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CORROSION OF GLASS-BONDED SODALITE AS A FUNCTION OF pH AND TEMPERATURE.*

Lester R. Morss, Mary Stanley, Chad Tatko, and William L. Ebert
Chemical Technology Division
Argonne National Laboratory
Argonne, IL 60439

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DISCLAIMER

CORROSION OF GLASS-BONDED SODALITE AS A FUNCTION OF pH AND TEMPERATURE

L. R. MORSS, M. L. STANLEY, C. D. TATKO, AND W. L. EBERT
Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

This paper reports the results of corrosion tests with monoliths of sodalite, binder glass, and glass-bonded sodalite, a ceramic waste form (CWF) that is being developed to immobilize radioactive electrorefiner salt used to condition spent sodium-bonded nuclear fuel. These tests were performed with dilute pH-buffered solutions in the pH range of 5-10 at temperatures of 70 and 90°C. The pH dependences of the forward dissolution rates of the CWF and its components have been determined. The pH dependences of the dissolution rates of sodalite, binder glass, and glass-bonded sodalite are similar to the pH dependence of dissolution rate of borosilicate nuclear waste glasses, with a negative pH dependence in the acidic region and a positive pH dependence in the basic region. Our results on the forward dissolution rates and their temperature and pH dependences will be used as components of a waste form degradation model to predict the long-term behavior of the CWF in a nuclear waste repository.

INTRODUCTION

The Electrometallurgical Treatment Program at Argonne National Laboratory (ANL) is developing a conditioning process for treatment of some of the U.S. Department of Energy spent sodium-bonded nuclear fuels that may not be suitable for direct geological disposal. In this process, uranium is electrorefined from spent fuel in a molten LiCl-KCl electrolyte, and fission products (Rb, Cs, Sr, Ba, rare earths) and actinides accumulate in the molten salt. To make the salt acceptable for disposition in a repository, the salt is blended with dried zeolite 4A, $Na_{12}(AlSiO_4)_{12}$, at 500°C. The salt-loaded zeolite is mixed with a glass binder in a 3:1 mass ratio of salt-loaded zeolite to glass. The mixture is processed at high temperature and pressure to convert the zeolite into sodalite, $Na_8(AlSiO_4)_6Cl_2$, forming glass-bonded sodalite, the ceramic waste form (CWF) [1]. This paper reports the dissolution rates of the sodalite and glass binder components of the CWF, as well as the CWF itself, as a function of temperature and solution pH. These rates will be used to provide parameters for the ceramic waste form model.

Several studies of the effects of pH and solution conditions on dissolution have been carried out on glasses and aluminosilicate minerals [2-7]. The equation for the dissolution rate of aluminosilicate minerals is based upon the model of Aagaard and Helgeson [8], who postulated the formation of an activated complex at the mineral surface, the decomposition of which is the rate-controlling step in dissolution:

$$\text{rate} = S\ \{\ k_0 \bullet 10^{(\eta \bullet \text{pH})} \bullet e^{(-E_a/RT)} \bullet (1 - Q/[H_4SiO_4]_{sat})\} \qquad (1)$$

where

rate = dissolution rate of material ($g \bullet d^{-1}$)
S = surface area of material (m^2)
k_0 = rate constant ($g \bullet m^{-2} \bullet d^{-1}$)
η = pH dependence factor
E_a = activation energy ($kJ \bullet mol^{-1}$), reflecting temperature dependence
R = gas constant (8.314×10^{-3} kJ $mol^{-1} \bullet K^{-1}$)

T = absolute temperature, K
Q = concentration of H_4SiO_4 in solution (mg/L)
$[H_4SiO_4]_{sat}$ = saturation concentration of H_4SiO_4 in solution (mg/L)

Our study has determined values of η, the parameter that represents the pH dependence of dissolution rate, from short-term corrosion tests of glass binder, sodalite, and CWF in dilute buffer solutions at pH values between 5 and 10 at 70 and 90°C.

EXPERIMENT

Monoliths of each material (glass binder, sodalite, and CWF) were prepared by hot isostatic pressing, cored, and cut into wafers nominally 10 mm in diameter and 1 mm thick. The wafers were polished with abrasives to a 600-grit finish.

The polished pellets were tested according to the MCC-1 procedure [9] in Teflon containers with buffered leachant solutions having the compositions and pH values shown in Table I. To achieve the ratio of 10 m^{-1} for the specimen surface area to leachant volume (S/V), a typical wafer with total surface area of 2.00 cm^2 was placed in buffer solution of volume 20.0 mL. The vessel was placed in a constant-temperature oven at 70 or 90°C for 1 to 10 days. The pH was measured before and after each test using an Orion Ross combination semi-micro electrode, calibrated with reference buffer solutions at 70°C or 90°C. All pH measurements were carried out with the test or reference solution in a constant-temperature bath.

TABLE I. Buffer Compositions Used in pH Buffer Tests and Measured Buffer pH Values

Buffer Composition	pH, 25°C	pH, 70°C	pH, 90°C
0.0095m KHph[a] + 0.0027m LiOH	4.85	5.01	5.07
0.0038m KHph[a] + 00031m LiOH	5.82	5.97	6.01
0.0263m TRIS[b] + 0.010m HNO_3	8.47	7.25	6.15
0.064m H_3BO_3 + 0.010m LiOH	8.39	8.10	7.94
0.012m H_3BO_3 + 0.010m LiOH	9.81	9.35	9.15
0.00098m HNO_3 + 0.0117m LiOH	11.96	10.66	10.23

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

The MCC-1 tests have been conducted at 90°C for 1, 2, 3, 5, 7, and 10 days, or at 70°C for 3, 5, 7, and 10 days. (Tests at 40°C are in progress.) The test durations were selected to be short enough that the rate of corrosion would be as close as possible to the forward rate. Results of MCC-1 tests with an alkali borosilicate glass at 90°C had previously shown that 3, 5, 7, and 10-day tests yield the forward rate [10]; tests at shorter durations may be affected by surface roughness, while tests at longer durations show the effect of the affinity term $(1\text{-}Q/ [H_4SiO_4]_{sat})$.

Termination of the tests required taking aliquots for pH measurement at the testing temperature and at 25°C. Aliquots were also taken after filtration and acidification for inductively coupled plasma-atomic emission spectroscopy or for inductively coupled plasma-mass spectroscopy. The vessels were then subjected to an acid stripping with 1% HNO_3 solution ; the concentrations of cations in the acid strip solutions were negligible.

RESULTS

The concentration of silicon in solution after test termination provides the best measure of matrix dissolution of glass-bonded sodalite, since both glass binder and sodalite have high silicon concentrations. The measured Si concentrations in solutions from buffered MCC-1 tests with each material (glass binder, sodalite, and CWF) were used to calculate the normalized mass losses, NL(Si) = $(m - m_{b,})/f_{Si} \bullet S$, where m is the mass of silicon in the test solution, m_b is the mass of silicon in the experimental blank, f_{Si} is the mass fraction of silicon in the material, and S is the sample surface area. At each temperature, the NL(Si) from tests at each buffer pH increased rapidly during the first three days, then increased more slowly to 10 days.

The normalized release rates, NR(Si) = $[NL(Si,t_2)-NL(Si,t_1)/(t_2-t_1)$, were calculated by linear regression of the 3- to 10-day releases for glass, sodalite, and CWF at 70°C and 1- to 5-day releases at 90°C; these release rates are listed in Table II. The logarithms of the NR(Si) data were plotted as a function of pH from tests at each temperature, as shown in Fig. 1. The logarithmic form of eq. (1) shows that the values of η are the slopes of the regression lines in Fig. 1.

$$\text{Log (rate)} = \log S + \log k_0 + \eta \bullet \text{pH} - E_a/RT + \log (1 - Q/[H_4SiO_4]_{sat})\} \quad (2)$$

These values of η in the acidic and basic regions are listed in Table III.

TABLE II. Normalized Dissolution Rates ($g \bullet m^{-2} \bullet d^{-1}$) of Sodalite, Binder Glass, and Ceramic Waste Form (CWF) as a Function of pH at 70 and 90°C [a]

pH	Sodalite, 90°C [b]	Glass, 70°C	Glass, 90°C	CWF, 70°C	CWF, 90°C
5.0-5.2	2.64±0.64	0.025±0.002	0.088±0.020	1.39±0.15	1.82±0.43
6.0	0.64±0.15	0.0093±0.0019	0.056±0.012	0.48±0.02	0.67±0.18
6.9-7.0	0.38±0.24		0.056±0.006		0.69±0.11
7.3		0.016±0.002		0.19±0.03	
7.9	0.98±0.29		0.93±0.21		1.29±0.13
8.3		0.22±0.01		0.40±0.03	
9.2	1.22±0.34		1.47±0.37		1.53±0.16
9.6		0.50±0.02		0.50±0.03	
10.2	2.55±1.21		5.3±1.3		3.27±0.80

[a] Uncertainties are standard errors.

[b] Measurements at 70°C are in progress.

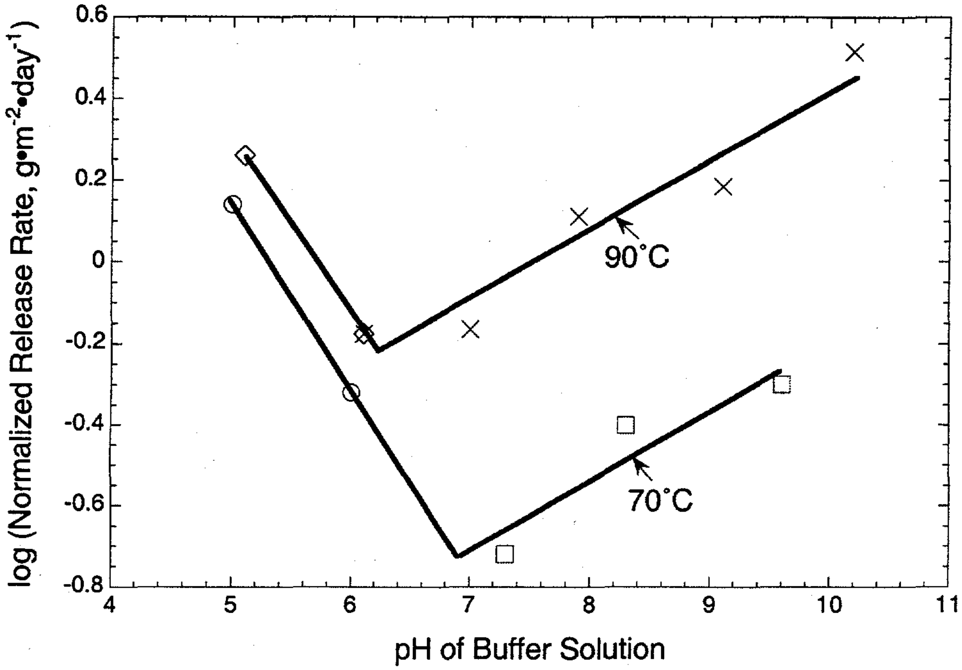

Fig. 1. Log (silicon release rate) from CWF as Function of pH in Buffered MCC-1 Tests at 70 and 90°C.

TABLE III. Values of η for Binder Glass, Sodalite, and CWF at 70 and 90°C (uncertainties of η are standard errors)

Material	η (acidic)	η (basic)
Glass (70°C)	-0.54*	0.63±0.24
Glass (90°C)	-0.20*	0.55±0.15
Salt-loaded Sodalite (70°C)	In progress	In progress
Salt-loaded Sodalite (90°C)	-0.47±0.12	0.23±0.05
CWF (70°C)	-0.46*	0.18±0.07
CWF (90°C)	-0.44*	0.17±0.03

*2-point fit; standard error estimated as ±0.2

DISCUSSION

Controlled-pH MCC-1 tests in the pH 5-10 region show normalized silicon mass losses that increase with test duration, rapidly in the first few days and then more slowly during 5-10 day test durations. Tentative dissolution rates have been calculated in the acidic and basic regions at 70 and 90°C. The dissolution rates are lower at 70°C than at 90°C at all pH values. The dissolution rates have a V-shaped behavior with minima at neutral solution pH values and increase as solution pH becomes more acidic or more basic.

The dissolution rates are consistent with dissolution rates for nuclear waste glasses and aluminosilicate minerals. The pH dependence of the dissolution of glass, salt-loaded sodalite, and CWF display the V-shape behavior reported for nuclear waste glass [4]. For the CWF as well as its components, the rate of dissolution is at a minimum near the point of neutral pH, which is 7.00 at 25°C, decreasing to 6.40 at 70°C and 6.21 at 90°C [11]. The results for salt-loaded sodalite are in fair agreement with dissolution tests of natural sodalite as a function of pH at 50°C: η(acidic) = -0.6 and η(basic) = 0.06 [12]. Other studies found a "flattened V" pH dependence. For example, Knauss and Wolery reported the dissolution rate of albite to be independent of pH over the range pH 3 to 8 [2] and the dissolution rate of muscovite to be pH independent between pH 5 and 7 [3]. Other aluminosilicate mineral dissolution rates are pH dependent over a wider pH range [5].

The dissolution rate of the CWF is expected to be a linear combination of the dissolution of its two components in the absence of synergism (interactive effects) between glass and sodalite dissolution. The pH dependence of the dissolution rate, η, is also expected to be a linear combination of the glass and sodalite rates, weighted in terms of the CWF composition of 75 mass % salt-loaded sodalite and 25 mass % glass. The results of Table III at 90°C indicate that the η(CWF) values derived from measured NL(Si,CWF) are consistent with the η(CWF) calculated from NL(Si, sodalite) and NL(Si, glass) weighted in the 3:1 ratio of sodalite to glass in the CWF. This weighting yields calculated η values for CWF of –0.40 in the acidic region and 0.31 in the basic region.

Additional buffered MCC-1 tests are being carried out at lower and higher pH values to better define the η values. Additional tests are also in progress at 40°C. Values of η at three temperatures will permit the calculation of E_a, which reflects the temperature dependence of the dissolution rate.

Other studies have found that the presence of Si in the neutral and basic pH range reduced the initial dissolution rate of waste glasses by a factor of 20 [7]. In the acidic region, Al was found to reduce the dissolution rate. We have initiated tests to determine the effect of dissolved Si and Al concentration on the dissolution of the glass and sodalite components of the CWF.

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