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RESISTANCE OF CERAMIC WASTE FORMS*

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EFFECT OF DIFFERENT GLASS AND ZEOLITE A COMPOSITIONS ON THE LEACH RESISTANCE OF CERAMIC WASTE FORMS

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ABSTRACT

A ceramic waste form is being developed at Argonne National Laboratory for waste generated during the electrometallurgical treatment of spent nuclear fuel. The waste is generated when fission products are removed from the electrolyte, LiCl-KCl eutectic. The ceramic waste form is a composite, fabricated by hot isostatic pressing a mixture of glass frit and zeolite occluded with fission products and salt. Past work has shown that the normalized release rate (NRR) is less than $1 \text{ g/m}^2\text{d}$ for all elements in a Material Characterization Center-Type 1 (MCC-1) leach test run for 28 days in deionized water at 90°C (363 K). This leach resistance is comparable to that of early Savannah River glasses. We are investigating how leach resistance is affected by changes in the cationic form of zeolite and in the glass composition. Composites were made with three forms of zeolite A and six glasses. We used three-day ASTM C1220-92 (formerly MCC-1) leach tests to screen samples for development purposes only. The leach test results show that the glass composites of zeolites 5A and 4A retain fission products equally well. The loss of cesium is small, varying from 0.1 to 0.5 wt%, while the loss of divalent and trivalent fission products is one or more orders of magnitude smaller. Composites of 5A retain chloride ion better in these short-term screens than 4A and 3A. The more leach resistant composites were made with durable glasses that were rich in silica and poor in alkaline earth oxides. The x-ray diffraction (XRD) results show that a salt phase was absent in the leach resistant composites of 5A and the better glasses but was present in the other composites with poorer leach performance. Thus, the data show that the absence of a salt phase in a composite's XRD pattern corresponds to improved leach resistance. The data also suggest that the interactions between the zeolite and glass depend on the composition of both.

INTRODUCTION

A ceramic waste form is being developed at Argonne National Laboratory for waste generated during the electrometallurgical treatment of spent nuclear fuel. The waste is generated when fission products are removed from the electrolyte, LiCl-KCl eutectic, used in the electrorefining step.

Early samples of the ceramic waste form were fabricated by hot uniaxially pressing a mixture of glass frit and zeolite occluded with fission products and salt [1, 2]. The leach resistance of the resulting waste form was evaluated with the Material Characterization Center-Type 1 (MCC-1) leach tests [3]. Most tests were run for 28 days in deionized water at 90°C (363 K), though a few were run in simulated J-13 well water and brine. Under these test conditions, all elements in the ceramic waste form had a normalized release rate of less than $1 \text{ g/m}^2\text{d}$, comparable to that measured in 1982 for Savannah River borosilicate glass [4].

Recently, the pressing method was changed from uniaxial to isostatic. This change facilitates fabrication of larger samples. Process parameters were subsequently modified [5]. The temperature was increased from $700\text{--}715^\circ\text{C}$ (973-988 K) to 750°C (1025 K), and the pressure from 6000 psi (41 MPa) to 25,000 psi (172 MPa). These conditions were necessary for deformation of the stainless steel can. The time at temperatures above 600°C (873 K) was minimal to prevent the formation of other crystalline phases during hot isostatic pressing. These changes prompted a re-examination of the effect of glass and zeolite compositions on leach resistance.

We are now investigating the leach resistance of ceramic waste forms prepared using three forms of commercially available zeolite A (designated 5A, 4A, and 3A). Zeolite A (all forms) can be represented by the formula, $\text{M}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$, where M represents a univalent charge-compensating cation [6]. The zeolite A structure contains both alpha and beta cages. The size of the pore (entrance) to the alpha cage is determined by the number and charge of the charge-compensating cations. The charge-compensating ions vary in the different forms: 5A contains calcium and sodium; 4A, only sodium; and 3A, potassium and sodium. The number preceding the letter A gives the

nominal pore size for the alpha cage, in angstroms. Different forms of zeolite A have different thermal stabilities. We investigated these zeolites to determine if differences in nominal pore size and/or thermal stability affect the leach resistance of their composites. We are also investigating the leach resistance of ceramic waste forms prepared with several glass compositions. Both the binding properties and durability of the glass are important. The glass matrix binds the zeolite powders and reduces the exposed surface area of the zeolite.

All samples were subjected to ASTM C1220-92 leach tests (the American Society Testing and Materials procedure for MCC-1 leach tests) for three days and examined with XRD. These screening tests allowed us to assess potential performance quickly. Leach resistance was evaluated by monitoring the loss of surrogate fission products, chloride, and boron from composite samples during leaching. Obviously, the most important characteristic of a waste form is its ability to retain fission products. The chloride loss is a measure of the chloride ion retention in the ceramic waste form and the boron loss is a measure of the glass durability. Each ceramic waste form sample was examined with XRD. Patterns obtained by this method were compared with those of the starting materials and other phases. The leach data and the XRD data were compared, and correlations were noted.

EXPERIMENTAL

Materials

Waste Salt. The materials used in these tests include simulated waste salt, zeolite A, and glass frit. Two waste salt compositions, given in Table I, were used. Both contained about 10 wt% fission products in KCl-44.2 wt% LiCl eutectic salt. The simulated fission product chlorides were obtained from Aldrich or Johnson-Matthey. They were 99.9 % purity or better, and all were packed under argon in glass ampoules. The LiCl-KCl eutectic salt was obtained from APL Engineered Materials, Inc. (Urbana, IL) and was also packed under an argon atmosphere. The various components were heated at 500°C (773 K) in a furnace well in a dry, argon or helium atmosphere glovebox. After melting, the salt was quenched and then crushed.

Table I. Salt Composition

ID#	Component Salts (wt%)										
	CsCl	KCl	LiCl	NaCl	BaCl ₂	SrCl ₂	CeCl ₃	LaCl ₃	NdCl ₃	PrCl ₃	YCl ₃
Salt 1	3.7	45.3	39.6	6.0	1.4	0.6	0.7	1.1	1.0	0	0.1
Salt 2	2.3	48.7	40.7	0.0	1.0	0.4	1.9	0.6	3.8	0.8	0.1

Zeolite. Three commercial forms of zeolite A were used: 5A, 4A, and 3A. They were obtained from the UOP-Molecular Sieves Division (Moorestown, NJ). The nominal compositions of the zeolites are given in Table II.

Table II. Zeolite Compositions

Zeolite Type	Components (Wt%)					
	Al	Ca	K	Na	Si	O
5A	18.1	9.7	NM ^a	4.4	17.9	Remainder
4A	19.0	NM ^a	NM ^a	16.2	19.8	Remainder
3A	16.5	NM ^a	10.1	8.0	16.3	Remainder

^aNM = not measured.

Glass. Six glass frits were tested. All were aluminoborosilicate glasses. These proprietary glass formulations are designated as G1, G2, G3, G4, G5, and G6, and their compositions are given in Table III. The glasses were obtained from either Bayer Chemicals (Baltimore, MD) or Corning (Corning, NY).

Table III. Glass Compositions

ID#	Glass Components (wt%)							
	Al ₂ O ₃	B ₂ O ₃	CaO	K ₂ O	Na ₂ O	SiO ₂	SrO	ZrO ₂
G1	8	17	1	1	7	65	0	1
G2	10	14	14	1	6	55	1	0
G3	6	10	11	1	3	61	8	0
G4	3	18	0	9	1	68	0	0
G5	6	11	1	1	7	72	0	0
G6	9	12	0	6	5	68	0	0

Composites. In the following discussion, composites are identified according to zeolite form and glass type. For example, 5A/G1 signifies a composite made with salt-occluded 5A zeolite and glass G1. Except where noted, all composites were prepared from mixtures containing equal weights of salt-occluded zeolite and glass. Two composites also contained an additional 10% dehydrated zeolite. The purpose of this test was to determine if the additional zeolite scavenges non-occluded salt.

Processing

Blending. The salt-occluded zeolite was prepared by mixing dehydrated zeolite and the crushed simulated waste salt in a rotating double-cone blender at 500°C (773 K) [7]. All of the salt-occluded zeolites used in these experiments contained 21 wt% salt. For simplicity in this text we refer to all of the salt-occluded zeolites by the zeolite form used in the blending process, i.e., 5A, 4A, or 3A.

Hot Isostatic Pressing. All composites were hot pressed using a two-step thermal profile that consisted of a temperature increase to 750°C (1023 K) followed by a fast cool down to 600°C (873 K), where the temperature was maintained for one hour. The profiles are discussed in more detail in another paper [5].

Test Method

After hot pressing, cored samples of the composite (ceramic waste form) were leached in deionized water at 90°C (363 K), for three days according to the ASTM C1220-92 procedure. The total mass loss was measured in each test. The leachates were analyzed with a variety of techniques. Chloride ion concentration was measured with a chloride ion selective electrode. Cesium and the rare earth ions were measured with inductively coupled plasma-mass spectroscopy (ICP-MS). The other ions were measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For most leachates, the ICP-AES detection limits were too low for barium (0.02 µg/mL) and strontium (0.005 µg/mL) to be measured. In later tests, ICP-MS was used to measure barium and strontium. In addition, a duplicate sample of each hot-pressed composite was crushed and examined for crystalline phases with XRD.

RESULTS

Leach Tests

The purpose of these experiments was to screen composites made with different zeolites and glasses and to identify the more promising compositions. The most important criterion for the ceramic waste form is that it immobilize fission products. Measurement of fission product loss involves several analyses and is relatively expensive. Therefore, only selected leachates were analyzed for fission products. The fractional loss of cesium is reported in Table IV as a percent. The fractional loss is defined as the ratio of the amount released into the solution relative to the amount initially present. The data are grouped according to zeolite and glass type. The release of fission products was found to depend on valence. Cesium, the only +1 ion, had a higher release than the higher valence fission products. The divalent fission products (barium and strontium) and the

trivalent fission products (cerium, lanthanum, neodymium, praseodymium, and yttrium) had very low releases, resulting in a concentration of less than 5 µg/L in the leachate. Cesium releases, by way of contrast, were on the order of 200 µg/L in the leachate. Low releases of cesium and very low releases of the divalent and trivalent ions were common to both 5A and 4A. Typical values for the fraction loss, in percent, for the divalent and trivalent ions are given in Table V for 5A/G1 and 4A/G1.

Table IV. Summary of Leach Test and XRD Results for Composites of Salt-Occluded Zeolite and Glass

Sample ID	Total Mass Loss (%)	Mass Loss for Cs (%)	Mass Loss for B (%)	Mass Loss for Cl (%)	Phases in XRD Patterns
5A/G1					
HO373	0.12	0.19	0.05	0.59	zeolite
HO424	0.16	0.23	0.05	0.96	zeolite
HO452	0.11	0.23	0.05	0.37	zeolite
HO521	0.12	0.30	0.09	0.45	zeolite
HO624	0.12	0.10	0.04	0.62	zeolite
HO653	0.09	0.46	0.04	0.49	zeolite
HO721	0.07	0.48	0.14	0.32	zeolite
HO741	0.12	0.36	0.09	0.51	zeolite
HO743 ^a	0.09	0.26	0.04	0.37	zeolite
5A/G2					
371	0.23	0.22	0.38	0.60	zeolite
453	0.85	NM ^b	0.31	0.89	other + salt
5A/G3, 5A/G4, 5A/G5, 5A/G6					
451 (G3)	0.48	NM ^b	0.68	0.92	other + salt + sodalite
832 (G4)	0.26	0.20	0.51	0.30	zeolite
834 (G5)	0.12	0.25	0.02	0.45	zeolite
835 (G6)	0.17	0.30	ND ^c	0.44	zeolite + other
4A/G1					
423	0.26	0.20	0.10	1.09	zeolite + salt
471 ^d	0.36	0.48	0.12	0.88	zeolite + salt
4A/G2					
421	0.44	NM ^b	NM ^b	1.60	zeolite + salt
472 ^d	0.43	0.40	0.35	0.85	zeolite + salt + sodalite
3A/G1					
491	0.57	NM	NM	1.67	zeolite + salt

^aSample contains 45% glass.

^bNM = not measured.

^cND = not detected.

^d10% dehydrated zeolite was added to zeolite/glass frit mixture prior to hot pressing.

Table V. Fractional Loss of Divalent and Trivalent Ions from 5A/G1 and 4A/G1

ID #	Zeolite/Glass	Fractional Loss of Higher Valent Ions (%)					
		Ba	Sr	Ce	La	Nd	Y
424	5A/G1	BDL ^a	BDL ^a	0.001	0.000	0.001	0.003
423	4A/G1	BDL ^a	BDL ^a	0.012	0.001	0.015	0.001

^aBDL = below detection limit of 0.02 µg/mL for Ba and 0.005 µg/mL for Sr

The total mass loss was used as a quality screen. On this basis, three zeolite/glass combinations stand out (5A/G1, 5A/G5, and 5A/G6). All of their mass losses were less than 0.2%. One combination 5A/G1 was studied extensively. Nine samples were prepared using several batches of 5A and several lots of glass frit. The mass losses were consistently low. The average for the 5A/G1 composites was 0.11% with a standard deviation of 0.03%. Two other combinations, 5A/G5 and 5A/G6, also had low mass losses in initial tests. The mass loss for all the other samples shown in Table IV varied from 0.2 to 0.9%, indicating that both zeolite and glass compositions affect leach resistance. For example, G1 composites with 4A and 3A had higher mass losses (0.3-0.6%) than with 5A. Likewise, 5A composites with G2 and G3 had higher mass losses (0.2-0.9%) than with G1. Possible reasons for the variation in mass losses include differences in the release of chloride and fission products and in the durability of the glass. Fractional losses for chloride, fission products, and boron were examined to gain insight into the leaching mechanisms.

The release of chloride is used to measure chloride dissolution. There are two sources of chloride: one from occluded salt within the zeolite's cages, and the other from "free" salt, which is sometimes seen in XRD patterns of the composites. In general, high chloride losses correlate with high total mass losses (e.g., see 4A/G2 and 3A/G1 composites in Table IV) and, as discussed below, generally track with the presence of "free" salt in the XRD pattern. This suggests chloride loss can be an important leaching mechanism. The data also show that the different forms of zeolite A have different chloride retention properties. The 5A/G1 composites had consistently lower chloride releases than the 4A/G1 and 3A/G1 composites. The 5A/G2 composites also had lower chloride releases than the 4A/G2 composites. Thus, 5A retains salt better than 4A and 3A, for the glasses tested. Additional work was recently started with 5A and other aluminoborosilicate glasses (G3-G6). As shown in Table IV, composites with G4, G5, and G6 had low chloride releases, whereas the composite with G3 had a relatively high release.

Comparison of the compositions of the zeolites, salt, and glasses shows that boron is the only major element present in the glass phase that is not present in the zeolite. Thus, the boron release provides an approximate measure of glass dissolution. The following data confirm that boron loss is a reasonable measure of glass durability. Leach tests of the pure G1 and G2 glasses showed that G1 was more durable than G2. The mass losses measured after a 3-day leach test for pure, hot isostatically pressed glasses were essentially 0% for G1 and 0.24% for G2. The releases from G1 glass of aluminum and silicon were very low, 0.00 and 0.03%, respectively. For G2, the releases of aluminum and silicon were significantly higher, 0.26 and 0.27%, respectively. As shown in Table IV, the fraction of boron leached was lower for G1 composites than for G2 composites, indicating that G1 is more durable in composites than G2. The durability of G3, G4, G5, and G6 has not been as extensively investigated as G1 and G2. The limited data in Table IV show boron releases were very low for G5 and G6, and these glasses appear promising for further testing.

The data in Table IV also show that the boron release was lower for 5A/G1 composites than for 4A/G1 composites. Thus, the form of the zeolite affects the performance of G1 composites.

X-ray Diffraction Results

Sister samples of the leached composites were examined with XRD. These patterns were compared with each other and with the starting materials used in their fabrication. This comparison showed that the composites could be divided into one of three types, according to the predominant crystalline phases. The three types are (1) zeolite, where the pattern of the composite is almost the same as the pattern of the initial zeolite, and there are no additional phases, (2) other, which designates unidentified phases, and (3) a mixture of zeolite, "free" salt, and, in some cases, sodalite. The phases identified in the XRD pattern for each composite are given in Table IV.

Figure 1A is the XRD pattern of 5A with 21 wt% salt. Figure 1B is the XRD pattern of a 5A/G1 composite. All of the XRD patterns for the 5A/G1 composites were similar. The 5A/G5 and 5A/G6 composites were also of this type. (The 5A/G6 composite contained an additional unidentified phase.) In Figure 1B, there is a broad, amorphous peak (between 20-30°) due to the glass component of the composite. Further comparison of Figures 1A and 1B shows that the two patterns are alike in some respects and different in others. For example, the positions of the lines present in both patterns are essentially the same. However, the relative intensities of some lines are very different. One strong line and several weak ones present in Figure 1A are absent in Figure 1B.

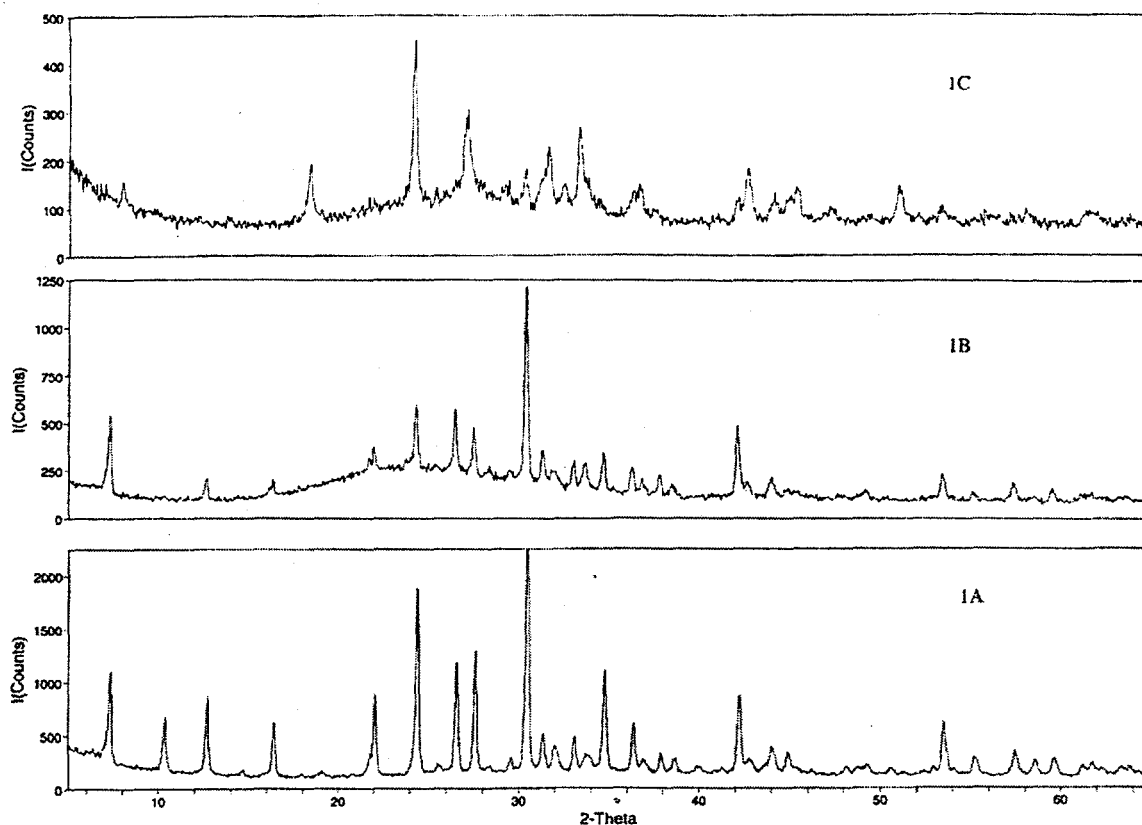


Fig. 1. X-ray Diffraction Patterns of 5A with 21 wt% salt (A) and Two Zeolite-Glass Composites, B (5A/G1, #452) and C (5A/G2, #453)

Figure 1C is an example of a XRD pattern that consists of "other" phases, and very little, if any, zeolite phase. This can be seen by comparing Figure 1A with Figure 1C, the XRD pattern for a 5A/G2 composite, #453. There is no longer a one-to-one correspondence between the positions of the lines in the XRD patterns for the composite and the zeolite. The XRD pattern of the 5A/G3 composite was also of this type. The "other" phases in these composites are, as yet, unidentified. Easily identified phases such as NaCl or sodalite were present in some of these composites. Samples with these phases are identified in Table IV.

The data indicate that the zeolite-glass interactions depend on glass composition. For example, three of the composites 5A/G1, 5A/G2, and 5A/G3 (#451, #452, and #453, respectively) had different XRD patterns even though they were made in the same hot pressing run and with the same batch of 5A. Glasses 2 and 3 interacted more strongly with 5A and caused it to transform to other crystalline phases. Glass 1 showed less tendency to effect a transformation of the zeolite.

A comparison of the XRD patterns for 4A and its composites, 4A/G1 and 4A/G2 showed that the patterns of the composites consisted of mixtures of zeolite, NaCl, and, in some, cases, sodalite. The same changes in the zeolite patterns observed in the 5A and 5A/G1 composites were also seen in the 4A samples. There was a one-to-one correspondence in the positions of the zeolite lines but relative intensities of some lines varied. Similar results were seen in the XRD patterns for 3A and the 3A/G1 composite.

Thus, the XRD results suggest that composites made from 5A are less likely to convert to other phases than those made from 4A. We have studied the effect of heating mixtures of 5A/G1 and 4A/G2 powders (prior to hot pressing) at 700°C (973 K). The 4A/G2 mixtures completely converted to sodalite within 4 hours, while the 5A/G1 mixture did not convert to sodalite, even after 24 hours.

The XRD results also show that differences in promoting transformation exist among various glasses. Examination of the compositions in Table III shows that the glasses that react with 5A (G2 and G3) contain more than 10% alkaline earth oxides. Glasses that are less aggressive contain 1% or less alkaline earth oxides.

CONCLUSIONS

Composites comprised of zeolite A containing 21 wt% salt and glass frit were hot isostatically pressed and then leached. Three forms of zeolite A and six glass frits were used. We investigated the effect of compositional changes in the zeolite and the glass by measuring short term leach resistance and crystal structure. The results were the following. First, both zeolite 5A and 4A retain fission products equally well. The release of cesium was small, varying from 0.1 to 0.5 wt%, while the release of divalent and trivalent fission products was one or more orders of magnitude smaller. Second, 5A/G1 composites retained chloride better than 4A/G1 and 3A/G1 composites. The chloride loss was especially high for the 3A/G1 composite. Third, several aluminoborosilicate glasses (G1, G5, and G6) acted as durable glass binders for 5A. The other aluminoborosilicate glasses either reacted with the 5A and transformed its XRD pattern (G2, G3) or were not durable (G4). Finally, test results correlated with the XRD results, i.e., the leach resistance was usually poor when the XRD pattern contained "free" salt, non-zeolitic phases, or sodalite.

Future work will be concerned with measuring the leach resistance for the more promising zeolite-glass composites for longer times. It is important to determine if the trends observed in the 3-day tests are also observed in tests for 28 days or longer. Other planned experiments are concerned with identifying conditions that affect glass reactivity, such as alkaline earth oxide concentration, and identifying other phases that immobilize cesium better.

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