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ABSTRACT

The leachability of Savannah River Plant (SRP) waste glass was assessed for leachants in the pH range of 3 to 11. A parabolic relationship was observed between leachability and solution pH in this range. At 40°C, leachability was lowest within a pH range of approximately 5 to 9. Most of the groundwaters in potential repository locations have pH values in this range. Below pH 5 and above pH 9, leachability of the waste glass increases. Leachability as a function of solution pH was studied first at room temperature and then in more detail at 40°C, 90°C, and 150°C using abbreviated MCC-1 and MCC-2 static leaching tests. These data were then correlated with the formation and stabilization of surface layers that are produced on the waste glass during leaching.

INTRODUCTION

The leaching behavior of Savannah River Plant (SRP) waste glass was studied as a function of temperature and solution pH. An integrated approach was used which combined leachate solution analysis with more detailed bulk and surface studies in order to obtain as much information as possible concerning the leaching process. This study is one part of a multiphase experimental program at Savannah River directed at assessing, understanding, and predicting the long-term chemical durability of SRP waste glass forms.[1,2]

SUMMARY

- A parabolic relationship of leachability versus solution pH was observed at room temperature, 40°C, 90°C, and 150°C. Glass corrosion at room temperature was at a minimum between pH values of 5 and 9. Above pH 9 and below pH 5, glass corrosion increased.
- Most pH values of repository groundwaters now under consideration generally fall within regions of minimum leachability.
- Protective surface layers form on waste glass samples during leaching in neutral and basic solutions. In the acidic leachant, no layers were observed at 40°C or 90°C; at 150°C, only an interaction zone was noted.
- There appears to be a direct correlation with adhered surface layer thickness and leachability.

- The thicknesses of adhered protective surface layers decrease in both neutral and basic solutions when temperature is increased from 90°C to 150°C. At 150°C, the surface layers also become depleted in elements such as Mg, Ca, and Ni. These data correspond to higher leach rates of the waste glass.
- The activation energies for leaching at pH 3 and 11 are very similar and relatively small. The activation energy for leaching at pH 7, where leach rates are lowest, is considerably higher.

EXPERIMENTAL PROCEDURES

A two-part experimental effort was used to evaluate the leachability of TDS/131 waste glass (Table 1). The first set of tests were scouting tests used to determine the functional relationship of leachability of waste glass in eight buffered solutions with pH values ranging from 3 to 11 (Table 2). The second set of tests focused on the three most important pH regions defined in the scouting tests and studied leachability in leachants of pH 3, 7, and 11 at 40°C, 90°C, and 150°C. These experiments were performed using standardized static leaching procedures. The leachability data derived from solution analyses were then correlated with more detailed bulk and surface analyses of the leached glass surfaces.

Scouting Tests (Powders)

Samples of 131/TDS waste glass were ground to 40- to 60-mesh size. The waste glass powder was then placed in polypropylene vials and filled with buffered leachant using a relatively high ratio of glass surface area to leachant volume (SA/V) of 10 cm^{-1}. The vessels were capped and placed in a constant-temperature oil bath for 5-day tests. During this time, a nitrogen gas stream flowed in the vials. The nitrogen was first passed over ascarite and a glass wool trap to remove carbon dioxide and any particulates which could influence the data. The pH values were recorded at the end of each test, and solution analyses were performed using colorimetry and atomic absorption.

MCC-1 and MCC-2 Tests (Solid Slices)

Glass slices were prepared and tested in accordance with Material Characterization Center (MCC) procedures.[3] The slices were prepared to a 600 grit surface finish for detailed surface studies, and modified MCC-1 and MCC-2 tests were performed. Glasses were tested in buffered solutions of pH 3, 7, and 11 at 40°C, 90°C, and 150°C for 28 days using ratios of SA/V = 0.1 cm^{-1}. All tests were conducted in Teflon® (Du Pont trademark) vessels, and units at 150°C were placed in high-pressure bombs. Solution analyses were performed using inductively coupled plasma spectroscopy and atomic absorption. Optical microscopy, scanning electron microscopy, x-ray energy spectroscopy, wide-angle x-ray diffraction, electron microprobe analysis, and Auger electron spectroscopy were used in the bulk and surface studies. A discussion of these techniques and their application are given elsewhere.[4,5]

RESULTS

Solution Analyses

A generally parabolic relationship was observed for silica dissolution versus pH of the solution as shown in Figure 1. Silica dissolution is perhaps the best measurement for long-term corrosion of the product.

From the scouting tests over the pH range of 3 to 11, glass corrosion increased for leachate pH values greater than 9 and less than 5. However, in the pH range of about 5 to 9 for the room temperature data, silica dissolution was at a minimum. Fortunately, most of the groundwaters of geologic sites being considered as potential repository locations have pH values which initially fall within this region of optimum product performance (Figure 1).[6] As a result of the data shown in Figure 1, three distinct regions of waste glass leaching can be defined, i.e., acid, neutral, and base leaching of waste glass forms. Each of these regions has different leachability characteristics due to solubility considerations and possible changes in the mechanism of corrosion of the glass. Qualitative and quantitative models have recently been proposed describing a 3-stage corrosion process for SRP waste glass systems.[7]

After the scouting tests were completed, a more detailed leaching study was performed using standard MCC-1 and MCC-2 static leach tests. Leachates were examined for Si, B, Na, Mn, Fe, Cs, Sr, and Mg concentrations after leaching experiments. The average concentrations of species of interest at 40°C, 90°C, and 150°C at pH values of 3, 7, and 11 are summarized in Table 3. Note from these data that as temperature increases, glass dissolution increases. The most corrosive leachant is generally the acid medium followed by basic solutions. The neutral leachant was usually significantly less corrosive than the other solutions tested.

A parabolic relationship of glass leachability based on silicon extraction versus leachate pH was observed at each of the temperatures studied and is summarized in Figure 2. These curves shift to higher leachabilities with increasing temperature. Leachabilities were then calculated for each set of data based on extraction of six individual species and are summarized for 90°C in Figure 3 for solution pH values of 3, 7, and 11. Note from these curves that all elements are readily leached from the glass in the pH 3 leachant. However, Sr, Fe, and Mn are found only in very small quantities after leaching in solutions of pH = 7 and 11. This indicates that these elements are important to the surface layers formed during leaching. The solution analyses further suggest that while surface layers may be formed from pH 7 and 11 leachates, these same types of layers are not produced upon leaching in a pH 3 medium.

Surface Studies

Distinct differences in surface layers or interaction zones were produced for glasses leached in solutions of pH 3, 7, and 11.

These differences were most pronounced at 150°C. At this temperature, the pH 3 leached glass produced a porous and very rough interaction zone composed of at least three separate layers. The resulting film contained many cracks and was not continuous over the surface of the glass. The most adherent and continuous film occurred for glasses leached at pH 7, while glasses studied at the extreme conditons of pH 11 and 150°C yielded a surface layer that was subject to spalling.

The surface layers formed during leaching at 90°C in pH 7 and pH 11 solutions were generally enriched in major components from the waste such as Fe and Mn, and minor frit species such as Mg. Silicon was depleted in most surface layers. The average enrichment of components of interest within the surface layers as indicated by electron microprobe analysis are qualitatively shown in Table 4 along with the corresponding layer thicknesses. Further analyses of the outermost portion of leached glass surface layers by Auger electron spectroscopy is given in Table 5, and profiles of key elements through the surface layer are shown in Table 6. Each of the three pH regions will now be discussed in more detail:

pH 3

The surface layers formed after leaching glasses at pH 3 at 40, 90, and 150°C are given in Figure 4, along with x-ray line profiles of Si. At 40 and 90°C, the interaction layer is approximately 1 or less in thickness. At 150°C, the zone is about 35μ and composed of at least 3 separate layers, as shown in the micrographs. A characteristic feature of this large interaction zone, which distinguishes it chemically from the 150°C surface layers produced at pH 7 and 11, is a large Fe depletion.

pH 7

Only a very thin surface layer was produced after leaching glass at pH 7 at 40°C. At this temperature, the leaching process was apparently so slow that no significant layer formation resulted in the time period of the experiment. At 90°C, the thickest adhered surface layers observed in the entire study were produced and were about 15μ in depth. At 150°C, the layers decreased in size to about 10μ but still adhered to the glass.

One of the most interesting observations involving the chemical composition of these layers was made on glasses leached at 90 and 150°C. At 90°C, surface layers were generally enriched in elements such as Mn, Mg, Ca, and Ni. At 150°C, these elements were severely depleted in the surface layers (Figure 5).

pH 11

For glasses leached in solutions of pH 11, surface layers were observed at each of the temperatures studied. Layer thicknesses were 2μ at 40°C, 10 at 90°C, and about a 6μ layer was still on the glass at 150°C (Figure 6). Spalling of the layers formed at 150°C was observed during the experiment. Changes in the chemical composition of the surface layers in going from 90 to 150°C at pH 11 are similar to the changes observed at pH 7.

DISCUSSION

In a repository environment involving defense waste glass forms, the peak surface temperature for the waste form during the thermal pulse period is only about 90°C. Storage temperatures will then approach relatively low values (<50°C) within the first 1000 years of isolation during which engineering barriers will provide zero release from the waste package. The tests performed at 150°C, therefore, do not represent expected repository conditions but were run to better understand the properties of the glass waste form.

Under expected repository temperatures, based on laboratory tests, one would expect minimum glass dissolution to occur in the pH range of about 5 to 9. Since most groundwaters in geologic repository sites under consideration fall within this range initially, one would anticipate optimum product performance or minimum leachability of the waste glass with respect to pH effects. Even with increasing pH in unbuffered leachants, as observed during leaching with deionized water, the leachate will still be partially buffered by constituents extracted from the glass. In addition, surface layers are observed to form even as pH increases. These layers can then partially protect the glass from the newly created basic leachant. Surface layer formation and stabilization is the most important consideration for long-term durability of the product.

Data on thickness of surface layers suggest that after moderate leaching times, the leachability of the product correlates to the thickness of the adhered surface layers. At 40°C, these layers are beginning to grow. At 90°C, they appear to have formed well within the time period of the experiment. The thickness of the surface layer produced from the pH 7 leachant at 150°C is very similar to the surface layer thickness produced from the pH 11 leachant at 90°C. These adhered layers, of about 10μ in thickness, correlated very well with leachability, and correspond to silicon concentrations found in solution of 63 and 69 ppm. In addition, for both of these systems, the surface layer thickness decreases from 90°C to 150°C, which also corresponds with increased leachability. As a result of the surface layers formed, leachability decreases with time.

Finally, an interesting observation was made by plotting log of leachability versus 1/T. The slope of these plots obtained from a least-squares fit represents the activation energy of the leaching processes. As noted in Figure 7, glasses leached at pH 3 and pH 11 have similar slopes corresponding to activation energies of 5.5 and 5.7 kcal/mole, respectively. These are relatively low activation energies and suggest low impedance to species dissolving from the glass. In contrast, the activation energy of pH 7 is considerably higher, at 14.0 kcal/mole. The relative standard deviation of the activation energies was less than 5%. Recall the parabolic relationship of leachability which shows an increase of glass leaching in pH 3 and 11 versus pH 7.

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TABLE 1

Composition of SRP 131/TDS Waste Glass (Doped with Cs and Sr)

Waste Glass		131 Frit	
Component	Wt %	Component	Wt %
Frit 131	68.2	SiO_2	57.9
CsCl	1.0	Na_2O	17.7
$SrCl_2$	1.0	B_2O_3	14.7
Fe_2O_3	14.1	TiO_2	1.0
MnO_2	4.1	Li_2O	5.7
AW-500*	3.0	MgO	2.0
Al_2O_3	2.8	ZrO_2	0.5
NiO	1.7	La_2O_3	0.5
SiO_2	1.2		
CaO	1.1		
Na_2O	0.9		
Coal	0.7		
Na_2SO_4	0.2		

* Linde AW-500 zeolite (calcium-aluminum-silicate)

TABLE 2

Leachant Compositions

pH	Buffered Solution *
3**	0.5M Glycine, 14 drops HCl
5	0.5M Glycine, <1 drop HCl
7**	50 ml of 0.1M Tris† + 46 ml 0.1M HCl
8	50 ml of 0.1M Tris + 29.2 ml 0.1M HCl
9 (A)	LiOH + H_2O
9 (B)	50 ml 0.1M Tris + 5.7 ml 0.1M HCl
10	LiOH + H_2O
11**	LiOH + H_2O

* All of the solutions were used in scouting tests.

** Buffered solutions of pH 3, 7, and 11 were used in the more detailed MCC-1 and MCC-2 static leach tests.

† Tris (hydroxymethyl) aminomethane.

TABLE 3

Leachate Concentrations After MCC-1 and MCC-2 Tests*

Temp.	Solution pH	Si	B	Na	Mn	Fe	Cs	Sr	Mg
40°C**	3	27.00	4.39	12.26	3.82	12.30	1.04	0.94	1.16
	7	0.20	0.13	0.48	0.10	0.04	0.01	0.02	0.01
	11	20.30	3.57	10.51	0.03	0.20	0.79	0.10	0.05
90°C**	3	105.00	15.57	44.59	13.64	47.25	3.89	3.37	4.13
	7	2.71	2.24	7.74	1.53	0.06	0.40	0.36	0.41
	11	63.36	14.13	42.50	0.07	0.23	2.65	0.27	0.13
150°C***	3	224.60	42.58	130.77	36.67	113.55	9.72	8.33	10.21
	7	69.27	13.17	38.46	10.64	3.10	2.97	2.53	3.39
	11	211.03	103.27	288.94	1.02	2.46	5.80	0.72	0.81

* Each concentration is the average of three samples leached under identical conditions and corrected with a blank.

** MCC-1 static leach tests.

*** MCC-2 static leach tests.

TABLE 4

Electron Microprobe Analysis of Relative Enrichment of Elements of Interest in Surface Layers

	pH = 3			pH = 7			pH = 11		
	40°C	90°C	150°C	40°C	90°C	150°C	40°C	90°C	150°C
Layer Thickness	<1μ*	<1μ*	20μ/15μ**	<1μ*	15μ	10μ	2μ	10μ	6μ
Si			+/-		-	-	-	-	-/-
Al			+/+		+/+	+/+	-	+	+
Fe			-/-		+	+	+	+	+
Mg			-/-		+/+	-	+	+	-/+
Ca			-		+	-	+	+	-
Mn			-		+	-	+	+	-
Ni			-		+	-	+	+	-
Na			-		-	-	-	-	-

* Surface layers too thin for microprobe analysis.

** Multilayers.

+ Denotes element enriched in surface layer compared to bulk glass.

- Denotes element deficient in surface layer compared to bulk glass.

TABLE 5

Auger Analysis of Relative Enrichment of Elements of Interest in Surface Layers (Approximately 15A°)

	pH = 3			pH = 7			pH = 11		
	40°C	90°C	150°C	40°C	90°C	150°C	40°C	90°C	150°C
Si	0.9			0.8	0.2	0.2	0.7	0.9	1.0
Al				1.6	2.3	10.8	2.8	0.9	0.8
Fe	1.3			3.3	7.5	4.0	3.5	0.8	2.2
Mg							96.0		17.0
Mn	2.0			4.0	7.0	8.0	7.0	9.0	
Ni				3.0			23.0		3.0
Ti	1.5			1.4	1.2	0.8		0.8	
O	0.9			0.5	0.9	0.5	0.6	1.1	1.0
Ca							0.9		

TABLE 6

Depth Profile and Relative Enrichment* of Selected Elements in Glass Surface Layer Produced from pH 7 Leachant at 90°C

Depth (μ)	Mn	Fe	Al	Si
0	38	11.9	3.9	0.09
0.05	37	6.4	4.5	0.08
0.15	24	8.8	3.9	0.12
0.20	27	8.4	3.7	0.09
0.25	29	10.0	4.0	0.01
0.30	23	9.9	3.1	0.15
0.45	20	10.4	2.5	0.11
0.60	16	10.0	2.3	0.12
0.90	19	11.1	2.3	0.01
1.2	18	11.4	1.9	0.01
1.5	19	11.2	2.3	0.01
1.8	17	14.0	2.2	0.01
2.1	16	12.0	1.9	0.01
2.4	22	11.2	2.5	0.01
2.7	16	12.6	1.9	0.11
3.3	11	10.5	1.7	0.09

* Numbers represent the ratio:

$$\frac{\text{(concentration of element in surface layer)}}{\text{(concentration of element in bulk glass)}}$$

Values greater than 1 indicate enrichment, less than 1 indicate depletion.

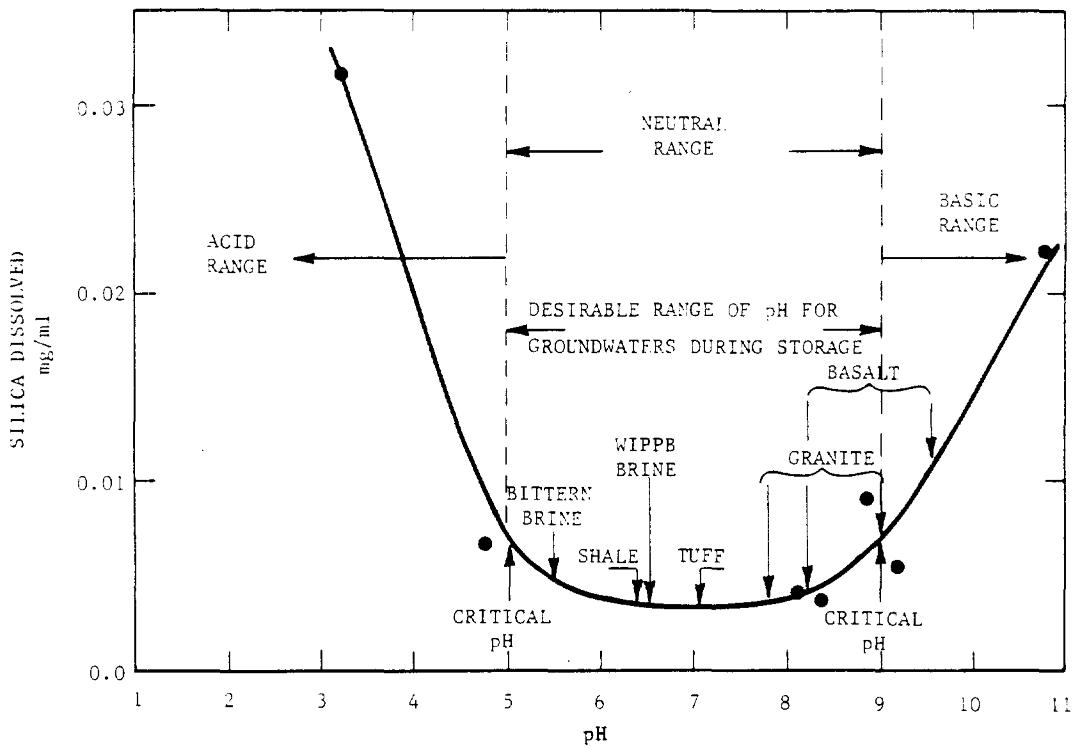

FIGURE 1. Silica Dissolution vs pH Curve

Scouting leaching tests - TDS/131 glass powder with SA/V = 10 cm^{-1} leached for 5 days in deionized water at room temperature.

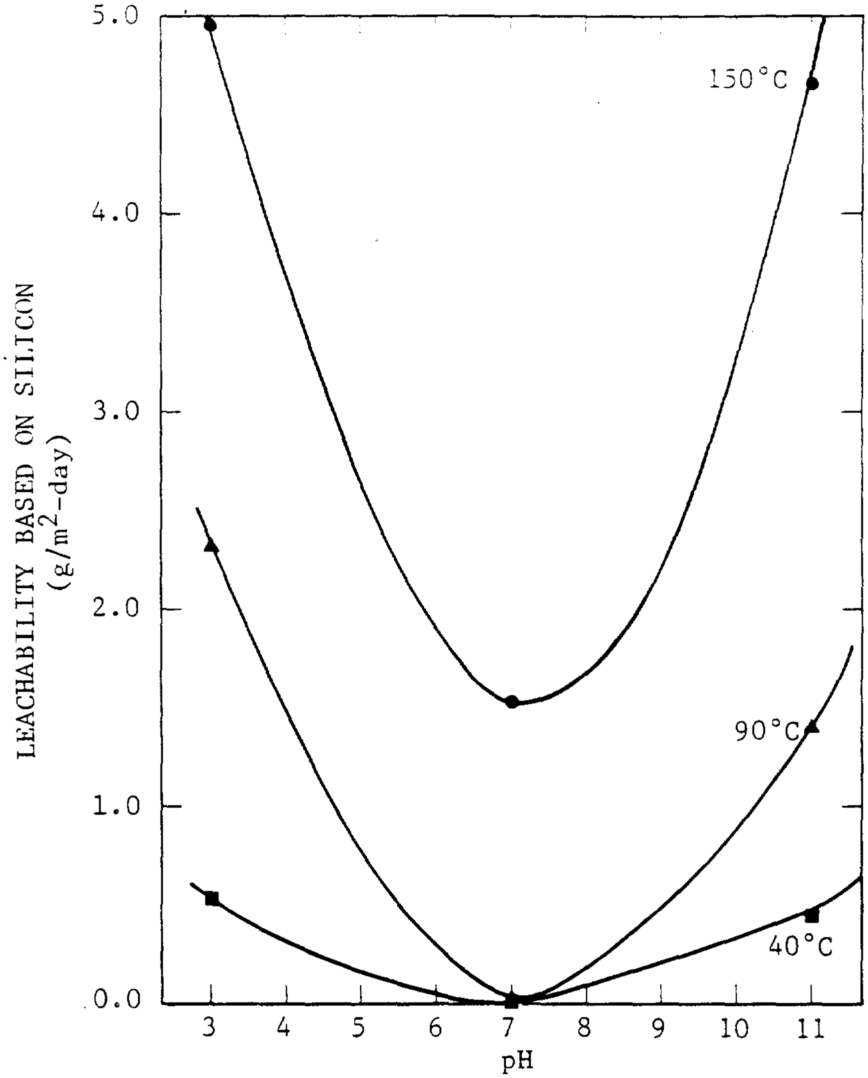

FIGURE 2. Leachability as a Function of pH at 40°C, 90°C, and 150°C
MCC-1 Tests
90°C/28 days

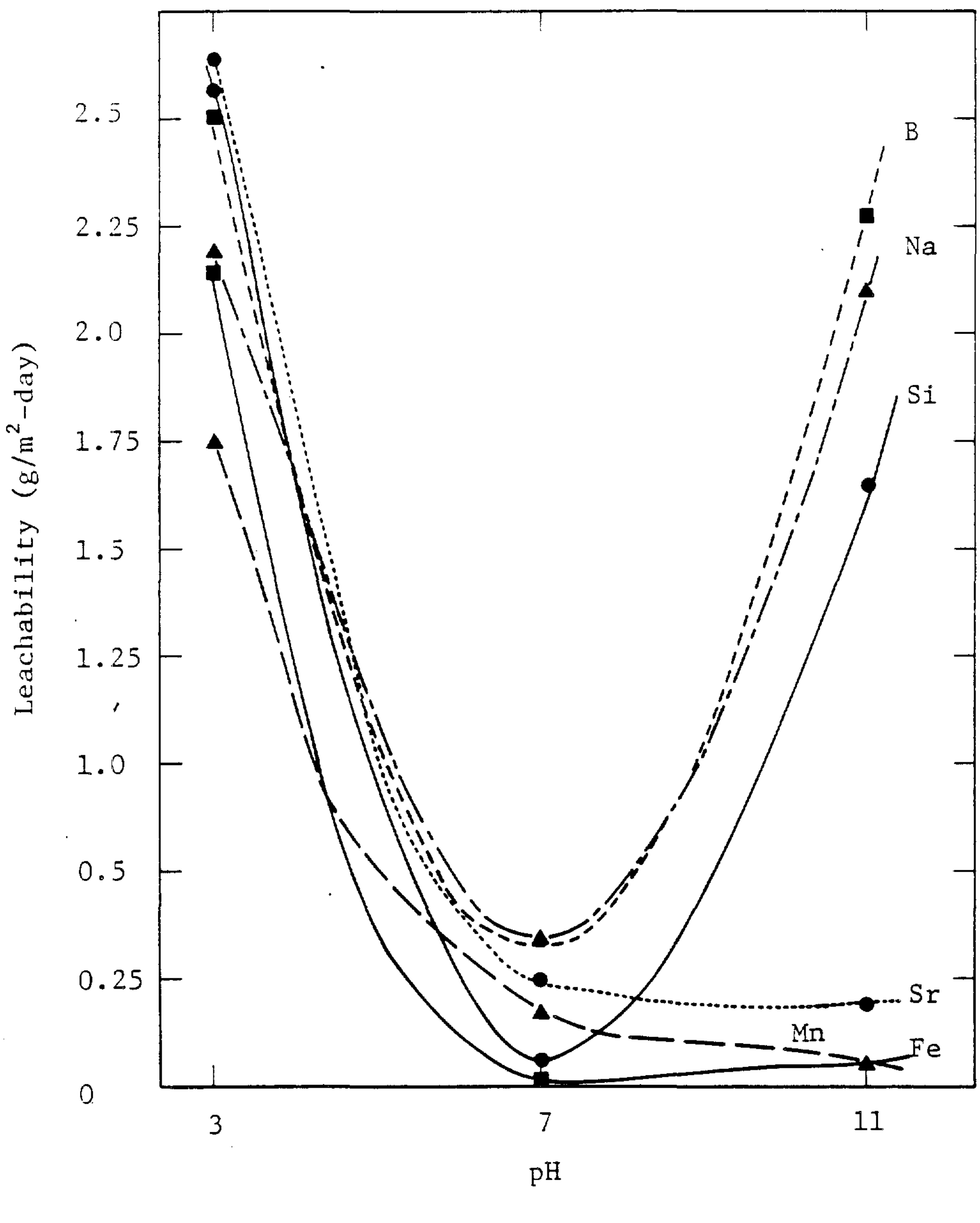

FIGURE 3. Leachability Curves

MCC-1 Tests
90°C/28 Days

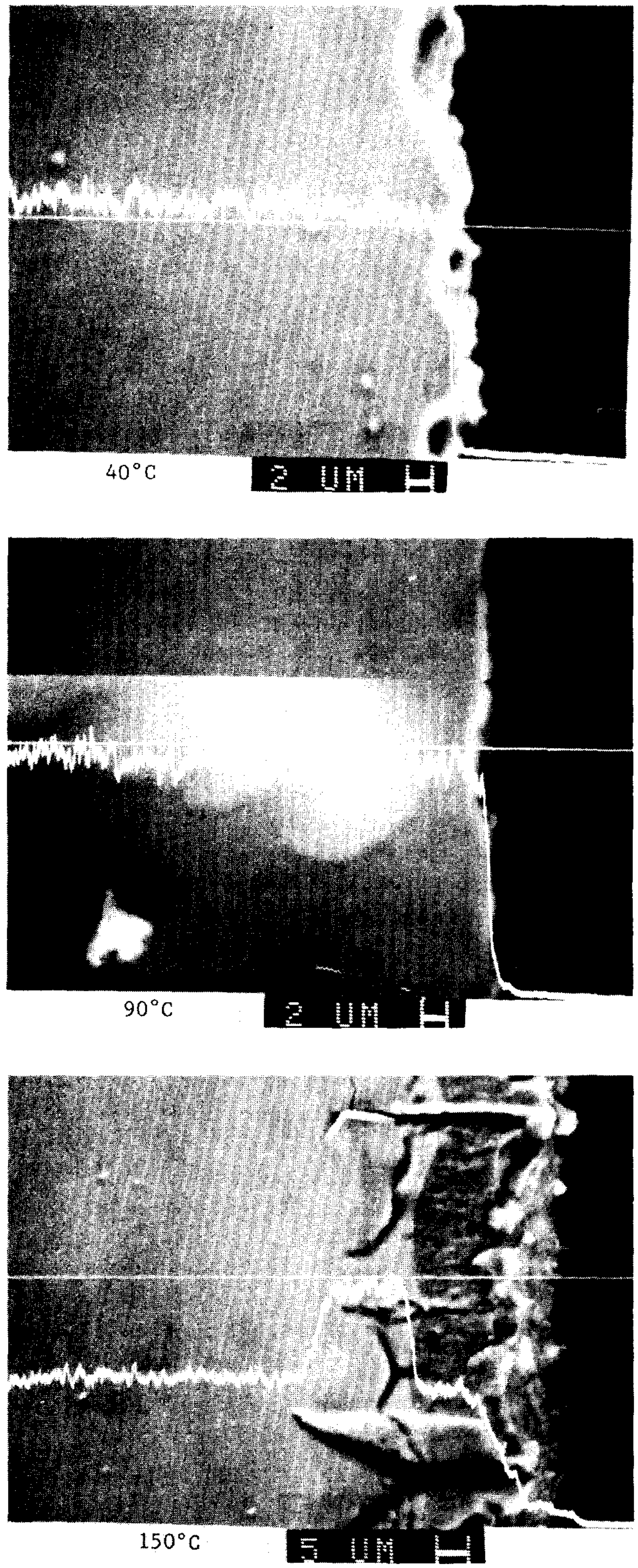

FIGURE 4. Si Profiles After Leaching in pH 3

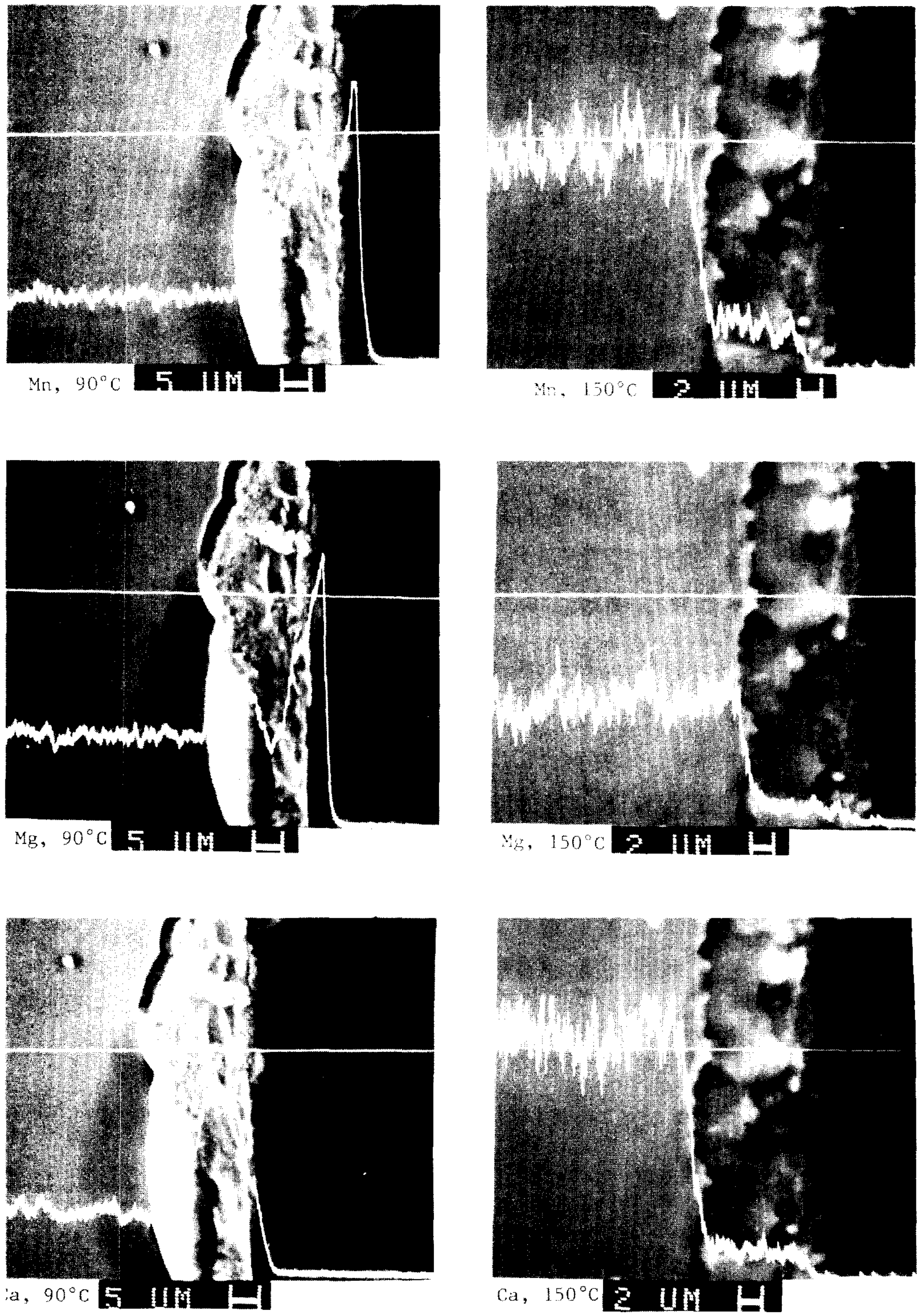

FIGURE 5. Profiles After Leaching in pH 7 at 90°C and 150°C

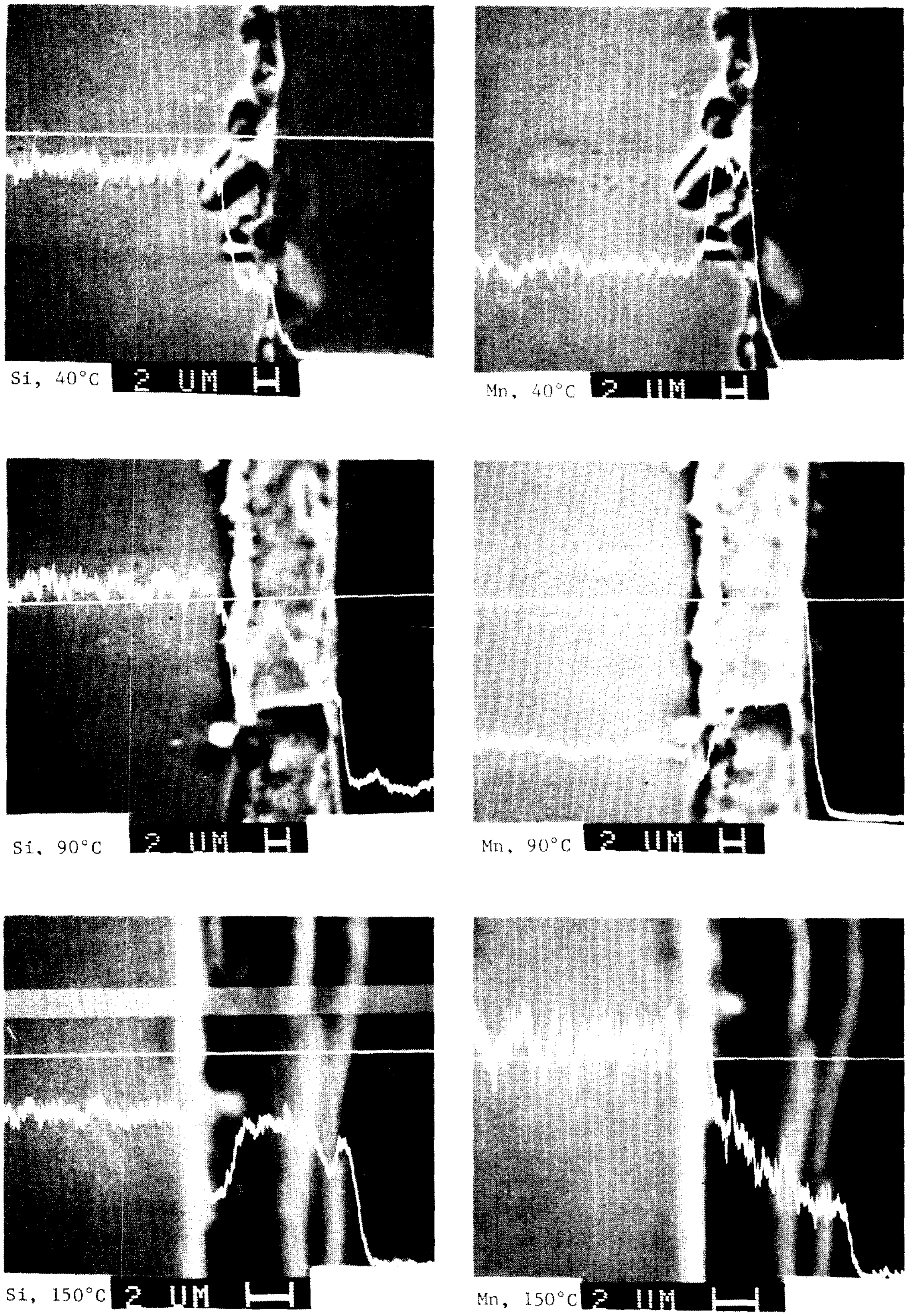

FIGURE 6. Profiles After Leaching in pH 11 at 40°C, 90°C, and 150°C

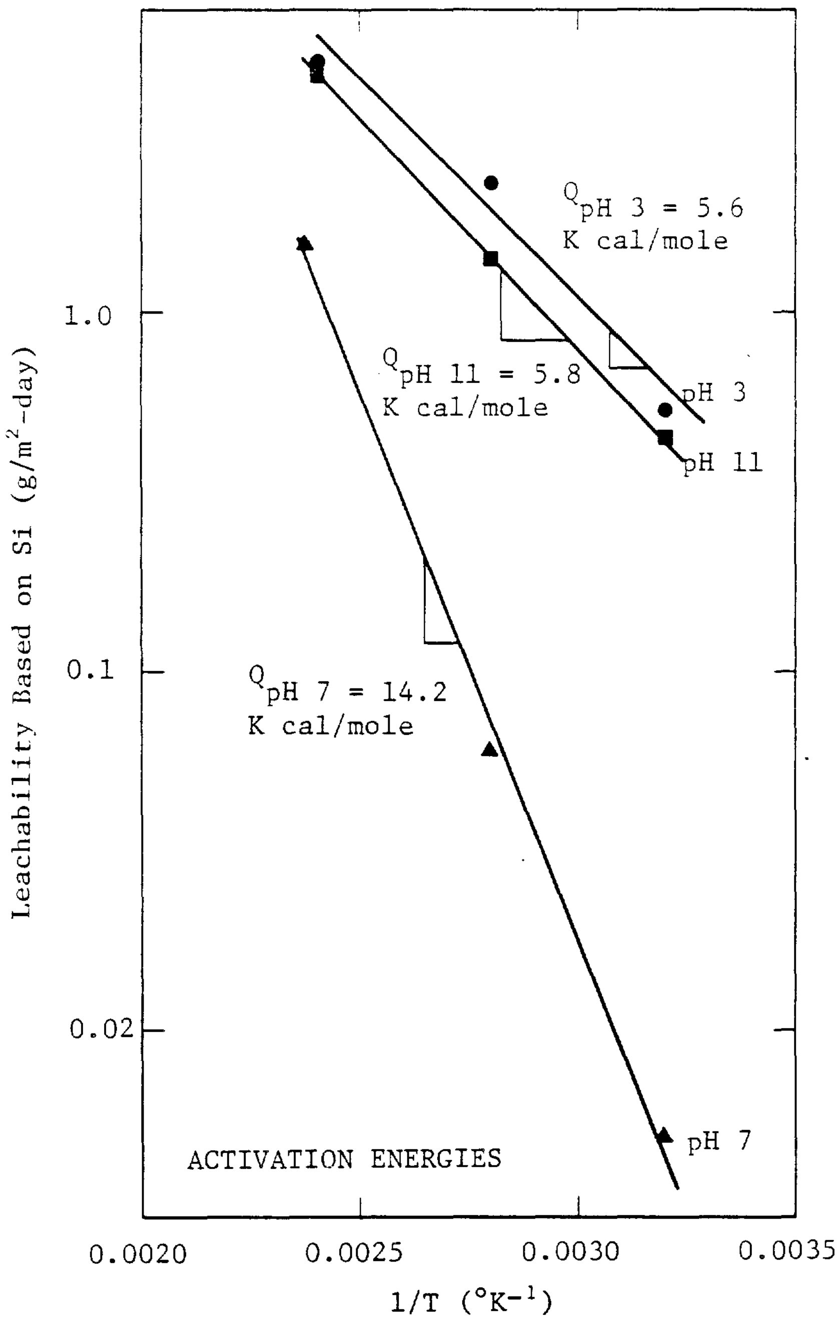

FIGURE 7. Leachability vs. Temperature at pH 3, 7, and 11