

COMPARISON OF THE CORROSION BEHAVIORS OF THE GLASS-BONDED SODALITE
CERAMIC WASTE FORM AND REFERENCE HLW GLASSES*

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ABSTRACT

A glass-bonded sodalite ceramic waste form is being developed for the long-term immobilization of salt wastes that are generated during spent nuclear fuel conditioning activities. A durable waste form is prepared by hot isostatic pressing (HIP) a mixture of salt-loaded zeolite powders and glass frit. A mechanistic description of the corrosion processes is being developed to support qualification of the CWF for disposal. The initial set of characterization tests included two standard tests that have been used extensively to study the corrosion behavior of high level waste (HLW) glasses: the Material Characterization Center-1 (MCC-1) Test and the Product Consistency Test (PCT). Direct comparison of the results of tests with the reference CWF and HLW glasses indicate that the corrosion behaviors of the CWF and HLW glasses are very similar.

INTRODUCTION

The Electrometallurgical Treatment Program at Argonne National Laboratory (ANL) is developing a ceramic waste form (CWF) for immobilizing salt wastes generated during conditioning of the U.S. Department of Energy's metallic spent nuclear fuel that may not be suitable for direct geologic disposal [1]. In this electrometallurgical treatment, the fission products and transuranic elements that accumulate in a molten LiCl-KCl electrolyte are electrochemically separated, then immobilized in metallic and ceramic waste forms. This paper addresses the ceramic waste form that is being developed to immobilize the waste salt. Fabrication of the ceramic waste form consists of several steps. The salt is mixed with dehydrated zeolite 4A during a blending process at 500°C [2]. The salt-loaded zeolite is then mixed with glass frit, loaded into stainless steel canisters, cold pressed, and then hot isostatically pressed at 900°C for one hour. The function of the glass is to aid the densification of the waste form [3]. During hot pressing, the zeolite converts to sodalite. The resulting waste form is comprised primarily of sodalite and glass with small amounts of other phases.

For the glass-bonded sodalite CWF to be qualified for disposal, it must meet the requirements set forth in the Waste Acceptance System Requirements Document (WASRD) for high-level waste. We designed a large matrix of tests to determine the corrosion mechanism following the methodology in the American Society of Testing Materials Standard Practice C1174-9 [4]. The objective of the testing program is to obtain information that culminates in a mechanistic model for waste form corrosion behavior that can be used to calculate the release rates of radionuclides in a disposal system.

Previous work with non-radioactive materials showed that a durable CWF could be produced using zeolite with particle sizes < 10 µm [2,3]. Waste forms made with this type of zeolite were referred to as glass bonded zeolite or glass bonded sodalite, depending on the crystalline structure. To facilitate remote handling, larger size zeolite particles were desired. After a careful study of particle size effects, a clay-bound granular zeolite 4A with particles from 74 to 250 µm was selected for fabricating the reference CWF [5].

In this paper, we present the results of MCC-1 and PCT conducted with the reference CWF and compare the results with the results of similar tests with HLW glasses. We also discuss the insight to model development that is provided by these test results.

EXPERIMENTAL

We prepared monolithic samples for MCC-1 tests [6] and crushed material for PCTs [7]. Monoliths were dry cut from the core with a diamond wafering blade, dry polished with 240 grit SiC abrasive paper, and ultrasonically cleaned for 2 min in 100% ethanol to remove fines. Samples were dried at 40°C, then stored in a desiccator until use. The thickness and diameter of the monoliths were about 0.2 and 1.1 cm, respectively. The geometric surface area of the monolith was about 2.7 cm². The MCC-1 tests were run in demineralized water at 90°C. The S/V ratio was 10 m⁻¹. Two tests were run for each time period.

Crushed CWF material was sieved with an ultrasonic sifter to isolate the -100 +200 sieve fraction for use in the PCTs. The fines were removed with sequential washes of 100% ethanol. Water was not used to avoid dissolving halite from the sample. Clean crushed material was dried and stored as described above. The PCTs were run in demineralized water at 90°C and simulated EJ-13 water for 7 to 182 days. Tests in demineralized water at 2,000 m⁻¹ were run in duplicate. Only single tests were run in EJ-13 water and in demineralized water at 20,000 m⁻¹ because of limited amounts of sample. The composition of the EJ-13 is given in Table 1.

Table I. Composition of Simulated EJ-13 Water*

Element	Concentration, mg/L	Element	Concentration, mg/L	Element	Concentration, mg/L
Li	0.07	Al	0.69	I	0.07
B	0.32	Si	39.3	Cs	0.0031
Na	50.35	Cl	10.62		

*EJ-13 water was prepared by equilibrating J-13 well water with crushed tuff rock (<100 mesh) at 90°C for two weeks, then cooling and filtering.

At the completion of each leach test, aliquots of the hot solutions were taken for pH and chloride analyses. The remaining solution was filtered with a 0.45-μm pore size cellulose acetate filter, and the filtrate was acidified with a few drops of high purity concentrated nitric acid. The empty vessel was then rinsed three times to remove any remaining test solution, and refilled with demineralized water, which was acidified with high purity, concentrated nitric acid (1% of the water's mass). The vessel was then heated overnight at 90°C. The resulting solution was filtered as before and is referred to as the "acid strip solution." The test and acid strip solutions were analyzed with inductively coupled plasma-mass spectroscopy (ICP-MS). The pH and chloride concentrations were measured with a pH electrode and a chloride ion selective electrode, respectively. The data were used to calculate the normalized elemental mass loss, NL(i), defined as

$$NL(i) = (C_i V_i + C_{as} V_{as} - C_{bi} V_{bi})/f_i S, \quad (1)$$

where C_i is the concentration of element i in the test solution, and V_i is the volume of the test solution. Corresponding meanings are attached to C_{as} and V_{as} , in the acid strip, and C_{bi} and V_{bi} , in the experimental blanks. The f_i is the mass fraction of element i calculated to be in the CWF, and S is the surface area in m². Mean NL values are reported for tests with two or more replicates.

The composition of the reference CWF was calculated from the amounts and measured compositions of the salt, zeolite 4A and glass constituents that were used to make the waste form. The compositions are given in Table II. The heterogeneity of the CWF complicates the measurement of its corrosion behavior. Most elements are present in more than one phase. Both

the glass and sodalite phases contain Al, Si, Na, and K. Small amounts of Na, Cl, I, and Cs are present in the sodalite phase and the halite phase, salt not contained in the sodalite's micro-structure. Boron is probably only in the glass phase.

Table II. Compositions (Mass%) of the Glass-Sodalite Ceramic Waste Form and its Constituents

Element	Glass	Zeolite	Salt	CWF ¹	Element	Glass	Zeolite	Salt	CWF
B	5.99	NM ³	NM	1.50	Ba	0.22	NM	0.79	0.08
Al	3.95	18.8	NM	13.6	Ce	NM	NM	1.22	0.10
Si	29.5	18.7	NM	19.9	La	NM	NM	0.64	0.05
Li	BDL ²	NM	5.49	0.44	Nd	NM	NM	1.96	0.16
Na	4.83	14.9	5.23	11.6	Sm	NM	NM	0.35	0.03
K	0.37	NM	21.1	1.81	Eu	NM	NM	0.03	0.003
Rb	NM	NM	0.23	0.02	Y	NM	NM	0.12	0.01
Cs	NM	NM	1.82	0.15	Cl	NM	NM	59.5	4.8
Sr	0.02	NM	0.54	0.05	I	NM	NM	0.12	0.01

¹ CWF = Reference ceramic waste form whose composition was calculated as a mixture of 25 mass% glass, 8 mass% salt, and 67 mass% zeolite.

² BDL = Below detection limit

³ NM = Not measured

RESULTS

Material Characterization Center-1 Tests

The MCC-1 tests have been run for 1, 3, 28, 91, and 182 days. Figure 1 shows the normalized mass losses versus time for several components of the reference CWF. The release is non-stoichiometric. The NL(i) decrease in order from Cl, I > Li, Na > Cs > Al, Si, > K, B, >Ba, Sr, > rare earths (Y, La, Pr, Nd, Sm, Eu) > Ce. (Not all NL(i) values are shown in the figure for reasons of clarity.) A general trend in the time dependence for all the elements is a high initial release rate for the first 28 days followed by a lower release rate after 28 days.

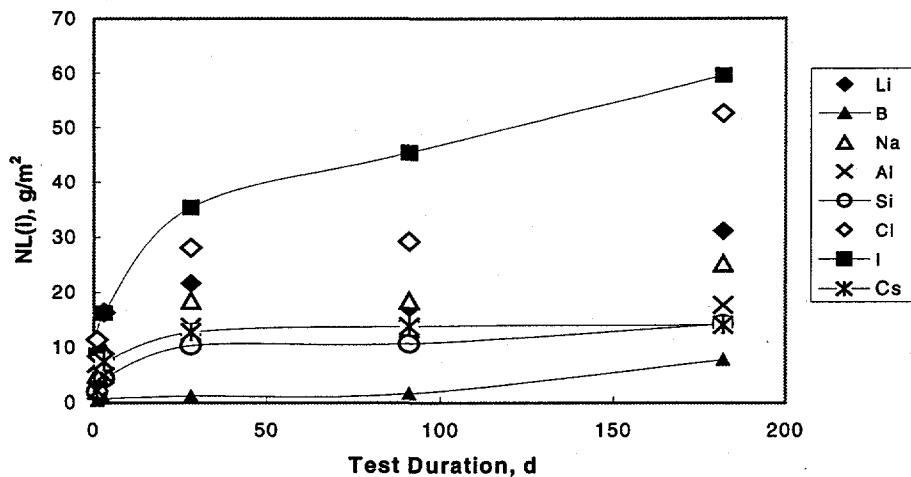


Figure 1. Normalized Elemental Mass Losses (NL) from the CWF in 1 to 182-Day MCC-1 Tests with Demineralized Water at 90°C. (The lines are a guide for the eye.)

Three aspects of this data, the forward rate, pH, and the measured Si concentrations, are of interest because they are used to describe glass corrosion and have been measured for several HLW glasses. The forward rate is the dissolution rate when there are no feedback effects from the solution. We measured the B and Si releases for 1 and 3 days, then derived the forward rate from a linear regression analysis, which included a zero intercept. Short-term data from other studies of HLW glasses are shown for comparison in Figure 2 [8,9]. Using B release, the forward rate for CWF corrosion was $0.25 \text{ g/m}^2 \cdot \text{d}$, lower than the 0.9 to $2 \text{ g/m}^2 \cdot \text{d}$ measured for other glasses, such as SRL-51S, SRL-202, SRL-165 and WV6. The forward rate for Si was $1.5 \text{ g/m}^2 \cdot \text{d}$, slightly higher than the $1.1 \text{ g/m}^2 \cdot \text{d}$ for the SRL-51S but comparable to WV6 and SRL-202U.

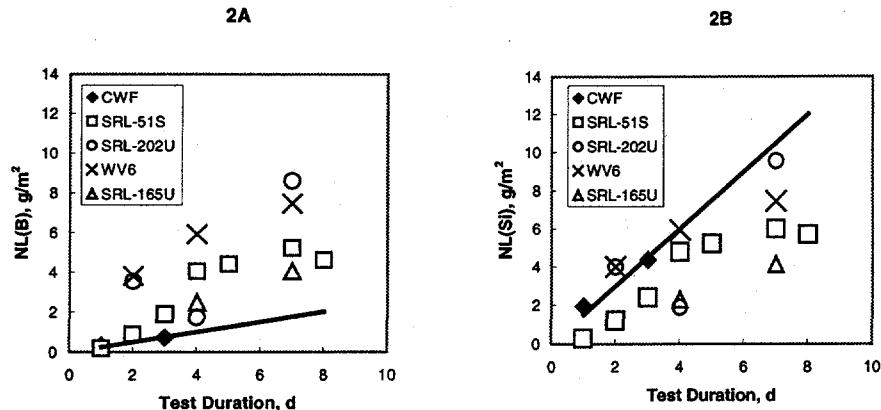


Figure 2. Normalized Losses for B (2A) and for Si (2B) in Short-Term MCC-1 Tests. (The line represents the best fit for the CWF data. Lines for the other data are not shown for clarity.)

The pH and Si concentrations in the various test solutions are given in Table III. The pH of the various test solutions for the CWF is about 9. The pH of the various demineralized water tests for many HLW glasses is about 10. The amount of dissolved Si increases slowly with time under MCC-1 test conditions and approaches the saturation values measured in the PCT, discussed below.

Table III. Measured Si Concentrations and pH in PCT and MCC-1 Tests

MCC-1 Test Duration, days	pH	[Si], mg/L	PCT Duration, (S/V=2000m ⁻¹) days	pH	[Si], mg/L	PCT Duration, (S/V=20000m ⁻¹) days	pH	[Si], mg/L
1	8.7	5.1						
3	8.7	8.2	7	9.1	15.4	7	8.9	12.1
28	8.9	19.7	28	8.8	22.9	28	8.9	19.0
91	8.8	20.9	91	8.7	28.0	91	8.8	36.2
182	8.8	28.6	182	8.6	17.1	182	8.8	28.2

Longer term NL(i) are available for several glasses, SRL-131, JSS-A (R7T7 glass with radioactive components), and PNL-76-68, for MCC-1 tests in demineralized water at 90°C for durations up to 1 year [10-13]. Release data for Si and Cs in Figure 3. These data show that the corrosion behavior of the matrix, measured by Si release, and Cs retention properties, measured by Cs release, are comparable in the CWF and HLW glasses. In general, the releases of B, Li, and Na, (not shown) are similar to those shown in Figure 3A.

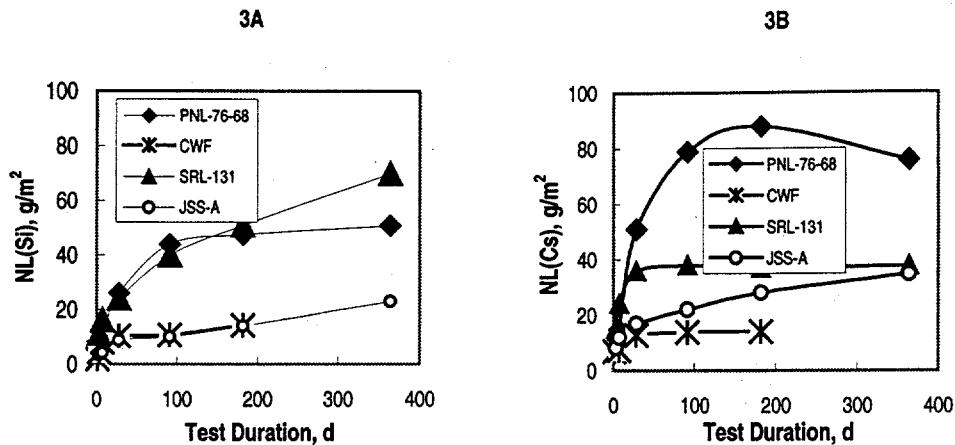


Figure 3. A Comparison of the NL(Si) (3A) and the NL(Cs) (3B) for Three HLW Glasses and the CWF in MCC-1 Tests in Demineralized Water at 90°C.

Product Consistency Tests for 7 Days

The Product Consistency Test Method A (PCT-A) is identified in the WASRD as the test for monitoring product consistency. We conducted five replicate PCT-A with the CWF. The mean NL values, the standard deviation, and the relative standard deviation were calculated to provide a measure of the consistency of the CWF and the uncertainty expected in longer term PCT. Values are given in Table IV for the elements discussed in this paper.

Table IV. Mean and Relative Standard Deviation (RSD) for Five Replicate PCT-A

Element	Mean NL g/m ²	RSD %	Element	Mean NL g/m ²	RSD %	Element	Mean NL g/m ²	RSD %
Li	0.33	20.2	Al	0.03	16.6	Cl	1.29	7.0
B	0.11	7.4	Si	0.04	9.1	I	0.64	12.8
Na	0.30	1.6	Cs	1.19	2.2			

In Figure 4, we compare the average results of PCT-A conducted with the CWF, EA glass, (the benchmark glass in the WASRD), SRL-51S, SRL-202 (two DWPF reference glasses), WV6 (West Valley reference glass), and R7T7 (COGEMA reference glass) [8,9,14].

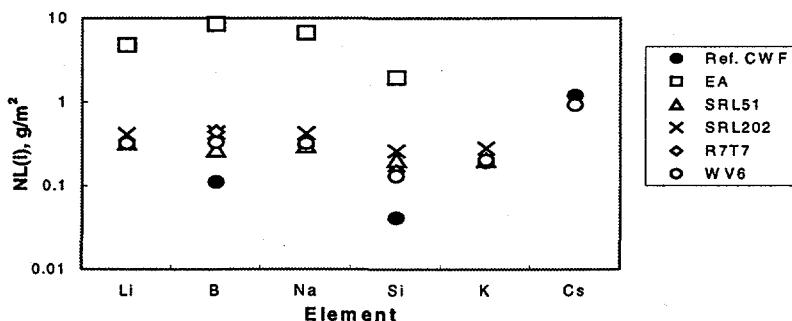


Figure 4. Normalized Elemental Mass Losses (NL) from the CWF and HLW Glasses in PCT-A.

The NL(i) from the reference CWF are comparable to or lower than the reference glasses and at least an order of magnitude smaller than the Environmental Assessment (EA) glass. (The EA glass does not contain Cs or K.)

Long Duration Product Consistency Tests

We conducted PCT for longer durations and at S/V ratio of $2,000 \text{ m}^{-1}$ to study the dissolution behavior as solution concentration of dissolved components increased. The time dependence of NL(i) varies with the elements, as shown in Figure 5. For example, the NL(Cs) decreases with time, which suggests that Cs is being incorporated into an insoluble alteration phase. Unfortunately, the concentration of Cs in the CWF (0.15 mass%) is too low to detect the distribution of Cs in the CWF or in alteration phases. The decrease in the amount of dissolved Cs with time is consistently observed in experiments in demineralized water and in EJ-13 at two S/V ratios, $2,000$ and $20,000 \text{ m}^{-1}$, as shown in Table V. The release of Cs is of importance because Cs-135 is a long-lived radioisotope and may be mobile.

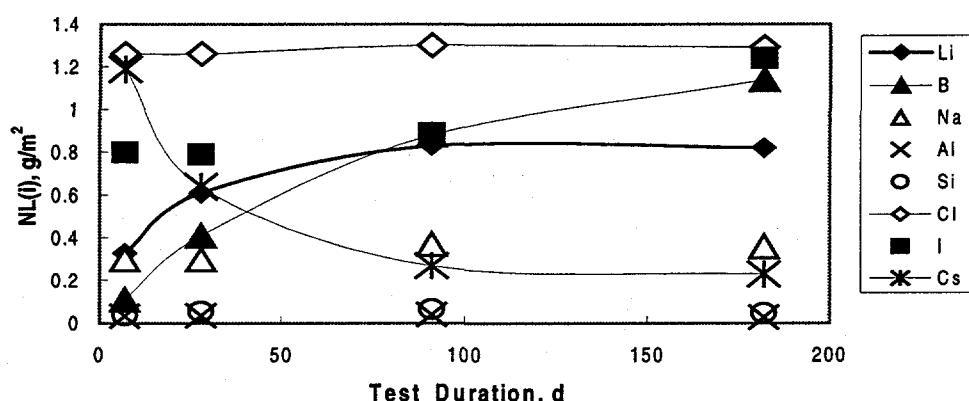


Figure 5. Normalized Elemental Mass Loss (NL) for the CWF in PCT with Demineralized Water at 90°C from 7 to 182 Days

Table V. Comparison of NL(Cs) in PCT from 7 to 182 Day Durations

Test Duration, d	NL(Cs), S/V = $2,000 \text{ m}^{-1}$		S/V = $20,000 \text{ m}^{-1}$	
	Water*	EJ-13	Water*	EJ-13
7	1.19	1.37	0.79	0.91
28	0.64	1.28	0.41	0.54
91	0.27	0.83	0.01	0.25
182	0.23	0.66	0.01	0.19

Also of importance is the release of iodine-129, another long-lived radioisotope. The CWF is a waste form capable of immobilizing iodine. The magnitude of NL(I) is lower than NL(Cl) for the four test durations, as shown in Figure 5. In tests with S/V ratios of $20,000 \text{ m}^{-1}$, the NL(I) varied from 0.4 g/m^2 at 7 days to 0.6 g/m^2 at 182 days and was well below the nearly constant 1.3 g/m^2 for NL(Cl). The release of iodine has one of the higher uncertainties (See Table IV) and considerable scatter is observed for NL(I). Longer term tests, which will help to establish the time dependence of the NL(I), are ongoing.

The time dependences of the NL(i) for Li, Na, and K are different. The NL for Li and K increases with time while NL(Na) is nearly constant. Since NL(Cl) is also nearly constant, the dissolution mechanism for Na and Cl (after the initial release) may be different from the dissolution mechanism for Li and K.

The NL for Al and Si are small, $< 0.05 \text{ g/m}^2$, and nearly constant. The NL(B), however, is relatively large and shows the largest increase with time.

The concentrations of measured Si are given in Table III for PCT with S/V ratios of 2000 and 20,000 m^{-1} for tests up to 182 days long in demineralized water. The saturation concentration for dissolved Si is 25-40 mg/L for the CWF, much lower than the 150-180 mg/L reported for HLW glasses [8,9].

The amount of Si released in tests with EJ-13 was also measured for the CWF. These data and those for several HLW glasses are given in Figure 6. The Si concentration in the EJ-13 blank is about 39 mg/L, represented by the line in the figure. The measured Si concentrations were lower for the CWF than for the glasses. These data confirm the 25-40 mg/L Si saturation value for the CWF.

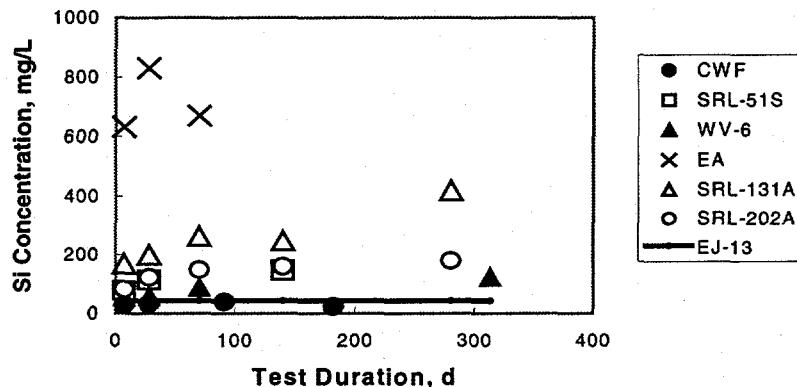


Figure 6. Measured Si Concentrations in EJ-13 Test Solutions with the CWF and HLW Glasses.

DISCUSSION

The intrinsic corrosion behaviors for the CWF and HLW glasses are similar. Corrosion for both the CWF and HLW glasses is characterized by a comparatively fast forward rate, followed by a slower long term rate in MCC-1 tests. The forward rates measured for B and Si are similar to those measured for HLW glasses. Another characteristic of glass corrosion observed in high S/V ratio tests with the CWF and HLW glasses is that measured Si concentrations approach saturation. The Si saturation concentration is lower for the CWF (25-40 $\mu\text{g/mL}$) than for the HLW glasses (150-180 $\mu\text{g/mL}$). Tests with EJ-13 and the CWF showed no significant increase in Si concentrations above that contained in the blank, confirming the low Si saturation value. Differences noted in the corrosion behavior between the CWF and HLW glasses usually indicate a more corrosion-resistant aspect of the CWF. The CWF immobilizes Cs and I, both of which have long-lived radioisotopes. The CWF also has the unique ability to immobilize chloride salts as well. The releases of Na and Cl did not vary appreciably after their initial release, indicating that salt release depends on corrosion of the sodalite framework.

CONCLUSIONS AND FUTURE WORK

MCC-1 and PCT have been completed for durations up to 182 days. The corrosion behavior measured for CWF is similar to that of HLW glasses. Forward rates and Si saturation concentrations measured for the CWF are either comparable or lower than those measured for

HLW glass. The CWF also immobilizes Cs and I, which is important because Cs-135 and I-129 are long lived radioisotopes of concern in repository performance. Future testing is concerned with measuring the corrosion properties of the two major phases. Tests to measure the pH and temperature dependence of the "pure" glass (no zeolite added), "pure" sodalite (no glass added), and the CWF are ongoing. Longer duration MCC-1 and PCT with the "pure" sodalite and "pure" glass are also ongoing. The results of these tests will allow determination of synergistic effects as well as a more complete understanding of the corrosion behavior of the CWF.

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