EFFECT OF DIFFERENT GLASSES IN GLASS BONDED ZEOLITE

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ABSTRACT

A mineral waste form has been developed for chloride waste salt generated during the pyrochemical treatment of spent nuclear fuel. The waste form consists of salt-occluded zeolite powders bound within a glass matrix. The zeolite contains the salt and immobilizes the fission products. The zeolite powders are hot pressed to form a mechanically stable, durable glass bonded zeolite. Further development of glass bonded zeolite as a waste form requires an understanding of the interaction between the glass and the zeolite. Properties of the glass that enhance binding and durability of the glass bonded zeolite need to be identified. Three types of glass, boroaluminosilicate, soda-lime silicate, and high silica glasses, have a range of properties and are now being investigated. Each glass was hot pressed by itself and with an equal amount of zeolite. MCC-1 leach tests were run on both. Soda-lime silicate and high silica glasses did not give a durable glass bonded zeolite. Boroaluminosilicate glasses rich in alkaline earths did bind the zeolite and gave a durable glass bonded zeolite. Scanning electron micrographs suggest that the boroaluminosilicate glasses wetted the zeolite powders better than the other glasses. Development of the glass bonded zeolite as a waste form for chloride waste salt is continuing.

INTRODUCTION

A mineral waste form is being developed at Argonne National Laboratory to immobilize chloride waste salt generated during the pyrochemical treatment of spent fuel.[1] The waste form is a two-phase composite material, referred to as glass bonded zeolite. The zeolite incorporates the waste salt (a very water soluble chloride salt) into its crystal lattice and the glass binds the zeolite in a durable solid matrix.[2,3] Currently we have been studying the effects of changes in glass composition on zeolite binding by measuring the durability of the glass bonded zeolite.

Past work has shown that glass bonded zeolite has adequate durability, i.e., the overall mass loss in leach tests is relatively low, the normalized release rate (NRR)

is less than 1 g/m^{2}d in 28-day leach tests at 363K in deionized water and brine, and the NRR decreases with time.[4] Development of glass bonded zeolite as a waste form requires an understanding of the chemistry of the interaction between the glass and the zeolite. We have started work to identify the characteristics of the glass that cause it to bind to the zeolite particles and form durable glass bonded zeolite. The parameters varied in this phase of our study are glass composition, incipient fusion point and softening point. Three sets of experiments were run, each using a different type of glass. In the first set, six boroaluminosilicate glasses were tested. In the second, two soda-lime silicate glasses were tested. In the third, two high silica glasses were tested.

For all three sets, each glass and the corresponding glass-zeolite mixture were hot pressed and then leached following the MCC-1 test procedure.[5] An unleached portion of each glass bonded zeolite was examined with scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). Failure modes were identified by comparing the leach test results and SEM micrographs.

EXPERIMENTAL

Commercial glasses were obtained from Miles Laboratory (Baltimore, MD) or Schott Glass Technologies Inc. (Duryea, PA). Most glasses were obtained in powder form, but a few were only available as blocks or chunks. The glass blocks were crushed with a grinder, finely ground by hand with an agate mortar and pestle, and sieved. The fraction that passed a 325 mesh screen (<43μm) was washed with water, then ethanol, and dried.

A high silica nuclear waste glass (SG7) that was developed for a sintering process was synthesized from its reagent grade constituent oxides because it was not available commercially.[6] The powders were mixed in a ball mill and heated until they fused, at 1873 K. After the melt appeared homogeneous (about 30 min), it was quenched in cold water. It was then processed as above.

The glass powders were loaded into a graphite die, cold pressed, then hot pressed in a uniaxial hot press. Standard conditions were an initial pressure of 28 MPa and a pressing temperature of 990 K. As the glass densified during hot pressing, the pressure dropped from its initial value to a lower value, depending on the glass. The pressure was allowed to drop until it stabilized. After stabilization, the glass was held at that reduced pressure for 20 minutes.

The salt occluded zeolite (referred to as zeolite in this paper) was prepared as reported earlier.[3,4] It contained 13 wt% aluminum, 13 wt% silicon, 11 wt% sodium, 6 wt% potassium, 2 wt% or less of each of the following: lithium, cesium, strontium, barium, cerium, lanthanum, neodymium, and yttrium. The chloride ion content was 11 wt%. The zeolite was in powder form and electron micrographs show that the particles are cubic [7]. Equal amounts of zeolite and glass were mixed in an argon glovebox. The pressing procedure was the same as above except that the pressure was maintained at 28 MPa.

The hot pressed pellets of glass and glass bonded zeolite were polished using a series of abrasive papers, cut with a Buehler diamond saw, and washed according to the MCC-1 leach testing procedure. Samples were leached for 28 days at 363 K in deionized water. The cation concentrations in the leachates were measured with inductively coupled plasma/atomic emission spectroscopy. The normalized release rate for each cation, i, was calculated from the equation

$$NRR = C_i V/f_i A d$$

where C_i is the concentration of i in the leachate (g/mL), V is the solution volume (mL), f_i is the mass fraction of i in the solid, A is the geometric surface area of the sample (m^2), and d is the duration of the test in days.

The incipient fusion point (IFP) was provided by the vendors. The softening point (defined as the temperature at which the viscosity of the glass is $10^{7.6}$ poise) was measured for two of the glasses by Corning Laboratory (Corning, New York). Softening points were obtained from the vendor for two other glasses.

RESULTS AND DISCUSSION

Set 1: Boroaluminosilicate Glasses

The major constituents of the glasses tested in this set are given in Table I. Glass A, the standard, was used in most of the early tests.[3,4] It is a boroaluminosilicate glass containing relatively high concentrations of calcium and strontium oxides and a small amount of zirconia. The new glasses, B-F, are similar but the concentrations of the major constituents were varied as follows: calcium oxide from 5.4 to 13.5 wt%, strontium oxide from 0.1 to 17.1 wt%, zirconia from 0 to 9.6 wt%, and silica from 46 to 61 wt%.

The durability of each hot pressed glass was measured with the MCC-1 leach test. The overall mass loss and the NRR for boron, sodium, and silicon are given in Table II. Five of the six glasses (A, B, D, E, F) had good durability. The two high zirconia glasses (D and E) had the lowest mass loss, 0.2 wt%, and NRRs of ~0.2 g/m^2d. Three of the glasses (A, B, and F) had an intermediate mass loss, 0.4 wt%, and NRRs of ~0.3 g/m^2d. Glass C failed the durability test because its mass loss was high, 1.4 wt%, and the NRRs exceeded 1 g/m^2d. Durability of these glasses did not increase with increasing silica concentration. The non-durable glass C contained 52.4 wt% silica and the durable glass E, 45.8 wt% silica.

The leach test results for the zeolite bonded with each of the glasses A-F are also given in Table II. The durability of the glass bonded zeolite did not always correspond with the durability of the glass. Five of the six glasses (A, B, C, D, and F) bonded with the zeolite and gave a durable product. The mass loss was 0.4 wt% and each NRR was less than 1 g/m^2d for the leach tests. Durable glasses

A, B, D, and F had the same performance as the non-durable glass C. Glass E, one of the more durable glasses, did not bind the zeolite and did not form durable glass bonded zeolite.

Table I. Glass Compositions

				Concentration (Wt %)							
No.	Al_2O_3	B_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	SrO	ZrO_2	IFP*	SP*
										(K)	(K)
Set 1											
A**	6.3	9.7	11.2	1.3	0.5	3.3	61.0	8.1	0.4	938	1108
B	9.7	13.9	13.5	0.8	0.4	6.5	55.0	0.1	<0.1	942	1023
C	4.5	15.0	5.4	0.1	0.1	4.4	52.4	17.1	1.5	948	
D	4.7	12.2	10.1	0.8	0.7	5.7	53.5	1.9	9.6	929	
E	11.2	4.3	13.5	2.9	1.2	7.3	45.8	0.1	12.4	943	
F	8.1	9.3	6.1	0.6	2.6	2.5	55.2	7.9	0.2	848	
Set 2											
G	<0.1	<0.1	7.9	7.4	0.1	8.0	65.0	0.2		792	981
H	1.1	<0.1	11.5	0.2	0.1	13.4	68.2	0.2			
Set 3											
SG7	8.6	8.4	2.4	<0.1	<0.1	8.1	69.7	<0.1			
I	5.9	4.9	3.2	2.0	1.0	8.7	69.1	<0.1		833	1042

*IFP = Incipient Fusion Point, provided by the vendors.
*SP = Softening Point, measured for glasses A and B; provided by the vendor for glasses G and I.
**The vendors preferred that the glasses not be identified by their tradename if the compositions were given.

Set 2: Soda-Lime Silicate Glasses

The second set of tests used soda-lime silicate glasses (Table I). These were a lead-free sealing glass (G) and a bottle glass (H). These glasses contain relatively high concentrations of silica, no boria, and little or no alumina. The sealing glass contains 6.7 wt% zinc oxide (not shown in Table II). As shown in Table II, the bottle glass (H) had about the same durability as the more durable boroalumino-silicate glasses (A, B, D, E, and F). The sealing glass (G), on the other hand, was less durable.

Zeolite was hot pressed with both glasses G and H. Neither bonded with the zeolite. The mass loss of the zeolite "bonded" with sealing glass (G) was high, 8 wt%. The pellet comprising the zeolite and container glass (H) was not leached because visual inspection showed that the powders had not densified. (The thickness of the pressed pellet was much larger than usual. In this case, the surface area is much greater than would be measured using the dimensions of the sample, and it is not possible to calculate the NRR accurately.)

Table II. Leach Test Results

Glass					Glass Bonded Zeolite				
Glass No.	Loss (wt%)		NRR (g/m^2d)		GBZ?*	Loss (wt%)		NRR (g/m^2d)	
		B	Na	Si			B	Na	Si
A	0.4	0.32	0.35	0.27	Yes	0.4	0.41	0.38	0.26
B	0.4	0.33	0.38	0.27	Yes	0.4	0.27	0.34	0.21
C	1.4	1.74	1.96	1.14	Yes	0.4	0.47	0.73	0.23
D	0.2	0.18	0.22	0.18	Yes	0.4	0.12	0.52	0.22
E	0.2	0.26	0.24	0.30	No	>4	NM	NM	NM
F	0.4	0.16	0.30	0.24	Yes	0.4	0.19	0.65	0.22
G	1.1	NM	1.17	1.07	No	>8	NM	NM	NM
H	0.4	NM	0.37	0.38	No	ND	NM	NM	NM
SG7	0.04	0.05	0.06	0.04	No	>2	NM	NM	NM
I	0.1	0.05	0.06	0.04	No	0.8	0.16	2.9	0.16

*GBZ: Was Glass Bonded Zeolite Formed?
NM = Not Measured
ND = Not Densified

Set 3: High Silica Glasses

In the third set of tests, two high silica glasses were used: SG7, and a commercially available glass (I) with a similar composition (Table I). SG7 is a glass that was developed especially for sintering and high durability.[6] As shown in Table II, both of these glasses were very high durable. Their mass losses and NRRs were significantly lower than those measured for the other glasses. However, neither of the high silica glasses formed durable glass bonded zeolite.

Comparison of Glass Composition and Other Properties

Comparison of the leach data shows that of the ten glasses tested, five bonded with the zeolite and five did not. The data in Tables I and II were examined to identify correlations between composition and binding properties of the glass/durability of the glass bonded zeolite.

Glass Composition: The five glasses that bind the zeolite contained intermediate concentrations of silica, 52-61 wt%. Glasses that contained less silica (E: 46 wt%) or more (G, H, SG7, and I: 65-70%) did not bind the zeolite. In addition, all of the glasses that did bond with the zeolite were richer in alkaline earths (AE) than alkalis (A). The opposite was true for glasses that did not bind the zeolite, i.e., they were richer in alkalis than in alkaline earths. (The values given in Table I were converted to equivalents of the metal and compared in this form.) Other ratios, e.g., aluminum to silicon, aluminum to alkali, or aluminum and boron to alkali do not

follow any pattern that correlates with zeolite binding or durability of glass bonded zeolite.

Incipient Fusion Point: The incipient fusion point (IFP) of the glasses tested, given in Table I, varies from 792 to 948 K. The IFP of glasses that bind the zeolite fall within the range of 848 to 948 K. The IFP of glasses that did not bind the zeolite vary from 792 to 943 K. Thus, no strong correlation exists between IFP and the durability of glass bonded zeolite or zeolite binding.

Softening Point: The softening points, in Table I, for the various glasses have a range of 981 to 1108 K. The two non-binding glasses (G and I) have softening points of 981 and 1042 K, respectively. The two binding glasses (A and B) have softening points of 1108 and 1023 K, respectively. These data demonstrate that the softening point is not an important variable in binding zeolite with glass.

Scanning Electron Microscopy

Scanning electron micrographs of several glass bonded zeolites are shown in Figures 1-4. Figure 1 is a micrograph of zeolite bonded with glass D, one of the high zirconia glasses. The area on the left-hand side is a relatively large, featureless area, which was identified by EDS as a glass phase. It has a high silicon concentration, intermediate zirconium concentration, and little or no chlorine. The other area on the right side of the micrograph contains small, distinct, approximately square particles. These particles are similar to zeolite particles in size and shape.[7] Analysis by EDS shows that these areas contain high concentrations of chlorine and intermediate concentrations of silicon and aluminum, i.e., the zeolite phase. The zeolite particles appear to be embedded in the glass matrix. Similar micrographs were obtained for zeolite bonded with glasses A and F.

For comparison, Figure 2 presents the micrograph of zeolite "bonded" with glass E, which had very poor durability. The microstructures in Figures 1 and 2 are similar in some respects. Analysis by EDS identifies glassy areas and areas comprised of zeolite particles. However, in Figure 2, there are two atypical features: small white particles scattered throughout and a large pore or hole near the bottom right hand corner. The white particles were determined (by EDS) to be a nearly pure zirconium phase. This separation of the zirconium phase was not observed in zeolite bonded with glass D, another high zirconia glass. The hole contains unbound zeolite particles unwetted by the glass. This can be seen more clearly in Figure 3, which is a micrograph of a cluster of unbound zeolite particles. Samples with poor durability have many such clusters. Such samples would be highly porous and have a much larger surface area than that calculated from their geometric shape, hence the NRR would be high (which are based on the calculated surface area) and their leach performance poor. The micrograph in Figure 4 is representative of the zeolite "bonded" with the high silica glasses (SG7 and I). The material appears "flaky". In other micrographs (not shown) many large areas of "dry" zeolite are visible. The microstructures indicate that the wetting properties of the glass may control zeolite binding.

Figure 1

Figure 2

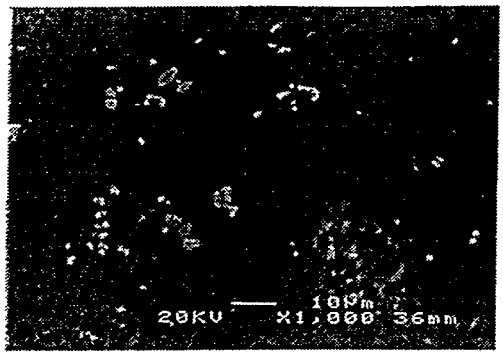

Figure 3

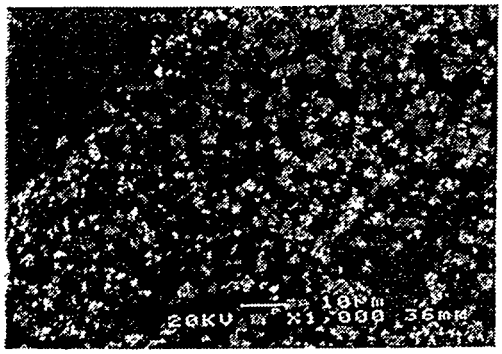

Figure 4

Figures 1-4 are scanning electron micrographs for various glass bonded zeolites. Figure 1 is typical of durable glass bonded zeolite. Figures 2-4 are micrographs of pellets with poor leach performance. See text for other details. Magnification is 1000 X.

CONCLUSIONS

The leach test data indicate that the durability of a glass itself, its incipient fusion point, or its softening point can not be used to predict the durability of zeolite bonded with that glass. Of the ten glasses investigated, the five that provided durable glass bonded zeolite had two characteristics: silica concentrations between 52 and 61 wt% and a molar ratio of alkaline earths to alkalis greater than one. The glasses that do not bind zeolite are rich in alkali metals and have silica concentrations below 52 or above 61 wt%. The SEM micrographs of the various glass bonded zeolites shows that the zeolite particles are embedded in the glass matrix or "wetted" when the durability is good. The zeolite particles appear "dry" and are clustered in "holes" when the durability or leach performance is poor.

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