate as a dispersant, and 0.5% aluminum phosphate as a suspending agent.

Additions of fine sand or silica are reported to improve the retention of soluble cations, particularly cesium, in cemented wastes [4]. This effect is thought to result from a modification of the calcium silicate hydrate gel that forms in hardening cement; the normal form of this gel does not adsorb cations, but more silica-rich forms do. In some tests, additions of up to 4% silica fume decreases leach rates marginally, but in other tests, fine sand appeared to increase rates slightly (compare #5 and 6 with #9 and 10). On the other hand, additions of silica fume produced a less workable grout while sand had the advantages of making a more fluid grout with longer set times.

Other tests have shown that exposure of the salt-mortar specimens to elevated temperatures during the curing period weakens them and increases the chloride leach rate. Exposure to saturated steam at 120°C for only three days during the first 115 days increased the leach rate by a factor of 2 to 4, and a similar exposure to 200°C steam increased the rate 4 to 8 times. Because the IFR salt waste matrix will contain considerable fission product heating, temperatures in the 80 to 150°C range are expected during the curing and interim storage period.

FUTURE WORK

Both fly ash and blast furnace slag have been found to be beneficial mortar additives for immobilizing IFR salt wastes. Work is underway on the effects of beta-gamma radiation on the IFR salt-mortar waste form. The dose from alpha particles will be negligible because the actinides will be removed from the salt before immobilization. Future work will be directed toward optimizing the mortar formulation to improve leach resistance and decrease the adverse effects of elevated temperatures. Silica additions will continue to be explored despite the equivocal results to date. Zeolites that adsorb cesium and strontium will be investigated. Future tests will measure the leach rates of specific fission product ions; it is expected that the leach rates of cesium and strontium will be considerably lower than the chloride rates determined to date.

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