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PROPERTIES OF GLASS-BONDED ZEOLITE MONOLITHS*

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ABSTRACT

It has been shown that mineral waste forms can be used to immobilize waste salt generated during the pyrochemical processing of spent fuel from the Integral Fast Reactor (IFR). Solid, leach resistant monoliths were formed by hot-pressing mixtures of salt-occluded zeolite A powders and glass frit at 990 K and 28 MPa. Additional samples have now been fabricated and tested. Normalized release rates for all elements, including iodide and chloride, were less than 1 g/m^2d in 28-day tests in deionized water and in brine at 363 K (90°C). Preliminary results indicate that these rates fall with time with both leachants and that the zeolite phase in the glass- bonded zeolite does not function as an ion exchanger. Some material properties were measured. The Poisson ratio and Young's modulus were slightly smaller in glass-bonded zeolite than in borosilicate glass. Density depended on zeolite fraction. The glass-bonded zeolite represents a promising mineral waste form for IFR salt.

INTRODUCTION

Glass-bonded zeolites are being developed as a high-level waste form for nuclear waste generated during the pyroprocessing of spent fuel from the Integral Fast Reactor (IFR) [1,2]. The IFR is an advanced reactor concept being developed at Argonne National Laboratory. One of the waste streams produced in the pyroprocess is a waste salt consisting of molten LiCl-KCl-NaCl and fission product (e.g., barium, cesium and strontium) chlorides. One advantage of using glass-bonded zeolites is that fission products in the salt waste can be immobilized without extensive chemical treatment. There are two major steps in the production of the waste form: (1) incorporating the waste into the structure and pores of a zeolite by treating the molten salt with the zeolite, and (2) converting the zeolite to a solid monolith by hot-pressing it with glass frit.

A preliminary evaluation of glass-bonded zeolites was based on the leach resistance of six specimens containing 50, 60, and 67 wt% zeolite (the remainder was glass) [2]. The leach tests followed the MCC-1 test procedure [3]. In these preliminary tests, each element had a normalized release rate (NRR) of less than 1 g/m^2d in 28-day tests in deionized water at 363 K. These results indicated that the glass-bonded zeolite was a promising waste form. However, additional testing was necessary to determine reproducibility, the effect of zeolite fraction, other measures of leach resistance, and some material properties.

Nineteen glass-bonded zeolite test specimens have now been fabricated using a standard set of pressing conditions. Waste forms having four different ratios of zeolite and glass frit were tested.The performance of these specimens was monitored through leach tests and material property measurements. All specimens were leached for 28 days in deionized water at 363 K. A few were leached for 56 days or in brine. In addition, a limited number of leachate samples were analyzed for chloride and iodide so that the NRRs for these anions could be determined. Material properties (Young's modulus, the Poisson ratio, Vickers hardness, and density) were measured for many of the specimens. Work continues on scoping experiments in which hot-pressing conditions (e.g., pressure) are varied. The results of these tests are summarized and used to evaluate the potential of glass-bonded zeolite as a waste form and to assess the importance of various experimental parameters, such as zeolite fraction and hot-pressing conditions.

EXPERIMENTAL

Zeolite Preparation

Zeolite samples were prepared as described elsewhere [2]. Briefly, zeolite A [$Na_7K_5(AlSiO_4)_{12}$] powders that had been pretreated with molten LiCl-KCl were contacted with simulated IFR waste at 773 K for 24 hours. Ion exchange and salt occlusion occurred. Most of the excess salt was removed with pressurized argon gas. The residual material, comprising salt-occluded zeolite and free salt, was blended with additional fresh zeolite to occlude the remaining salt. The blending operation consisted of mixing at room temperature and heating at 723 K [4]. These steps were repeated until the intensity of the NaCl peak at d = 2.83 Å in the xray diffraction spectrum became quite small, indicating that only a negligible amount of free salt . emained. At this point, the blended zeolite was ready for densification.

Hot-pressing Parameters

Approximately 4 g of blended, salt-occluded zeolite (hereafter referred to as zeolite) and glass frit were mixed at room temperature, then loaded into a 1-in. graphite die. The die had been previously coated with boron nitride, which functioned as an inert barrier and lubricant. The powdered samples were cold-pressed to 41 MPa and then placed in a uniaxial hot press. To minimize volatilization, the chamber was back- filled with nitrogen to atmospheric pressure, and an initial pressure of 28 MPa was placed on the sample. Most samples were pressed with a hold pressure of 28 MPa and a hold temperature of 990 K. The heating rate was 20 K/min. Typical hold times were 10-20 min after ram pressure stabilization. In a typical run, the ram pressure, monitored by an external gauge, increased as the temperature was ramped up. As the glass transition temperature was approached, the ram pressure began to decrease and continued to decrease as the sample densified. The pressure was manually increased if it fell below 28 MPa. The hold time was measured after the ram pressure stabilized. Some preliminary experiments have been completed in which the hot-pressing parameters were varied. In these tests, the pressure was varied from 28 to 56 MPa and the temperature from 970 to 1005 K.

Leach Test Method

The Materials Characterization Center leach test procedure (MCC-1) was followed, with one exception: all polishing and cutting operations were done dry rather than with a lubricant [3]. Each specimen (a disc approximately 2.54 cm in diameter and 0.3 cm thick) was polished to 600 grit and cut into 4 quarters with a diamond wafering blade. A different quarter was used in each leach test and for the material property measurements, as described below. Deionized water and brine leachants were used. The brine was prepared as specified in the MCC-1 procedure. The leach test results are calculated in terms of the normalized release rate (NRR), defined as

$$NRR = C_i V / f_i A d, \quad (1)$$

where C_i is the concentration of the element i in the leachate, V is the volume of the leachant, f_i is the fraction of the element i present initially in the glass-bonded zeolite, A is the geometric surface area, and d is the duration of the test. Each specimen was weighed to 0.1 mg before and after the leach test to determine mass loss. The solids (zeolite, glass, and crushed glass-bonded zeolite) were dissolved in various acid solutions. The procedures varied for different elements [5]. The concentrations of the cations in the dissolved solids and leachates were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectroscopy (ICP-MS), and the concentrations of chloride and iodide by ion chromatography. Typical compositions of the zeolite and glass are given in Table I.

TABLE I. Typical Compositions of Zeolite and Glass (wt %)

Element	Zeolite	Glass	Element	Zeolite	Glass
Al	14.6	3.3	I	0.08	NM
B	NM[1]	2.86	K	5.50	1.28
Ba	0.76	0.17	Li	1.92	0
Ca	NM	7.85	Na	9.94	2.29
Cs	1.68	0	Si	14.2	26.3
Cl	12.0	NM	Sr	1.05	6.78

[1]Not measured.

Other work [2] showed that measured f_i for the cations in the glass-bonded zeolite were the same as the f_i calculated from the equation

$$f_i \text{ (glass-bonded zeolite)} = f_i \times \text{wt\% (zeolite)} + f_i \times \text{wt\% (glass)}. \qquad (2)$$

Material Property Measurements

Densities were measured in ethanol using Archimedes' method. At least three measurements were made per specimen. Specimens were weighed dry, then submerged in ethanol for a minimum of 18 h. Samples were then weighed suspended in ethanol, as well as "wetted."

The Poisson ratio and Young's modulus of elasticity were determined by making ultrasonic velocity measurements with an ultrasonic analyzer and a digital oscilloscope that measured longitudinal and transverse travel times of pulsed sound [6]. Vickers hardness, H_v, was measured from a standard Vickers diamond indentation with loads ranging from 1 to 5 kg.

RESULTS AND DISCUSSION

Leach Tests

Leach resistance is one of the more important properties used for evaluating the performance of a waste form. Two criteria used in measuring the leach resistance of borosilicate glass have been adopted for evaluating the glass-bonded zeolite [7]. These criteria are (1) that the NRR of each element be less than 1 g/m^2d in 28-day, 363 K leach tests and (2) that these NRRs decrease with time. For the first series of leach tests, all specimens were leached for 28 days in deionized water at 363 K. These specimens were fabricated from mixtures containing 50, 60, 67, and 75 wt% blended zeolite (the remainder was glass frit). Objectives of these experiments were to determine whether leach resistant specimens could be reliably produced and whether the zeolite fraction affected the leach resistance of the composite. Consequently, the data in this series of experiments are grouped according to zeolite fraction. The mass loss and NRRs for all the cations were determined as described above.

28-Day Tests: All specimens containing 67 wt% blended zeolite or less met the criterion of having a NRR of less than 1 g/m^2d for each element. For the two specimens containing 75 wt% zeolite, the NRRs were less than 1 g/m^2d for all elements except potassium. The average values of the NRRs for each element are plotted versus the blended zeolite fraction in Figure 1. The release rates of the matrix elements (Al, B, and Si) and the divalent cations (Ba and Sr) were only slightly affected by increasing the amount of zeolite from 50 to 75 wt%. The NRRs of the univalent cations (Cs, K, Li, and Na) increased more markedly with increasing amounts of zeolite. Interestingly, the NRR for cesium was smaller than the NRRs for the other univalent cations in all cases. The average mass loss in the specimens with 50 wt% blended zeolite was 0.33 ± 0.05 wt%, while for the others it was 0.38 ± 0.03 wt%. These data suggest that leach resistant glass-bonded zeolites can be reliably produced and that composites containing equal amounts of glass and zeolite have slightly better leach resistance than composites with more than 50 wt% zeolite.

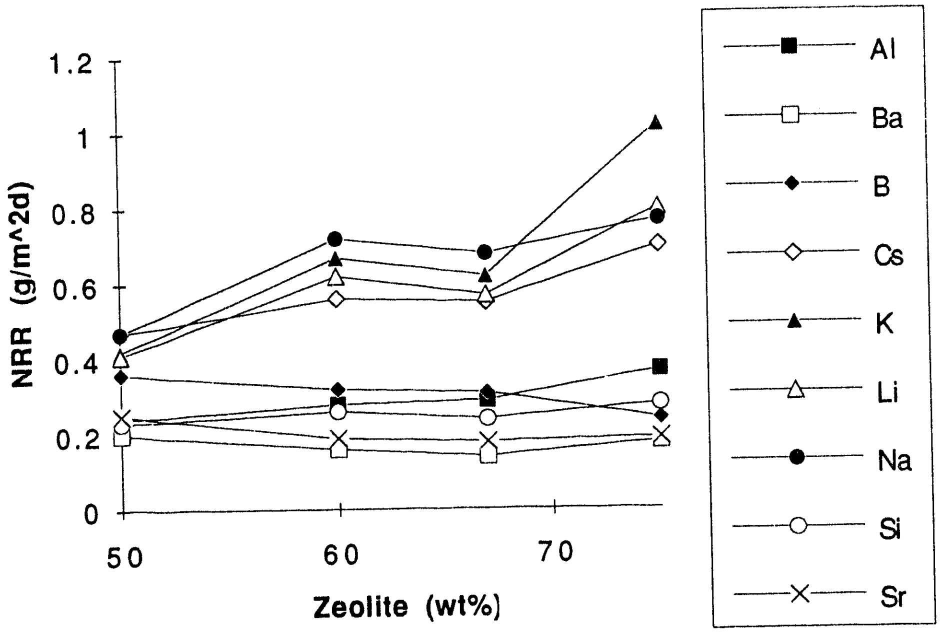

Figure 1. Normalized Release Rates for Four Zeolite-Glass Compositions

56-Day Tests: Five specimens were leached for 56 days. The average mass loss was 0.35 ± 0.04 wt% for the 28-day tests and 0.40 ± 0.07 wt% for the 56-day tests, an increase of about 15%. The compositions of the 28- and 56-day leachates were nearly the same and the NRR for each element decreased. The average NRRs for the 56-day and corresponding 28-day tests are given in Table II, Part A. The 56-day NRRs for many of the elements are about 50% of the 28-day NRRs suggesting that initial release predominates. The decrease in the NRRs was smaller for some elements, notably calcium and boron: for these elements the 56-day NRRs were 60-70% of their 28-day NRRs. Because boron and calcium are found only in the glass phase, the glass may be less corrosion resistant than the zeolite.

Brine Tests: Another criterion for evaluating the glass-bonded zeolite as a waste form is that the ion exchange properties of the zeolite should not adversely affect the leach resistance of the composite. We have therefore started leach tests of glass-bonded zeolite in brine. The objectives of these tests are to determine whether the zeolite phase in the glass-bonded zeolite functions as an ion exchanger and if so, whether the ion exchange properties alter the leach resistance of the composite. The brine is a concentrated solution of $MgCl_2$, KCl, and NaCl, containing 29.4, 25.3 and 35.4 mg/mL of Mg, K and Na, respectively. Ion exchange is therefore favored in brine by mass action and should be observable by comparing the NRRs of the minor elements in the brine and deionized water leachates.

TABLE II. Normalized Release Rates (g/m^2d) in 28- and 56-Day Leach Tests in Deionized Water and Brine

	Part A[1]		Part B[2]		Part C[3]	
Duration (days) Leachant	28 water[4]	56 water	28 water	28 brine	56 brine	28 water
Element	Normalized Release Rates (g/m^2d)					
Al	0.30	0.13	0.28	0.00	0.05	0.28
Ba	0.21	0.08	0.22	0.43	0.30	0.18
B	0.31	0.19	0.35	0.49	0.34	0.33
Ca	0.19	0.14	0.17	0.70	0.25	0.39
Cs	0.60	0.32	0.61	0.57	0.26	0.51
K	0.73	0.38	0.63	*	*	0.48
Li	0.60	0.35	0.54	0.42	0.23	0.49
Na	0.67	0.37	0.71	*	*	0.58
Si	0.25	0.11	0.23	0.15	0.17	0.23
Sr	0.23	0.11	0.24	0.51	0.22	0.23

[1]Zeolite content of specimens: two at 50 wt%, one at 60 wt%, and two at 75 wt%.
[2]Zeolite content of specimens: one at 50 wt%, and one at 60 wt%.
[3]One specimen containing 67 wt% zeolite.
[4]Water=deionized water.
*Constituent of brine.

Two specimens were leached in brine for 28 days. In the brine tests, the mass losses of the specimens were low, less than or equal to 0.08 wt% and the NRR for each element was less than 1 g/m^2d. The average NRRs in brine and in deionized water are given in Table II, Part B. In comparison to the water NRRs, the brine NRRs are about the same for cesium and lithium but higher for the divalent ions and boron. Because the zeolite phase is the only source of cesium and lithium (see Table I), and the glass phase the only source of boron and calcium, one may tentatively conclude that ion exchange has occurred primarily between the brine and the glass but not between the brine and the zeolite. Further studies are ongoing to determine whether the increase in the NRRs for the divalent metals (Ba and Sr) common to both phases is due to release from the glass or the zeolite phase or both. The NRRs for aluminum and silicon are lower in brine than in deionized water. These elements are common to both phases, and it is not clear why their concentrations are depressed in the brine, while the boron release is enhanced.

One specimen was leached in brine for 56 days. The specimen's mass was the same, within 0.1 mg, before and after the leach test. The brine and deionized water NRRs for this specimen are given in Table II, Part C. Comparison of the 28- and 56-day brine NRRs is limited because of the small number of samples and because of the differences in the corresponding 28-day NRRs in deionized water at 363 K. A tentative conclusion is that, for most elements, the NRRs decrease with time and the initial release predominates. The small increases in the NRRs for aluminum and silicon may not be significant. Further tests are planned.

Chloride and Iodide Release: Another criterion for evaluating the leach resistance of glass-bonded zeolite is that the NRRs for the chloride and iodide be less than 1 g/m^2d in 28-day tests and that they decrease with time. Fifteen deionized water and brine leachates were analyzed for iodide. In twelve of these leachates, the iodide concentration was below the detection limit of 0.1 μg/mL. There was no appreciable difference in the iodide concentrations in deionized water and brine leachates, indicating that anion exchange does not occur. Because the brine contains about 160 mg/mL chloride, conditions should favor anion exchange by mass action. In the remaining three leachates, the NRR for iodide varied from 0.6 to 1.8 g/m^2d. The specimens that released the larger amount of iodide had been hot-pressed under nonstandard conditions. As will be discussed below, it is believed that the NRRs can be controlled by pressing conditions.

A few leachates were also analyzed for chloride. The average NRR for chloride was 0.6 g/m^2d in two 28-day tests and 0.4 g/m^2d in two 56-day tests for specimens made under standard conditions with equal amounts of zeolite and glass. Thus, chloride ion release is comparable to the release of univalent cations in magnitude and in time dependence.

Changes in Hot-pressing Conditions: Several specimens were fabricated under different pressing conditions and leach tested to determine if pressing conditions affect leach resistance. In the first series of tests, we used higher pressures (42 and 56 MPa) because micrographs of the glass-bonded zeolite revealed porosity. Other work indicated that higher pressures reduced porosity in similar types of samples [8]. The results of the leach tests were that the NRRs for the more leachable elements, including chloride and iodide, were slightly higher in specimens pressed at 42 or 56 MPa than in those pressed at 28 MPa. It may be that higher pressures cause microcracks in the specimens. Other experimental variables that appear to adversely affect leach resistance were free salt in the blended zeolite, incomplete densification, and higher pressing temperatures. These results identify important parameters in the blending and hot-pressing operations.

Material Properties

The material properties of borosilicate glass have been measured to determine its strength and fracture resistance. A testing program to measure the material properties of glass-bonded zeolite has therefore been initiated. The densities varied with the zeolite fraction. Measured values were 2.39, 2.36, 2.33 and 2.31 g/cm^3 for waste forms with 50, 60, 67 and 75 wt% zeolite, respectively. A 4 g sample of the glass frit was also hot-pressed under the standard pressing conditions (28 MPa and 990 K). Its density was measured as 2.60 g/cm^3. By using this value and the measured density of the specimens containing equal amounts of glass and zeolite, the densities for specimens containing 60, 67 and 75 wt% zeolite were calculated as 2.36, 2.33 and 2.30 g/cm^3. The agreement between the calculated and the measured densities indicates that the densities are additive and that the glass-bonded zeolite is a composite material. The two phase nature of the glass-bonded zeolite is also apparent from micrographs taken with a scanning electron microscope.

The Poisson ratio, Young's modulus and Vickers hardness were also measured. The average values are given in Table III. We found that these properties did not vary significantly with zeolite fraction or with pressing conditions. There is insufficient data to determine whether the mechanical properties of borosilicate glass and the glass-bonded zeolite are similar. However, the preliminary data indicate only small differences in the properties that have been measured for both waste forms. The measurement of other mechanical properties requires larger samples and these will be measured when larger samples of glass-bonded zeolite are available.

TABLE III. Mechanical Properties of Glass-bonded Zeolite (GBZ) and Two Glasses

Material	Poisson Ratio	Young's Modulus (GPa)	Hardness (GPa)
GBZ, 50% zeolite	0.15 ± 0.01	60.4 ± 1.5	4.6 ± 0.3
GBZ, 60% zeolite	0.15 ± 0.01	58.8 ± 1.3	4.4 ± 0.4
GBZ, 67% zeolite	0.16 ± 0.01	57.7 ± 0.5	4.4 ± 0.2
GBZ, 75% zeolite	0.15 ± 0.01	58.3 ± 0.3	4.6 ± 0.2
glass[1]	0.15	70.4	NM[2]
EA glass[3]	0.18	66.9	NM

[1]Glass user as binder in glass-bonded zeolite. See text for details.
[2]NM=not measured.
[3]EA=Environmental Assessment Borosilicate Glass, see Reference 9.

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