Hydrothermal Reactions of Nuclear Waste Solids A Preliminary Study

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September 1978

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SUMMARY

A simulated high-level waste glass, Supercalcine, and some common ceramic and metallic solids were exposed to hydrothermal conditions at 350°C and 250°C for time periods ranging from three days to three weeks.^(a) Most of the experiments were done in salt brine, but the glass study did include deionized water tests so that the influence of salt could be better understood.

Under the extreme hydrothermal conditions of these tests, all of the materials examined underwent measurable changes. The glass is converted to a mixture of crystalline phases, depending upon conditions, giving NaFeSi₂O₆ as the primary alteration product. The rate of alteration is higher in deionized water than in salt brine; however, under equivalent test conditions, 66% of the cesium originally in the glass is released to the salt brine, while only 6% is released to deionized water. Rubidium and molybdenum are the only other fission product elements significantly leached from the glass. Evidence is presented which shows that sintered Supercalcine undergoes chemical changes in salt brine that are qualitatively similar to those experienced by glass samples. High concentrations of cesium enter the aqueous phase, and strontium and molybdenum are mobilized.

Scouting tests were made with a variety of materials including commercial glasses, granite, UO₂, Al₂O₃, steel, and waste glasses. Weight losses under hydrothermal conditions are in a relatively narrow band, with glass and ceramic materials showing 3 to 20 times greater weight losses than 304L stainless steel in the 250°C test used.

The conclusion from these studies is that virtually all solid materials show hydrothermal reactivity at temperatures between 250°C and 350°C, and that these extreme conditions are not desirable. Further work is needed to establish kinetic parameters for the hydrothermal reactions.

(a) These conditions were selected to accelerate the hydrothermal reaction; actual temperature during waste storage, even for a high-activity waste, should be less than 200°C if water is present during the first 100-yr time period following closure of the repository. At 1000 yr the temperature will be less than 100°C for both wet and dry storage.

CONTENTS

SUMMARY	iii
INTRODUCTION	1
EXPERIMENTAL	3
RESULTS AND DISCUSSION	5
LEACHABILITY CONSIDERATIONS	5
GLASS CYLINDER BEHAVIOR	6
PHASE BEHAVIOR	14
SUPERCALCINE TEST	16
COMPARATIVE TESTS	21
CONCLUSIONS	27
REFERENCES.	29
ACKNOWLEDGMENTS	31

LIST OF FIGURES

1	Cross Section of 76-68 Glass Exposed to Saturated Salt Brine at 350°C for Three Weeks.	8
2	Cross Section of 76-68 Glass Exposed to Deionized Water at 350°C for One Week	9
3	Concentration Profile Through the Reaction Zone Shown in Figure 4	10
4	Reaction Zone of 76-68 Glass Exposed to Salt Brine at 350°C for One Week	11
5	Reaction Zone of 76-68 Glass Exposed to Deionized Water at 350°C for One Week	13
6	X-Ray Diffraction Traces of Powdered 76-68 Glass After One-Week Hydrothermal Tests at 350°C	15
7	Photomicrographs of Supercalcine Exposed to Salt Brine at 350°C for Three Days	19
8	Cesium Concentration Profile Across the Reaction Zone of a Supercalcine Pellet	20
9	Effect of Temperature on HLW Glass Leach Rates	23
10	Durability of 76-68 Glass as a Function of Time	24
11	Cross Sections of 76-68 Glass Exposed to Salt Brine at 250°C.	25

LIST OF TABLES

1	Constituents of the Hydrothermal-Glass Reaction Tests . . .	4
2	Composition of 76-68 Glass	4
3	Leachability Results for Glass Tests	5
4	X-Ray Fluorescence Analyses of Residual Glass Powders . . .	7
5	Oxide Composition of Supercalcine SPC-4	17
6	Proposed Supercalcine Phases	18
7	Supercalcine Leachability Results	18
8	Results of Scouting Autoclave Leach Tests	22

INTRODUCTION

Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy (DOE), has been studying the reaction of high-level waste (HLW) glass in aqueous solutions at high temperatures. This document presents the results of initial studies of these hydrothermal-glass reactions and a limited evaluation of Supercalcine and other materials.

Storage conditions in geologic repositories have not yet been defined. It has been reported that temperatures as high as 300⁰ to 400⁰C in salt and nonsalt formations could be reached by a close-packed array of high-activity HLW canisters.⁽¹⁾ These estimates can be assumed to be an upper limit on possible temperatures and will probably not be seen in actual wet repositories. We estimate that in salt storage the presence of water around the glass will decrease the maximum glass surface temperature to that of the surrounding rock -- to about 150⁰C maximum. The temperature drop occurs because of a major improvement in near-field heat transfer. These temperatures will occur within the first 100-yr period for high-activity waste, and will fall below 100⁰C in 1000 yr (in either wet or dry storage). Safety and economic considerations will of course be used to define allowable conditions.

Since glasses are known to alter to crystalline products under certain time and temperature conditions,^(2,3) and since water accelerates this process,⁽⁴⁾ it is clear that hydrothermal tests with waste glasses are needed to determine the importance of any changes that occur. Concerning repository design, kinetics for the processes occurring must be defined--particularly the dependence upon temperature--so that controls can be specified, if needed.

The experiments were designed to facilitate the study of simulated HLW glass behavior under hydrothermal conditions. High temperatures and large surface area samples were used to accelerate the formation of hydrothermal reaction products. The intent was simply to determine the reaction products

of the glass-water reaction at high temperatures and to obtain some preliminary information on reaction kinetics. Salt brine was used to simulate a salt formation repository. Deionized water was used as a reference point to other glass durability tests and to give an idea of the behavior of HLW glass in groundwaters of low ionic strength.

Previous studies of the effect temperature has upon glass durability indicated, as expected, that the rate of attack increases as the temperature increases. Between 25°C and 100°C, HLW glass leach rates increase by factors ranging between 10 and 100.⁽⁵⁾ Industrial glass has been tested to temperatures greater than 250°C with similar increases in leach rates.⁽⁶⁾ McCarthy et al. have examined the hydrothermal alteration of the same glass studied in this work.⁽⁷⁾ They report that in deionized water at 300°C the glass altered to several crystalline phases. The major product of their test, $\text{NaFeSi}_2\text{O}_6$, was also found in this study.

In this report we first present the experimental details, then discuss the testing results of waste glass, Supercalcine, and other materials. Our conclusions follow those discussions.

EXPERIMENTAL

Glass samples and deionized water were reacted together with combinations of salt and canister material, as shown in Table 1. The glass used in the tests is the simulated HLW glass designated 76-68[PW-8a-3(1:2)76-101]; its composition is shown in Table 2.⁽⁸⁾ Each test included 10 g of glass ground to -325 mesh, plus a solid cylinder of glass 1.3 cm in diameter and weighing at least 2 g. The powdered glass provided a large surface area that ensured complete reaction, and an evaluation of the reaction depth into the glass cylinder provided preliminary kinetic data.

Deionized water is the standard leachant used in most leach tests; it was used in the hydrothermal studies as a reference point to these other leach tests. Adding 100 g of crushed salt to the 125 ml of water yielded a saturated salt brine even at the high temperatures used in these experiments. The salt came from the 2621-ft level of the site being considered for the Waste Isolation Pilot Plant (WIPP), and was provided by Sandia Laboratories of Albuquerque, New Mexico. Stainless steel (4.2 g of -100 mesh 304 SS) was added in two tests to determine the influence of a canister material on the hydrothermal-glass reactions.

Each test was run at 350°C in a 300-ml Hastelloy C autoclave vessel. The equilibrium operating pressure ranged from 1750 psi to 2510 psi, depending upon the constituents of the test. Tests 1 through 3 ran for one week, and Tests 4 through 6 ran for three weeks. Temperatures were measured with a Chromel-Alumel thermocouple inserted into a thermowell within the solution. Pressures were measured continuously with a Bourdon tube.

After each test the solution concentrations of ions that dissolved from the glass were measured. These results were compared with x-ray fluorescence analyses of the residual powdered solids and of the glass cylinder. Crystalline phases were identified by x-ray diffraction. The glass cylinder was characterized using metallography and scanning electron microscopy (SEM) with x-ray fluorescence capabilities.

TABLE 1. Constituents of the Hydrothermal-Glass Reaction Tests

<u>Test Number</u>	<u>76-68 Glass</u>	<u>Deionized Water</u>	<u>Salt</u>	<u>304 Stainless Steel</u>
1,4	x	x	x	x
2,5	x	x	x	
3,6	x	x		

TABLE 2. Composition of 76-68 Glass

<u>Oxides</u>	<u>Wt%</u>	<u>Oxides</u>	<u>Wt%</u>
Rb ₂ O	0.13	Pr ₆ O ₁₁	0.53
SrO	0.38	Nd ₂ O ₃	1.67
Y ₂ O ₃	0.21	Sm ₂ O ₃	0.33
ZrO ₂	1.77	Eu ₂ O ₃	0.07
MoO ₃	2.28	Gd ₂ O ₃	0.05
RuO ₂	1.07	U ₃ O ₈	4.58
Rh ₂ O ₃	0.17	Fe ₂ O ₃	9.77
PdO	0.53	Cr ₂ O ₃	0.41
Ag ₂ O	0.03	NiO	0.20
CdO	0.03	P ₂ O ₅	0.48
TeO ₂	0.26	Na ₂ O	12.51
Cs ₂ O	1.03	SiO ₂	39.80
BaO	0.56	B ₂ O ₃	9.47
La ₂ O ₃	0.53	CaO	2.00
CeO ₂	1.19	ZnO	4.97
TiO ₂	2.97		

It should be pointed out here that the inclusion of both bulk and powdered samples in a single experiment complicates subsequent data interpretation. Leach rates and chemical back-reactions of the solid cylinder are affected by the high surface area of the powder. As the experiments described are comparative by design, this is mentioned only to ensure that leach rate values are not used in any absolute sense without due consideration of the effects of surface-area-to-solution-volume ratios.

RESULTS AND DISCUSSION

LEACHABILITY CONSIDERATIONS

The durability of HLW products is usually measured by the weight loss of the test sample or by chemical analysis of the solution that the sample contacted. Leach rates based upon weight loss of each glass cylinder are shown in Table 3. The table also lists the fraction of cesium and strontium that left the glass and entered the solution. Within experimental error, the glass cores from Tests 3 and 6 in deionized water lost weight at the same rates as did samples in salt brine (Tests 1, 2, 4). Solution analyses, however, show that salt significantly affects the leachability of the glass. Most of the cesium originally in the glass is released to the salt brine, while only 6% is released to deionized water. Most of the cesium found in

TABLE 3. Leachability Results for Glass Tests

Test	Leach Rate Based on Weight Loss ($\text{g}/\text{cm}^2\text{-d}$)	Percent of Element in Solution							
		Cs	Rb	Sr	Mo	Si	B	U	Zn
1	4.0×10^{-3}	66	72	3.6	54	0.2	71	<0.1	0.5
2	4.6×10^{-3}	80	82	3.4	59	0.2	73	<0.1	0.3
3	5.3×10^{-3}	6	16	0.2	49	2.2	100	0.1	<0.1
4	4.5×10^{-3}	95	90	4.8	62	0.2	96	<0.1	0.3
5	(c)	70	96	3.4	5 ^(d)	0.1	89	0.2	0.6
6	4.0×10^{-3}	4	20	0.4	63	1.9	86	0.2	<0.1

-
- (a) Weight loss of a cylinder of material divided by its geometric surface area and time.
- (b) Each test included roughly 80% glass powder and 20% solid glass cylinder by weight. The majority of ions in solution were leached from the powder.
- (c) Sample damaged during removal from autoclave.
- (d) Does not include molybdenum that precipitated when the solution was acidified.

solution comes from the powdered glass rather than from the glass cylinder. As expected, the leaching behavior of rubidium is similar to that of cesium. Ten times more strontium leached into salt brine than leached into deionized water. More than 50% of the molybdenum and boron were released to the solution--their dissolution behaviors apparently unaffected by the type of solution. In all tests, releases of uranium and zinc to the solution were less than one percent of the original glass inventory. Only silicon was found in higher concentrations in deionized water than in salt brine.

X-ray fluorescence analyses of the reacted glass powder verified the depletion of cesium, rubidium, and molybdenum from the glass. Table 4 lists the percent of the original glass concentrations measured in the powders after Tests 1 through 5. Fluorescence data was not available for Test 6. Aside from cesium, rubidium, and molybdenum, the elements detected by x-ray fluorescence showed only small deviations from the unreacted glass concentrations.

From these observations and the data reported in later sections, several points may be made regarding the behavior of HLW glass in hydrothermal environments:

- Increasing temperature greatly increases the rate of attack upon the glass.
- Salt brine enhances solubility of cesium, rubidium, and strontium.
- Weight loss measurements must be coupled with elemental analyses to understand durability measurements.

GLASS CYLINDER BEHAVIOR

While the glass cylinders showed similar weight loss rates in deionized water and in salt brine, their physical appearances were significantly different. The cylinders treated in deionized water swelled and developed large cracks into the interior, and the color throughout the glass cylinder changed from black to a light, milky green. The one-week salt brine samples showed only surface discoloration and no cracks. After three weeks in salt brine some cracks developed in the cylinder surface.

TABLE 4. X-Ray Fluorescence Analyses of Residual Glass Powders

Element	Percent of Original Glass Concentrations				
	Test 1	Test 2	Test 3	Test 4	Test 5
Cs	23	12	100	16	17
Rb	0	17	89	0	0
Sr	96	94	100	93	100
Mo	31	28	6	23	31
Ba	100	92	100	91	91
Fe	100	100	97	100	100
Ni	100	100	87	100	100
Zn	100	99	100	98	100
Zr	100	100	100	100	100
Ru	100	99	100	97	100
Pd	100	100	100	97	100
Te	100	100	94	94	100
Y	100	100	100	100	100
La	100	93	96	95	100
Ce	100	100	98	95	100
Pr	100	88	100	100	100
Nd	100	89	100	100	100
U	100	88	100	99	100

Figures 1 and 2 show polished cross sections of the three-week salt brine cylinder (Test 4) and the one-week deionized water cylinder (Test 3), respectively. The Test 4 sample has an inner core of unreacted glass surrounded by a reaction layer 0.21 cm thick. The Test 3 sample reacted through its entire 1.3-cm diameter. Large cracks are clearly evident. The dark regions correspond to residual RuO_2 and $(\text{Fe,Ni,Cr})_3\text{O}_4$ undissolved in the original glass. Numerous small crystals ($<1\ \mu\text{m}$) seen in the reaction zone are too small to be analyzed by microprobe. They appear to be embedded in unreacted glass.

FIGURE 1. Cross Section of 76-68 Glass Exposed to Saturated Salt Brine at 350°C for Three Weeks

FIGURE 2. Cross Section of 76-68 Glass Exposed to Deionized Water at 350°C for One Week

Concentration profiles across the reaction zone of each sample were made using the energy dispersive x-ray (EDX) attachment to the SEM. Figure 3 shows the profile and Figure 4 shows the corresponding micrograph of the reaction layer of the one-week salt brine sample (Test 2). Peak height is plotted as a function of position for the reaction layer, which is 0.07 cm thick. Positions 2 through 11 correspond to the region where the glass has

FIGURE 3. Concentration Profile Through the Reaction Zone Shown in Figure 4

FIGURE 4. Reaction Zone of 76-68 Glass Exposed to Salt Brine at 350°C for One Week

altered and formed some crystalline phases. In this region silicon, uranium, and zinc (not shown) appear in lower concentrations than in the unreacted glass indicated by positions 18 and 19. Uranium seems to diffuse to a high-concentration region centered at position 3. Calcium and titanium (not shown) show higher concentrations in the alteration region than in the bulk glass. Cesium and molybdenum are undetectable in this region. Iron remains at its bulk-glass concentration throughout the reaction zone.

Positions 12, 13, and 14 designate a region where all detected elements except cesium return gradually to their unreacted glass concentrations. This area corresponds to the devitrification front Lofgren identifies for natural rhyolite glass.⁽⁴⁾ In this front and in the alteration region behind it, ions diffuse to nucleation sites and crystals begin growing. Uranium provides a prime example of this mechanism, since in all salt brine tests it is concentrated in a zone just beneath the surface of the sample. Its chemical form in this region has not been determined.

Positions 15, 16, and 17 correspond to a region described in the literature as a hydration layer.^(2,4,9) The glass matrix absorbs water, hydrolyzing the Si-O-Si bonding. The water absorption also strains the glass and may cause the observed microcracks within the hydration layer, although these may also be caused by drying the sample prior to examination. The concentration profile through the HLW glass indicates that cesium and possibly other alkali metals are diffusing out of this hydration layer. Position 18 is just beyond the hydration front, and the composition at positions 16 through 18 is actually not measurably different from that of the unreacted glass.

Figure 5 shows the region of the one-week deionized water test cylinder (Test 3) across which a concentration profile was made. The profiles do not reveal any significant variations in elemental concentrations across the sample radius. Since this sample has altered through its entire radius, no hydration layers are visible.

The behavior of this HLW glass may be compared to the behavior of natural glasses. Marshall reports hydrothermal reaction rates of perlite in terms of the time required to alter the glass to a depth of 100 μm as a function of temperature.⁽⁹⁾ At present, data on waste glass are available only for tests done at 250°C and 350°C, and these tests were not done under entirely constant conditions of sample surface areas and solution volumes. The data do suggest a temperature dependence comparable to natural glasses, but the alteration rates are higher. Extrapolation of alteration rates for the waste glass to lower temperatures, nevertheless, suggests adequate durability for geologic times. Alteration rates are so highly dependent upon temperature that a glass which alters to a depth of 1 cm in one week at 350°C requires about 10^5 yr to alter to this depth at 100°C. More data is needed to verify this conclusion, though the work on natural glasses is supportive.

In summary, examination of glass cores from the hydrothermal-glass reaction tests at 350°C shows that:

high-level waste glasses behave similarly to natural glass--first hydrating, then altering to crystalline products.

FIGURE 5. Reaction Zone of 76-68 Glass Exposed to Deionized Water at 350°C for One Week

- the rate of alteration of the HLW glass studied is higher than that of natural glass.
- salt brine reduces the rate of alteration by a factor of approximately 50, compared to the rate in deionized water.

PHASE BEHAVIOR

The powdered glass from each test was analyzed by x-ray diffraction to study the alteration products of the hydrothermal-glass reaction. Figure 6 shows part of each diffraction trace for the unreacted glass and for the residuals (i.e., after washing the salt away) from Tests 1, 2, and 3. The major reaction product is a silicate with the composition $\text{NaFeSi}_2\text{O}_6$. This is the same pyroxene mineral (acmite) identified by McCarthy in his studies.⁽⁷⁾ We did not find the $(\text{Na,Cs})_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$ phase that McCarthy found, probably because uranium is reduced to the +4 state by the Hastelloy autoclave in our own experiments. Residual RuO_2 in the original glass remains unreacted. The stability of the $(\text{Fe,Ni,Cr})_3\text{O}_4$ phase typically found in HLW glasses is not known because of direct overlap with reflections from the $\text{NaFeSi}_2\text{O}_6$ phase. The 304 stainless steel present in Tests 1 and 4 apparently was not reactive, as its expected diffraction pattern is present (at a higher 2θ than shown).

Although examination of the glass cylinder clearly shows deionized water to be more destructive than salt brine, the reaction products for the glass powder are similar for each solution. The major difference in the diffraction patterns for the crystalline phases lies in the region of 20° to 30° 2θ , where two major phases and one or two secondary phases remain to be identified. The crystals generated in these tests are generally sub-micron in size. Crystals large enough to be characterized (ideally $>5\ \mu\text{m}$) require higher temperatures and/or longer times for growth. Intensity measurements, when compared to standard crystalline mixtures, indicated that about 50% of the powdered glass was converted to crystalline products. There was little difference in the products from the one- and three-week tests, suggesting that "equilibrium" was approached. Contrary to suggestions of some workers,⁽⁷⁾ it is not obvious that fully crystalline products arise from hydrothermal reactions of these very complex glasses.

FIGURE 6. X-Ray Diffraction Traces of Powdered 76-68 Glass After One-Week Hydrothermal Tests at 350°C

SUPERCALCINE TEST

Supercalcine is a ceramic alternative to glass as a waste form, and is being developed by PNL and Pennsylvania State University. The concept and some evaluations have been reported by Rusin et al.⁽¹⁰⁾ The elemental concentrations for the variation studied (SPC-4) and the various phases present (assumed compositions) are given in Tables 5 and 6. The Supercalcine was exposed to hydrothermal conditions similar to those described previously for glass. A pellet of sintered Supercalcine, 12 g of -325 mesh Supercalcine, 120 g of -325 mesh NaCl, and 150 ml of deionized water were combined in a 500 ml Hastelloy C autoclave for 67 hr at 350°C and 1600 psi.

Solution Analysis

Table 7 shows the percentages of cesium, rubidium, strontium, molybdenum, and silicon found in the solution. After three days as much rubidium and strontium had dissolved from the Supercalcine as had dissolved from glass in seven days. Approximately 50% of the cesium was released to the solution. Molybdenum showed significantly different behavior in Supercalcine than in glass; less than 1% of the molybdenum was found in the solution from the Supercalcine test, while more than 50% was dissolved in the glass test.

Solids Examination

The sintered pellet survived the hydrothermal conditions with only slight discoloration and with a net weight gain rather than a weight loss. Figure 7 shows photomicrographs of a cross section of the pellet, revealing a reaction zone approximately 0.02 cm thick. A phase identified by microprobe analysis as $(Ca_{.1}Sr_{.8}Ba_{.1})MoO_4$ grew on the surface of the sample. Although the analysis was only semiquantitative, note the major difference between the actual and the assumed compositions (Table 5). We believe the crystal growth resulted from the transport of elements from the powder to the surface of the pellet, since the pellet itself did not show major depletion of these elements. This is not true, however, in the case of cesium. A cesium concentration profile obtained by SEM-EDX is shown in Figure 8. Similar to glass, Supercalcine is largely depleted of cesium at the surface--the depletion in fact extending to greater depths than might

TABLE 5. Oxide Composition of Supercalcine SPC-4

Oxide	Grams of Oxide per Liter of Calcined SPC-4	Weight Percent of Oxide
RE ₂ O ₃ (a)	34.07	20.4
Gd ₂ O ₃	27.69	16.6
ZrO ₂	13.04	7.8
Fe ₂ O ₃	8.00	4.8
P ₂ O ₅	7.10	4.3
MoO ₃	13.68	8.2
Cs ₂ O	7.61	4.6
BaO	4.13	2.5
SrO	2.81	1.7
Cr ₂ O ₃	0.91	0.5
Rb ₂ O	0.94	0.6
Na ₂ O	0.31	0.2
RuO ₂	0.80	0.5
NiO	0.38	0.2
CdO	0.26	0.2
Ag ₂ O	0.23	0.1
CaO	3.47	2.1
SrO	4.26	2.6
Al ₂ O ₃	7.55	4.5
SiO ₂	29.34	17.6
	166.58	100.0

(a) RE = 0.133 Nd + 0.051 Ce + 0.014 La + 0.003 Pr +
0.002 Sm + 0.002 others; 0.002 RE is a stand-in for
Am+Cm.

TABLE 6. Proposed Supercalcine Phases

<u>Phase</u>	<u>Weight, g/liter</u>	<u>Wt%</u>
$\text{Ca}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$	42.5	25.5
$\text{Ca}_2\text{Ce}_8[\text{SiO}_4]_6\text{O}_2$	11.2	6.7
$\text{Cd}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$	1.9	1.1
$\text{Ag}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$	1.9	1.1
REPO_4	23.5	14.1
ZrO_2	13.1	7.8
SrMoO_4	16.8	10.1
BaMoO_4	8.0	4.8
$\text{CsAlSi}_2\text{O}_6$	16.9	10.1
$\text{RbAlSi}_2\text{O}_6$	2.6	1.6
$\text{NaAlSi}_2\text{O}_6$	2.0	1.2
$\text{Ni}(\text{Fe})_2\text{O}_4$	1.2	0.7
$\text{Fe}(\text{Cr})_2\text{O}_4$	1.4	0.8
Fe_2O_3	6.7	4.0
RuO_2	0.8	0.5
CaO	0.1	0.1
Al_2O_3	7.5	4.5
SiO_2	<u>8.9</u>	<u>5.3</u>
	167.0	100.0

TABLE 7. Supercalcine Leachability Results

<u>Element</u>	<u>Percent of Waste in Solution</u>
Cs	46.0
Rb	80.0
Sr	3.3
Mo	0.6
Si	0.5

FIGURE 7. Photomicrographs of Supercalcine Exposed to Salt Brine at 350°C for Three Days

FIGURE 8. Cesium Concentration Profile Across the Reaction Zone of a Supercalcine Pellet

be thought by examining the micrographs in Figure 8. The photomicrographs show increased porosity in the reaction zone, which probably permits easier solid/solution phase interactions than occur with a glass.

X-ray diffraction analysis of the powdered Supercalcine before and after the hydrothermal test shows only small changes in the phase assemblage as evidenced by diffraction intensity and unit cell dimensions. The pollucite phase--assumed to "fix" cesium--shows no intensity change, but the lattice parameter changes from 13.68 Å to 13.72 Å. A rapid Na-Cs ion exchange reaction, coupled with the incorporation of water into the pollucite structure, accounts for the cell dimension change. Although Na^{+1} is smaller than Cs^{+1} , the openness of the structure and the incorporation of water preclude any understanding of composition changes simply from lattice constant measurements. The same statement is true about the diffraction intensity, which may remain nearly constant as ion exchange reactions proceed.

The results of this preliminary test show that under hydrothermal conditions in salt brine, Supercalcine undergoes significant alteration reactions. Certainly more than one experiment is needed to accurately study and determine the hydrothermal behavior pattern of any waste form; nevertheless, this test suggests that Supercalcine and glass behave in a similar fashion.

COMPARATIVE TESTS

Prior to the more detailed experiments discussed in previous sections, scouting tests were run to evaluate the relative durability of several waste-related materials. Small, solid samples of canister materials, glasses, and ceramics were exposed to a simulated Waste Isolation Pilot Plant (WIPP) salt brine (80% saturated) for 72 hr at 250°C and 1000 psi. The 50 ml of solution for each test was contained in an 80-ml Inconel pressure bomb. Durabilities were measured strictly by weight loss. As was pointed out earlier, a weight loss measurement tells only part of the story, since glasses in particular may be altered extensively without a large weight change, and since weight loss data does not reveal the behavior of specific elements leached. Also, metals may oxidize without material loss, consequently showing a weight increase.

With the limitations of a weight loss measurement in mind, the results of the scouting tests presented in Table 8 may be discussed. Within experimental error, all of the glass and ceramic materials are as durable as the standard borosilicate glass (NBS-717). The three metals show the highest durability, but the short durations of these scouting tests may not be adequate to reveal true corrosion behavior.

The test of 76-68 glass in 150 ml of brine solution, when compared to the 50 ml test, suggests that there is a waste-volume-to-solution-volume effect. This parameter has been shown to be important by previous lower-temperature leach studies. Increasing the solution-to-waste ratio apparently increases the amount of waste taken into solution because of concentration levels needed to establish "equilibrium."

TABLE 8. Results of Scouting Autoclave Leach Tests^(a)

Sample Material	Leach Rate, g/cm ² -day ^(b)		
	50 ml Brine Solution	150 ml Brine Solution	50 ml Deionized Water
Soda-lime-silica glass (NBS No. 710)	3×10^{-3}		
Borosilicate glass (NBS No. 717)	5×10^{-4}		
Waste glass 72-68[PW-4b-7(2.8)73-1]	7×10^{-4}		
Waste glass 76-68[PW-8a-3(2.0)76-101]	2×10^{-4}	2×10^{-3}	8×10^{-3}
Granite	6×10^{-4}		
UO ₂ fuel pellet	2×10^{-4}		
Alumina	2×10^{-4}		
Sintered Supercalcine (SPC-2)		4×10^{-4}	
304L stainless steel	4×10^{-5}		
Inconel-601	4×10^{-5}		
Carbon steel	7×10^{-5}		

(a) Samples immersed in simulated WIPP brine for 72 hr at 250°C and 1000 psi.

(b) Based upon weight loss and geometric surface area.

Some kinetic data can be obtained by combining the results of these scouting tests with tests at 25°C, 100°C, and 350°C. Figure 9 shows an Arrhenius plot of the weight loss data of 76-68 glass in salt brine and deionized water. Deionized water represents a "worst" case based upon weight loss alone. The activation energies calculated from the slopes of the lines are 9 kcal/mole in salt brine and 8 kcal/mole in deionized water.

Other tests at 250°C also provided weight loss rate-versus-time data. Figure 10 shows weight loss data as a function of time for the 250°C and 350°C tests with 76-68 glass. At 250°C there is no further weight loss apparent after one week of testing. At 350°C in 125 ml of 100% saturated brine, the weight loss continues to increase after three weeks. Micrographs of the samples from the 250°C tests are shown in Figure 11. They show that the initial alteration layer depth produced after three days does not

FIGURE 9. Effect of Temperature on HLW Glass Leach Rates

increase in direct relation to time. The reaction products apparently provide some protection against rapid hydrothermal attack. There is some evidence that cracks in the altered zone allow access of water to the unreacted glass, but swelling of the glass and growth of crystals along the crack may tend to seal the openings. Longer-duration tests are needed to establish whether crack sealing actually does occur. Tests of glass in a waste canister are needed to understand the "effective" surface area in view of this potential for self-sealing of cracks.

FIGURE 10. Durability of 76-68 Glass as a Function of Time

FIGURE 11. Cross Sections of 76-68 Glass Exposed to Salt Brine at 250°C

CONCLUSIONS

- High-level waste glass behavior is similar to natural glass behavior under hydrothermal conditions: the glass hydrates and then crystallizes.
- The rate of alteration of the HLW glass studied is higher than the rate of alteration of natural glasses.
- High-level waste glass alteration rates are lower in salt brine than in deionized water.
- Even with complete alteration of the glass, most waste elements remain insoluble.
- Cesium, rubidium, strontium, and molybdenum show moderate-to-high solubility levels in salt brine--more than an order of magnitude higher than the levels observed in deionized water.
- $\text{NaFeSi}_2\text{O}_6$ is the primary alteration product in both salt brine and deionized water treatments for the glass studied.
- The stainless steel canister material does not affect elements released to the solution phase.
- Supercalcine shows hydrothermal reactivity that is qualitatively similar to that of glasses. Cesium, rubidium, and strontium reveal the same solubility trends found for the glass.
- Additional hydrothermal experiments are needed to more completely define hydrothermal behavior of glass, particularly with respect to the temperature dependence for alteration, and within the temperature range more likely to be encountered (e.g., 100^o to 200^oC).
- Based upon weight loss comparison, the hydrothermal durabilities of waste glass, commercial glasses, and common ceramic oxides are all comparable.

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