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S.-Y. Jeong, L. R. Morss, and W. L. Ebert
Chemical Technology Division
Argonne National Laboratory
Argonne, IL 60439

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ABSTRACT

A glass-bonded sodalite ceramic waste form (CWF) has been developed to immobilize electrorefiner salt wastes from electrometallurgical treatment of spent sodium-bonded reactor fuel for disposal. A degradation model is being developed to support qualification of the CWF for disposal in the federal high-level waste disposal system. The parameter values in the waste form degradation model were previously determined from the dissolution rates measured in MCC-1 tests conducted at 40, 70, and 90°C. The results of several series of tests that were conducted to confirm the applicability of the dissolution rate model and model parameters are presented in this paper: (1) Series of MCC-1 tests were conducted in five dilute buffer solutions in the pH range of 4.8 – 9.8 at 20°C with HIP sodalite, HIP glass and HIP CWF. The results show that the model adequately predicts the dissolution rate of these materials at 20°C. (2) Tests at 20 and 70°C with CWF made by pressureless-consolidation (PC CWF) indicate that the model parameters extracted from the results of tests with HIP CWF can be applied to PC CWF. (3) The dissolution rates of a glass made with a composition corresponding to 80% glass and 20% sodalite were measured at 70°C to evaluate the sensitivity of the rate to the composition of binder glass in the CWF. The dissolution rates of the modified binder glass were indistinguishable from the rates of the binder glass.

INTRODUCTION

Spent sodium-bonded nuclear fuel is being conditioned for disposal using an electrometallurgical technique developed at Argonne National Laboratory (ANL). A glass-bonded sodalite ceramic waste form (CWF) was developed for disposition of radioactive salt recovered from the electorefiner during conditioning [1]. The CWF is prepared by first mixing zeolite 4A with waste salts at ~500°C to occlude the waste-loaded salt within cages of the zeolite crystal lattice. The salt-loaded zeolite is then mixed with commercial borosilicate glass frit (75 mass % salt-loaded zeolite and 25 mass % glass) and vitrified at ~915°C. When heated, the salt-loaded zeolite transforms to sodalite, $Na_8(AlSiO_4)_6Cl_2$, and the glass frit melts to encapsulate the sodalite. The resulting waste form consists of sodalite inclusions fixed in a glass matrix. The CWF can be made using either hot isostatic pressing (HIP) or pressureless-consolidation (PC) processes. The PC process has been selected for immobilizing EBR II fuel.

The dissolution behavior of the CWF has been modeled with the expression [2]

$$\text{rate} = k_0 \bullet 10^{(h \bullet \text{pH})} \bullet e^{(-E_a/RT)} \bullet (1 - Q/K) \qquad (1)$$

where *rate* is the dissolution rate of the CWF, k_0 is the intrinsic rate constant, η is the pH dependence, E_a is the temperature dependence (activation energy), Q is the ion activity product, and K is apparent solubility product of the CWF. Series of MCC-1 tests were conducted at 40, 70, and 90°C to provide model parameter values for for HIP CWF and for its two major components, sodalite and binder glass. [3] In short-term MCC-1 tests, the value of the affinity term (1-Q/K) remains near one and the parameter values are readily determined from tests conducted at controlled temperature and pH values. Separate parameter values were measured for the HIP CWF, binder glass, and sodalite. As is the case for high-level waste glass waste forms, different parameters values are used in the dissolution rate expression for acidic and alkaline solutions. The model parameter values for the acid and base legs are given in Table 1.

Table 1. Model Parameter Values for Sodalite, Binder Glass, and CWF

	Acid Leg			Base Leg		
	$\log k_0$, $g/(m^2 \bullet d)$	η	E_a, kJ/mol	$\log k_0$, $g/(m^2 \bullet d)$	η	E_a, kJ/mol
Sodalite	10.7	-0.42	56	8.26	0.22	71
Binder Glass	11.1	-0.36	72	6.36	0.64	83
CWF	11.9	-0.40	65	10.7	0.19	84

The tests described in this paper were conducted to confirm the applicability of these rate expressions for waste forms made by different process, with slightly different compositions, at a temperatures outside the range used to determine the model parameters.

Although single-pass flow-through (SPFT) tests are commonly used to measure model parameter values, we used the MCC-1 method to determine the model parameter values for HIP CWF. This is because the MCC-1 method has been standardized (ASTM C 1220-98), whereas the SPFT test method has not been standardized, and far fewer tests and solution analyses are required to determine parameter values using the MCC-1 test method than using the SPFT test method.

Previous tests to determine model parameter values were conducted at 40°C and higher to generate sufficiently concentrated solutions for reliable analyses. [2] A series of MCC-1 tests was conducted at 20°C in five dilute buffer solutions over the pH range of 4.8 – 9.8 with HIP sodalite, HIP glass and HIP CWF for comparison with the rates calculated at 20°C using Eq. 1 with the model parameters in Table 1 for each material. Although model parameter values were determined during waste form development using materials made by HIPing, a pressureless consolidation (PC) process has since been developed and selected for inventory reduction phase for EBR II waste instead of the HIP process. Tests and analyses have shown that the waste forms made by HIP and PC are almost identical. The major difference is that the PC CWF has a slightly higher porosity and inclusion phases are more uniformly distributed throughout the binder glass in the PC CWF than in the HIP CWF. The dissolution rates of binder glass and CWF that had been processed by PC were measured and compared with the dissolution rates of HIP CWF under the same conditions to confirm that the model parameters determined based on tests with HIP CWF could be applied to PC CWF..

The parameter values determined from tests with binder glass will likely be used to provide an upper bound to the dissolution rate of the CWF. [2] Electron microscopy studies of sodalite granules and the intergranular binder glass in both HIP CWF and PC CWF have shown that the size of sodalite inclusions decreases with the process time and the concentrations of silicon and aluminum in the binder glass near sodalite inclusions were higher than in binder glass further removed from the sodalite. These observations indicate that a small amount of the sodalite dissolves into the binder glass during processing. In order to evaluate whether changes in the binder glass composition due to the dissolution of small amounts of zeolite or sodalite affect the dissolution rates of the binder glass, a modified binder glass with a composition equivalent to a homogeneous mixture of 80 mass % glass and 20 mass % sodalite was prepared and its dissolution rate measured at several pH values at 70°C.

EXPERIMENTAL METHOD

The CWF is composed of 75 mass % salt-loaded sodalite with 25 mass % glass binder. The CWF and binder glass were prepared by either the hot isostatic pressing (HIP)) or pressureless consolidation (PC) process [1]. The modified binder glass was batched from oxides and carbonates to yield a composition equivalent to a homogeneous mixture of 80 mass % glass and 20 mass % sodalite. This composition represents a likely maximum amount of zeolite and sodalite that may dissolve into the binder glass under normal processing conditions. The oxide and carbonate reagents were mixed, heated in Pt/Rh crucibles to 500°C to decompose carbonates, heated to 1150°C and held at this temperature for one hour, quenched to room temperature, and crushed to – 60 mesh. The crushed glass was remelted at 1150°C, poured into a mold, cooled at a rate of 24°C/hour to 550°C, annealed for two hours at 550°C, and furnace cooled to room-temperature. The compositions of the as-received modified binder glass and binder glass are listed in Table 2.

Table 2. Compositions of the As-Received and Modified Binder Glasses, in oxide mass %.

Component	Binder glass	Modified binder glass
Al_2O_3	7.5	12.3
B_2O_3	19.3	15.4
CaO	1.3	1.0
K_2O	0.4	1.4
Li_2O	0.0	0.3
Na_2O	6.5	10.1
SiO_2	63.1	57.7

Monoliths of each material were cored and cut into wafers nominally 10 mm in diameter and 1 mm thick for use in MCC-1 tests. The faces of wafers were polished to 600-grit final finish and the samples were washed with demineralized water to remove fines. The MCC-1 tests were conducted with in Teflon containers with buffer solutions. The ratio of the sample surface area

to solution volume (S/V) used in the tests was nominally 10 m^{-1}. The compositions and pH values of buffer solutions measured at different temperatures are shown in Table 3.

Table 3. Compositions and pH values of buffer solutions used in the MCC-1 tests.

Buffer composition	pH at 20°C	pH at 25°C	pH at 40°C	pH at 70°C	pH at 90°C
0.0095 m KHph[a] + 0.0027 LiOH	4.84	4.86	4.96	5.03	5.18
0.0038 m KHph[a] + 0.0031 m LiOH	5.95	5.87	5.99	6.20	6.25
0.0100 m HNO_3 + 0.012 m TRIS [b]	7.35	7.51	7.14	6.57	6.29
0.064 m H_3BO_3 + 0.010 m LiOH	8.37	8.39	8.31	8.27	8.14
0.012 m H_3BO_3 + 0.010 m LiOH	9.81	9.84	9.68	9.56	9.37

[a] KHph: Potassium hydrogen phthalate
[b] TRIS: Tris(hydroxymethyl)aminomethane

The test durations were 2-10 days for 70°C tests and 7-91 days for 20°C tests. The test durations were selected to be short enough to maintain dilute test solutions so that the dissolution rate would be as close as possible to the forward rate. At the end of the tests, the test solutions were analyzed with inductively coupled plasma-mass spectroscopy (ICP-MS)

RESULTS AND DISCUSSION

The concentrations of Si in the test solutions were used to calculate the normalized Si mass losses (NL_{Si}).

$$NL_{Si} = (C_{Si}-C^{b}_{Si})/\{(S/V)f_{Si}\} \quad (2)$$

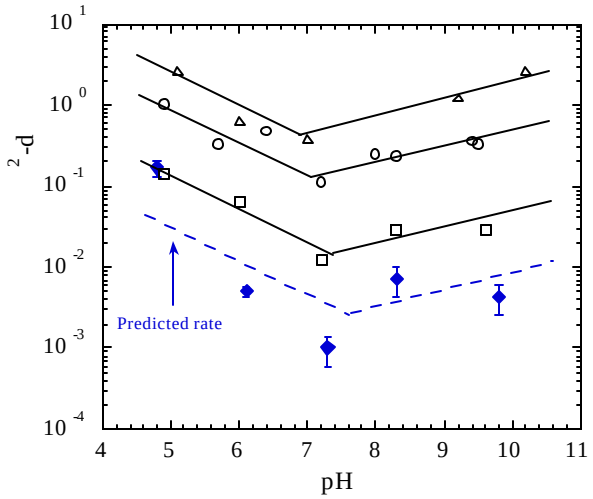
where C_{Si} is the measured concentration in the test solution, C^{b}_{Si} is the measured concentration in the blank test solution, S/V is the sample surface area to solution volume ratio, and f_{Si} is the mass fraction of Si in the CWF, binder glass, or sodalite. Normalized dissolution rates, NR_{Si} = ? NL_{Si}/? t, were the slope of the linear regression fit of the NL_{Si} values. The Si concentration was used to calculate the dissolution rate because Si is present in both the sodalite and binder glass. Boron was not use because it is not present in the sodalite phase.

Predictability of Rate Expression

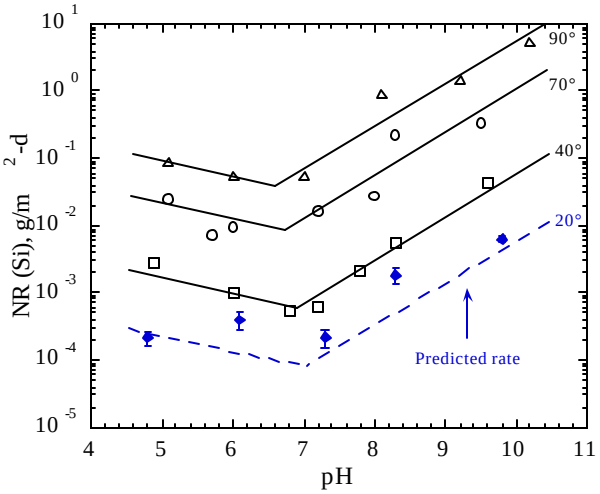
The parameter values for the pH and the temperature dependence of CWF dissolution rate in the degradation model were derived from the dissolution rates of HIP sodalite, HIP binder glass, and HIP CWF in MCC-1 tests conducted at 40, 70, and 90°C [2]. Those test results and the solid V-shaped lines calculated from the regression parameters in Table 1 are shown in Figs. 1a-c [2]. Note that the regression of the data from tests at 40, 70, and 90°C were constrained to determine one value of η and one value of E_a each for the acid and base legs. The dashed V-shaped lines in Figs. 1a-c were calculated using the expressions for the acid and base legs at 20°C.

In order to confirm the predictability of model parameters derived from test at higher temperature, series of MCC-1 tests were conducted with HIP sodalite, HIP binder glass, and HIP

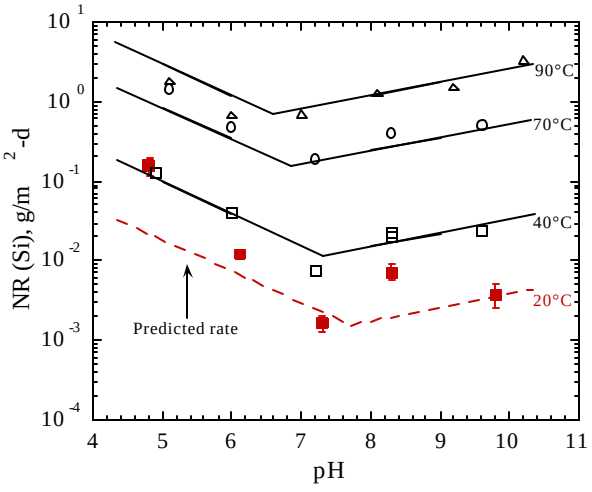
CWF in five buffer solutions in the pH range of 4.8 – 9.8 at 20°C. Dissolution rates were obtained by linear regression of the normalized Si mass losses [NL(Si)]. The NR(Si) values are plotted vs. pH in Figs. 1a-c. On average, the measured dissolution rates at 20°C are slightly greater than the rates predicted by the rate expression. As expected, the scatter in the rates measured at 20°C is greater than that for rates measured at higher temperatures. This is probably because the Si concentrations are nearer the analytical detection limit in the 20°C test solutions. We note that while the agreement between the measured and predicted rates of the CWF at 20°C are fair at best, the accuracy of the model for HLW glasses extrapolated to 20°C will probably be no better. This is inferred based on comparison of the predicted and measured dissolution rates of the binder glass, which has a composition similar to HLW glasses (Fig. 1b).



(a) HIP Sodalite



(b) HIP Binder Glass



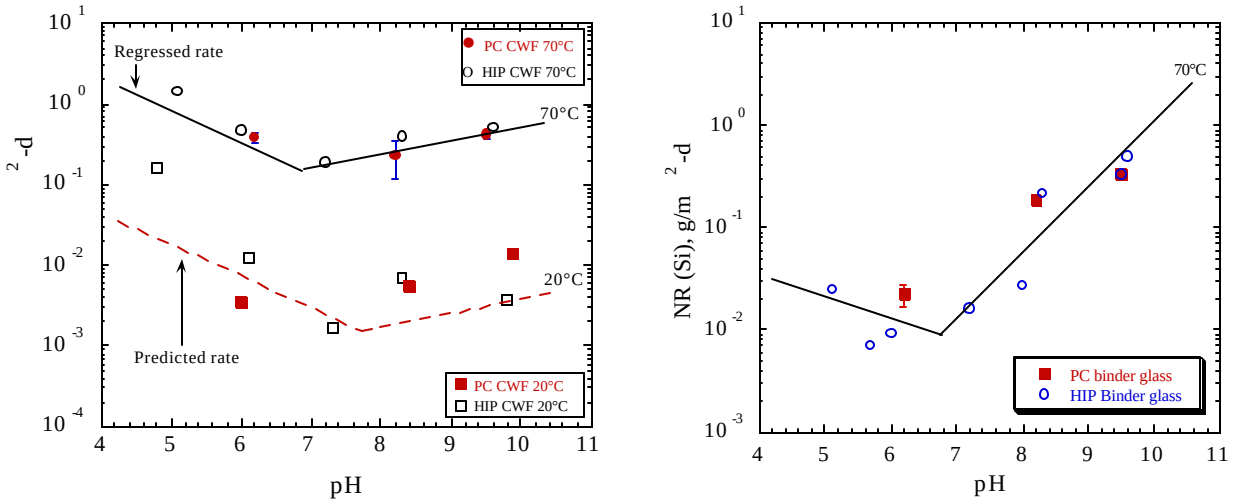
(c) HIP CWF

Fig. 1. Measured dissolution rates at (?) 20, (?) 40, (o) 70, and (Δ) 90°C vs. pH for (a) HIP sodalite, (b) HIP binder glass, and (c) HIP CWF. The solid V-shaped lines are calculated from the model (see Eq.1 and Table 1).

Although there is appreciable scatter in the measured rates, the deviations of NR(Si) from the model prediction lines in Fig. 1 are small in terms of the actual dissolution rates. We note that the dissolution rates of sodalite and CWF at pH 4.8 are significantly higher than model predictions and exceed the expected test uncertainty. These results may indicate that the dissolution mechanism of sodalite in acid solutions is different at 20°C than at higher temperatures. Otherwise, the results indicate that the models adequately predict the dissolution rates of sodalite, binder glass, and CWF at 20°C.

Effect of CWF Consolidation Method

The MCC-1 tests were conducted with the PC binder glass and PC CWF in three buffer solutions in the pH range of 6 – 10 and 70°C to confirm that the parameter values determined from materials made by HIP could be applied to materials made by PC. The normalized Si mass losses from PC CWF and PC binder glass were plotted as a function of test duration and regressed to determine the dissolution rate. For each material, the NR(Si) values are plotted as a function of pH in Fig. 2. The pH and temperature dependence for the forward Si dissolution rates of PC binder glass and CWF were indistinguishable from those of HIP binder glass and CWF at 20 and 70°C within the test uncertainty. These results show that the model parameters determined from the results of tests with HIP CWF can also be applied to PC CWF.



(a) HIP and PC CWF (b) HIP and PC binder glass

Fig. 2. NR(Si) as function of pH for (a) CWF at 20 and 70°C, and (b) binder glass at 70°C. The lines are from the model rate expression. .

Effect of Glass Composition

The dissolution rates of the modified binder glass, which had a composition corresponding to 80% glass and 20% sodalite, were measured at several pH values at 70°C and compared with those of the as-received binder glass to evaluate the sensitivity of the dissolution rate to glass composition. The dissolution rate at each pH value was obtained by linear regression of the normalized Si mass losses as a function of pH. The dissolution rates of the modified binder glass are compared with the dissolution rates of binder glass in Fig. 3. The V-shaped line in Fig. 3 is

the modeled dissolution rate of the HIP binder glass at 70°C. The dissolution rates and pH dependence of the two glasses in the basic region are indistinguishable within testing uncertainty. These results indicate that the dissolution rate of the binder glass in CWF is not significantly affected by the dissolution of small amounts of sodalite.

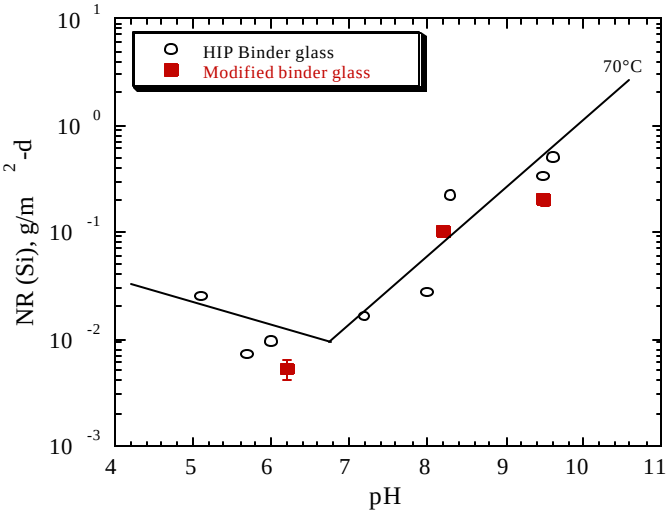


Fig. 3. NR(Si) as function of pH for the modified and as-received binder glass in buffered MCC-1 tests at 70°C. The line is the modeled rate at 70°C.

CONCLUSIONS

The predictability of the dissolution models for CWF and its major components using parameter values derived from the results of MCC-1 tests at 40, 70, and 90°C were evaluated. The results of a series of MCC-1 tests in five buffer solutions in the pH range of 4.8 – 9.8 at 20°C with HIP binder glass and HIP CWF show that the model parameters measured for HIP CWF over the temperature range of 40 – 90°C can adequately predict the dissolution rate at 20°C. The dissolution rates of binder glass and CWF processed by pressureless-consolidation method were similar to those for HIP binder glass and HIP CWF. These results show that the model parameters measured for HIP CWF can be applied to PC CWF. The dissolution rates of a glass with a composition corresponding to 80% binder glass and 20% sodalite were indistinguishable from the dissolution rates of the binder glass at 70°C. Thus, the rate expression for the binder glass, which is used as an upper bound for the dissolution rate of the CWF, is not sensitive to moderate changes in the glass composition.

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