
Solubility Effects in Waste-Glass/Demineralized-Water Systems

H. T. Fullam

June 1981

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Pacific Northwest Laboratory
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by Battelle Memorial Institute



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Pacific Northwest Laboratory
Richland, Washington 99352



SUMMARY

A study was carried out at the Pacific Northwest Laboratory (PNL)^(a) to determine the solubility limits of various elements present in waste glasses in demineralized water as a function of temperature. The work represents one segment of the Waste/Rock Interaction Technology (WRIT) Program, which is funded by the Office of Nuclear Waste Isolation (ONWI) under contract to the Department of Energy.

The work was limited to the study of aqueous systems involving demineralized water and four glass compositions at temperatures of up to 150°C. No attempt was made to identify the ionic species present in the aqueous solutions or the solid phases that control the solubilities of the various elements.

Two methods were used to measure the solubility of glass components in demineralized water. One method involved approaching equilibrium from subsaturation, while the second method involved approaching equilibrium from supersaturation. The first method simply required contacting the glass with water at a constant temperature and monitoring the solution pH and composition as a function of time. The solubility measurements were carried out at four temperatures: 35°C, 65°C, 95°C and 150°C. Four different nonradioactive waste glass compositions were studied. Naturally occurring elements were used as standins for the actinides and fission products normally found in the radioactive waste glasses. The glasses contained uranium (as depleted uranium) at the normal concentrations.

The second (supersaturation) method used to determine the solubility of glass components involved holding a glass-water mixture at an elevated temperature for an extended period of time, evaporating the resulting solution to a small volume, holding the concentrated solution at a controlled lower temperature, and then analyzing the solution for dissolved species. Using the second method, solution concentrations were determined at a final temperature of 35°C.

The compositions of the aqueous solutions were determined primarily by induction-coupled plasma spectrometry (ICP). In addition, the uranium concentration was determined using a Scintrex U-A3 uranium analyzer and the zinc and cesium concentration was determined by atomic absorption.

The system that results when a waste glass is contacted with demineralized water is a complex one. The dissolution behavior of the various glass components and their solubility limits in the resulting solution are affected by a number of variables. Solubility measurements were obtained under a variety of conditions, and the solution concentrations and solubility limits determined varied greatly, depending on the test conditions. The two methods used to determine the solubility limits gave very different results, with the supersaturation method yielding much higher solution concentrations than the subsaturation method for most of the elements present in the waste glasses. The data indicate that these differences were due to the fact that the solution compositions were not determined under identical conditions

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with the two methods. The results show that it is impossible to assign solubility limits to the various glass components without thoroughly describing the glass-water systems. This includes not only defining the glass type and solution temperature, but also the glass surface area-to-water volume ratio (S/V) of the system and the complete thermal history of the system. The solubility data presented in this report were obtained under specific sets of conditions; this data may not be applicable to systems in which the conditions vary significantly from those specified in this report. The data presented can be used, however, as a guideline for estimating the solubility limits for glass components in aqueous systems.

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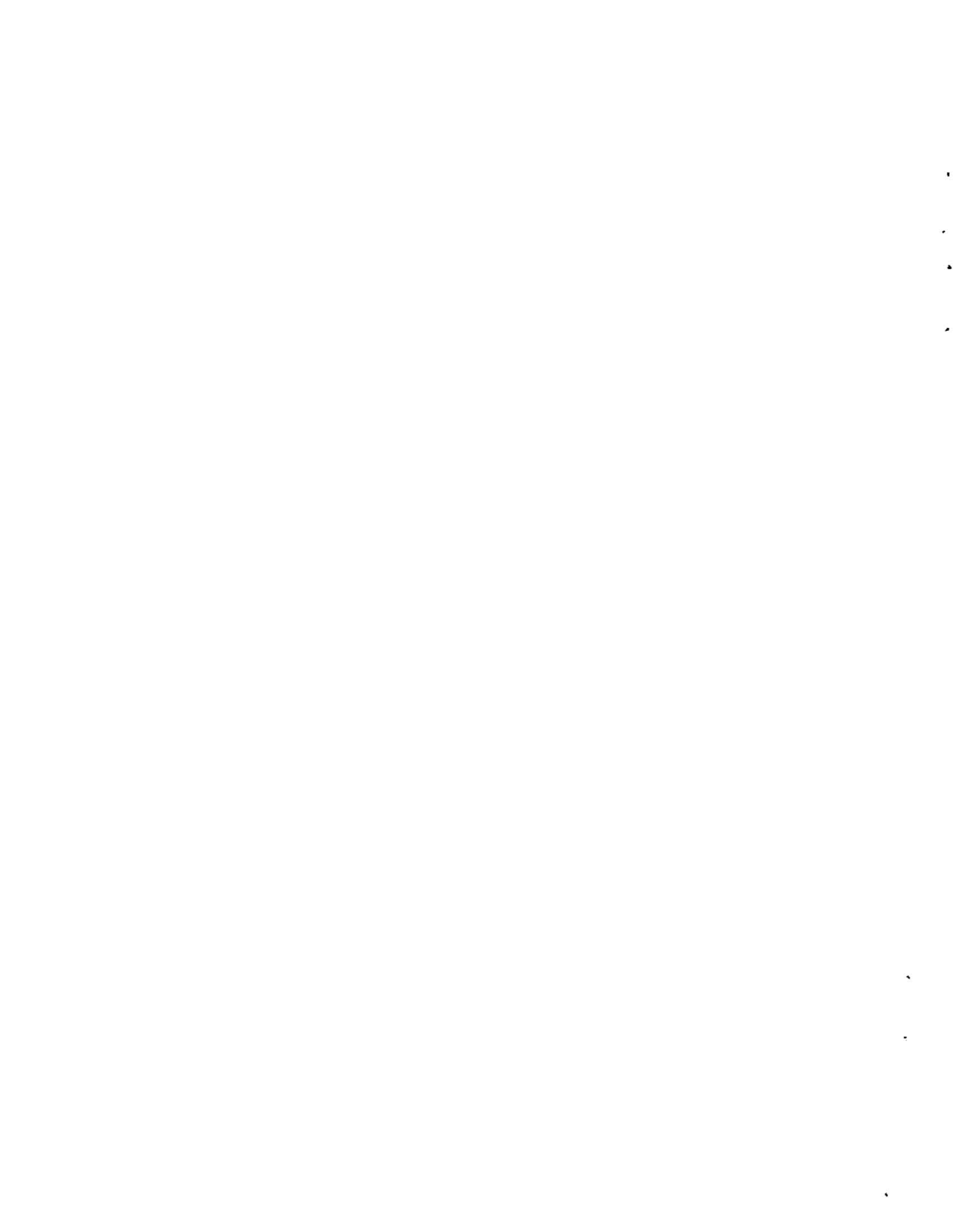
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1.0 INTRODUCTION

The safe geologic disposal of radioactive nuclear wastes requires a thorough understanding of potential interactions between the geologic media and the waste material (and its containment system). The WRIT Program is one of several programs under way at PNL that are designed to help obtain the data needed to show that the wastes can be safely stored in geologic repositories. The WRIT program is funded by ONWI under contract to the Department of Energy.

Two of the basic objectives of the WRIT Programs are: 1) developing a basic understanding of both the mechanisms of radionuclide release from the wastes and the subsequent interactions with the containment (engineered-barrier) system and geologic media; and 2) developing effective models for predicting leaching behavior, retardation characteristics, and release processes for the radionuclides in the repository environment. To accomplish these objectives, it is necessary to have a thorough understanding of the dissolution behavior of the waste in the aqueous media present in a repository and of the solubility limits for selected individual components of the waste in the aqueous solutions. To help understand the effects that solubility limits can have on the dissolution behavior of waste glasses, a study was carried out to measure the solubility of individual elements of selected waste glasses in demineralized water over a temperature range of 35⁰C to 150⁰C. The results of this study are summarized in this report.



2.0 EXPERIMENTAL

2.1 OBJECTIVES

The primary objective of this WRIT study was to determine the solubility limits in water of various elements found in waste glasses. A secondary objective was to determine what effects the solubility limits have on the dissolution of the glasses. The work was limited to a study of aqueous systems involving demineralized water and four glass compositions at temperatures of up to 150°C. No attempt was made to identify the solid phases that control the solubilities of the various elements or the species present in the aqueous solutions.

2.2 EXPERIMENTAL PROCEDURES

Two different methods were used to determine the solubility of glass components in demineralized water. Using the first method, equilibrium was approached from subsaturation, while with the second method equilibrium was approached from supersaturation. The first method simply involved contacting crushed glass with demineralized water at a controlled temperature and monitoring the solution pH and composition as a function of time. The second method involved holding the glass-water mixture at an elevated temperature for an extended period of time, cooling the system, holding it at 35°C for an extended time, and then determining the pH and composition of the aqueous phase at the lower temperature.

Two modifications of the subsaturation method were used, depending on the test temperature.

1. A weighed amount of crushed glass of known particle size and surface area was placed in a polypropylene or Teflon flask. A known volume of demineralized water was added, and the flask was sealed. The flask was placed in a constant-temperature water bath and held at temperature for an extended time. Samples of the aqueous solution were taken at periodic intervals for chemical analysis and pH determinations. The solution samples for chemical analysis were obtained using a 0.3 μm Millipore® filter, a polypropylene filter-holder, and a polypropylene syringe. The filter-holder containing the filter disc was placed directly into the solution and allowed to come to thermal equilibrium before the sample was taken. As the sample entered the syringe it was acidified to about 0.1M H^+ with high-purity nitric or hydrochloric acid. The solution pH was determined at the test temperature. The tests were carried out at 35°C, 65°C, and 95°C and lasted up to 7650 hours. Polypropylene flasks were used for the tests at 35°C and 65°C. Teflon flasks were used for the 95°C tests. Control of the bath temperature was maintained within about $\pm 1^\circ\text{C}$ at 35°C and 65°C and about $\pm 2^\circ\text{C}$ at 95°C. No attempt was made to continuously agitate or stir the flasks during testing, but each flask was shaken briefly before a sample was taken. All of the tests were carried out at known glass-surface area-to-water volume (S/V) ratios. Systems of different initial S/V ratios were prepared by holding the initial water volume constant and varying the amount and/or particle size of the glass used. The

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flasks used in the tests were about 80% filled with glass and solution, the remaining space being filled with air. Whenever an aqueous sample was taken, the flask was opened and the solution exposed to fresh air. This could result in the absorption of CO_2 , which could in turn affect the results obtained. No attempt was made to carry out the tests in an air- or CO_2 -free system. The tests were designed so that a large amount of undissolved glass was always present, even after several thousand hours' contact.

The procedure described above was limited to temperatures of less than 100°C because of sampling difficulties and limitations of the plastic flasks. A modification of the procedure was used, therefore, for solubility measurements at 150°C .

2. In the second modified procedure a piece of glass of known geometric surface area was placed in a gold ampule (Figure 1). The ampule, which had a 0.5-in. ID, was crimped at the midpoint so that the glass sample was held in the upper section. A known volume of demineralized water was placed in the lower section of the ampule, and it was welded shut. The ampule was placed in a small pressure vessel (fabricated from 304L stainless steel) that was partially filled with water. The vessel was sealed and inverted so that the water in the ampule completely covered the glass sample. The pressure vessel was placed in a oil bath and held at 150°C for the required time. The vessel was then removed from the oil bath and immediately inverted so that the solution drained away from the glass sample before it began cooling. After the vessel was cooled, it was opened and the gold ampule removed and opened. The glass sample was removed and the solution in the ampule transferred to

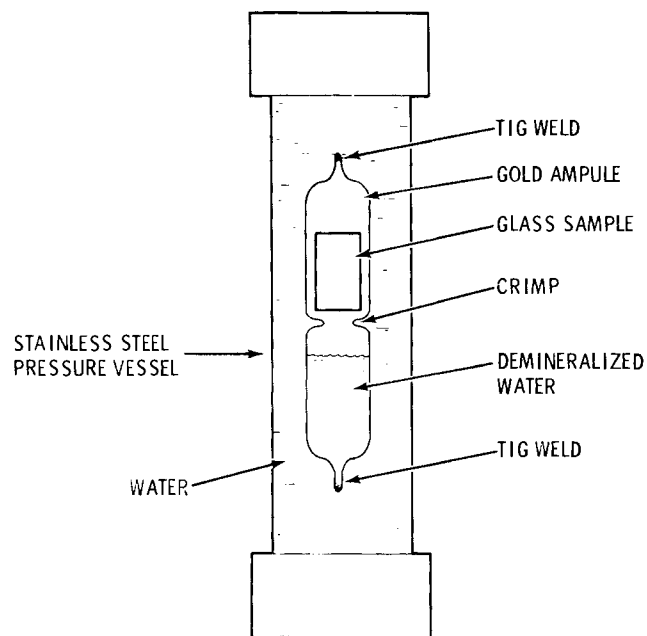


FIGURE 1. Sketch of Equipment Used in the 150°C Solubility Measurements

a plastic bottle. The solution's pH was determined at room temperature. The solution was then acidified to 0.1M H⁺ with high-purity nitric acid. The gold ampule was washed twice with 0.1M high-purity nitric acid to dissolve any solids that precipitated as the solution cooled. The original solution and combined wash solution were then analyzed for dissolved species. In order to determine the change in solution composition and pH as a function of time, it was necessary to run a series of tests with each ampule being held at 150°C for a different length of time. Each series of tests lasted up to 768 hours. The same S/V, based on the geometric surface area of the glass sample, was used for each test.

In the second method used to determine solubility limits for glass components in demineralized water, equilibrium was approached from supersaturation. Three modifications of the supersaturation method were used.

1. A small quantity of powdered glass was dissolved in 500 ml of demineralized water at 90°C to 100°C in a sealed polypropylene bottle. The resulting solution was divided into several unequal fractions. Each fraction was placed in a polypropylene bottle, evaporated to a small volume (2 ml to 5 ml), and held at a constant temperature of 35°C for several days. The pH of each fraction was then measured and a filtered sample taken for analysis.
2. Several grams of powdered glass were contacted with demineralized water at 85°C or 95°C for several weeks in a sealed polypropylene bottle. The glass-water slurry was then evaporated at 100°C until a small volume of liquid remained. The residue was equilibrated at 35°C for several days, then its pH was measured and a filtered sample taken for analysis.
3. Several grams of powdered glass and about 10 ml of demineralized water were placed in a gold ampule and the ampule was welded shut. The ampule was then heated in an autoclave at either 150°C or 250°C for several days. The ampule was removed from the autoclave while warm and transferred to a 35°C water bath. The temperature of the ampule was maintained above 35°C throughout the transfer. The ampule was held at 35°C for several days in a water bath and then opened. A filtered sample of the solution was taken for chemical analysis and the solution pH was determined at 35°C.

In all of the tests the analytical samples were taken and acidified to 0.1M H⁺ with high-purity nitric acid using 0.3 μm Millipore filters and the filter holder/syringe system previously described.

Blank tests were run on the different plastic flasks and bottles used in the tests to see if they contributed impurities to the glass-water systems. No problems were detected with any of the materials. Similarly the filter disc, filter holders, syringes and vials used to obtain and hold the analytical samples were analyzed to determine if dissolved species were deposited on their surfaces. Again, no problems were detected with any of the materials.

In addition to the solubility tests, a large number of tests were carried out to determine the effects of various parameters on the pH of the solutions produced when a waste glass was contacted with water. Most of the pH experiments were carried out at room temperature

(nominally 23°C), and lasted up to 7800 hours. No attempt was made to control the temperature in the room temperature tests. Glass-water mixtures were held in sealed plastic bottles and the pH of the resulting solution was determined as a function of contact time. The tests were limited to a single waste glass--76-68--that is described in the following section.

2.3 MATERIALS

Four glass compositions were used in the solubility studies. Three of the glasses were simulated waste glasses that had been prepared using depleted uranium and naturally occurring elements as standins for the actinides and fission products found in the radioactive waste glasses. The nominal compositions of the three waste glasses are given in Table 1.

TABLE 1. Nominal Compositions of the Waste Glasses Studied

Component	Glass Composition, wt%		
	76-68 PW-8a-1	77-107 PW-9-1	77-260 PW-7c-1
Glass Frit			
Al ₂ O ₃			2.0
B ₂ O ₃	9.5	13.0	9.0
CaO	2.0	2.0	1.0
CuO			3.0
K ₂ O		4.0	2.0
Na ₂ O	7.5	2.0	8.0
SiO ₂	40.0	38.0	36.0
TiO ₂	3.0	3.0	6.0
ZnO	5.0	5.0	
	<u>67.0</u>	<u>67.0</u>	<u>67.0</u>
Waste			
Ag ₂ O	0.03	0.05	0.02
BaO	0.56	1.13	0.55
CdO	0.03	0.08	0.03
CoO	0.11	0.20	0.10
Cr ₂ O ₃	0.41	0.21	0.02
Cs ₂ O	1.02	1.98	0.78
Fe ₂ O ₃	9.68	0.90	1.19
Gd ₂ O ₃			10.14
MnO ₂			0.11
MoO ₃	2.27	4.41	1.92
Na ₂ O	5.00	3.47	3.14
NiO	0.52	0.16	0.31
P ₂ O ₅	0.48	0.40	2.36
Rb ₂ O	0.13	0.25	0.11
RE(a)	4.76	9.24	3.84
RuO ₂	1.06	2.20	0.85
SrO	0.38	0.72	0.29
TeO ₂	0.26	0.50	0.22
U ₃ O ₈ (b)	4.54	3.80	5.40
ZrO ₂	<u>1.76</u>	<u>3.30</u>	<u>1.68</u>
	<u>33.00</u>	<u>33.00</u>	<u>33.00</u>
	100.00	100.0	100.0

(a) A commercial rare earth mixture having the nominal composition in wt%: 0.2, Y₂O₃; 24.0, La₂O₃; 48.0, CeO₂; 5.0, Pr₆O₁₁; 17.0, Nd₂O₃; 3.0, Sm₂O₃; 0.8, Eu₂O₃; and 2.0, Gd₂O₃

(b) U₃O₈ prepared from depleted uranium.

Approximately 1 kg of each glass was prepared specifically for the solubility studies using the standard laboratory procedure (Mellinger and Chick 1979).

The fourth glass studied was a special formulation 79-339, which is a high alumina glass that is reported to have a low dissolution rate in water (Chick and Buckwalter 1979). The composition of the 79-339 glass, which did not contain the simulated fission products and actinides found in the waste glasses, is given in Table 2.

Each glass was crushed and dry ball-milled using a porcelain jar and alumina balls. The pulverized glass was screened and the surface area of each sized fraction was determined by the BET method using krypton (Brunauer, Emmett and Teller 1938). The results obtained with 76-68 glass are given in Table 3. The other glasses gave similar results. The sized-glass fractions were then used in the experimental tests.

TABLE 2. Nominal Composition of 79-339 Glass

<u>Component</u>	<u>wt%</u>
Al ₂ O ₃	6.04
B ₂ O ₃	10.48
CaO	0.93
Cs ₂ O	0.04
Fe ₂ O ₃	14.43
MnO ₂	1.33
Na ₂ O	9.59
SiO ₂	<u>57.16</u>
	100.00

TABLE 3. Surface Area of Crushed 76-68 Glass as a Function of Particle Size

<u>Sieve Size(a)</u>	<u>Surface Area(b), cm²/g</u>
-4 + 20	60
-20 + 40	200
-40 + 70	380
-70 + 100	590
-100 + 140	750
-140 + 200	1130
-200 + 230	2310
-230 + 325	2690
-325	4930

- (a) U.S. Standard Sieve Series.
 (b) Determined by the BET Method using krypton (Brunauer, Emmett, Teller 1938).

The solubility studies were carried out in demineralized water that was prepared using a Corning model LD-5 water purifier. The treated water had a pH of 6.1 to 6.5 and a resistivity of greater than 2×10^6 ohm-cm. Analysis of the water by induction-coupled plasma spectrometry (ICP) showed that silicon (at 0.03 ppm) was the only element present above the detection limit for the instrument.

2.4 ANALYTICAL PROCEDURES

The various aqueous samples were analyzed for dissolved elements using the ICP. The elements determined by ICP, and the detection limit for each, are given in Table 4. In addition, the uranium concentration in the samples was determined using a Scintrex U-A3 uranium analyzer and the cesium and zinc concentration was determined by atomic absorption. No attempt was made to analyze the waste glasses for silver, rubidium, and the rare earth elements, praseodymium, samarium, and yttrium. No attempt was made to analyze for anionic species present in the aqueous samples.

TABLE 4. Detection Limits for Elements Using the Induction-Coupled Plasma Spectrometer

<u>Element</u>	<u>Detection Limit, ppm</u>	<u>Element</u>	<u>Detection Limit, ppm</u>
Al	0.03	Mn	0.002
As	0.08	Mo	0.01
B	0.01	Na	0.01
Ba	0.002	Nd	0.02
Ca	0.01	Ni	0.01
Cd	0.004	P	0.1
Ce	0.04	Pb	0.06
Co	0.01	Ru	0.05
Cr	0.02	Sb	0.05
Cu	0.004	Si	0.02
Eu	0.002	Sr	0.002
Fe	0.005	Te	0.06
Gd	0.01	Ti	0.002
K	0.3	Zn	0.02
La	0.008	Zr	0.008

3.0 RESULTS AND DISCUSSION

When a waste glass is contacted with demineralized water, the components of the glass begin to dissolve and the pH of the resulting solution changes. The rate of dissolution of the glass components and the rate of change of solution pH are highly dependent on the initial S/V ratio of the system. Long-term contact of the water and glass at a constant temperature in a closed static system results in the solution pH and the concentrations of many of the dissolved elements reaching apparent equilibrium levels. The equilibrium levels attained appear to depend on the initial S/V ratio as well as the system temperature. When glass-water mixtures are maintained at a high temperature for an extended period of time, evaporated to a small volume, and then held at a lower temperature, the resulting solution pH and concentrations of dissolved species are much higher than the equilibrium values attained when the system is equilibrated at the lower temperature. It is not possible, therefore, to define the apparent solubility limits and equilibrium pH for a glass-water system without defining the S/V ratio for the system and its thermal history. The factors affecting solution pH, dissolution behavior, and apparent solubility limits for various elements in the glass are discussed in the following sections.

3.1 SOLUTION pH

When a waste glass is exposed to demineralized water at a constant temperature in a static system, the pH of the solution will change as components of the glass dissolve. The magnitude and rate of the pH change is dependent on the type of glass, the S/V ratio of the system, the solution temperature, and the contact time. If the system is held at a high temperature, and then cooled and held at a lower temperature, the solution pH is much higher than when the system is held at the lower temperature for an equivalent time.

In general, when the S/V ratio of the glass-water system is low, the pH of the solution gradually increases until it appears to reach an equilibrium value after extended contact. When the S/V value is large, the solution pH increases rapidly to a maximum and then gradually decreases until a constant value is attained. For very large S/V values, the initial increase in pH is too rapid to measure with a standard pH electrode and meter. Figure 2 shows how the solution pH varied during the first few hours of contact at room temperature for 76-68 glass-water mixtures having different S/V values. Similar results were attained with the other three glasses. Figure 3 shows the effects of long-term contact at room temperature on the pH of the 76-68 glass-water mixtures. The tests lasted up to 7650 hours, and in each case the pH of the solution appeared to reach a constant value after prolonged contact. There is, however, considerable spread in the data that makes it difficult to determine if a constant pH has actually been reached. As will be shown later, some components of the glass are continuing to dissolve, even after 7650 hours of contact, which indicates the pH may be slowly changing.

The data presented in Figure 3 show that 76-68 glass-water systems having a high S/V ratio exhibit a minimum in the pH curve. The minimum in the pH curve at high S/V ratios was observed in all of the tests with 76-68 glass but was not observed with the other glasses. As will be

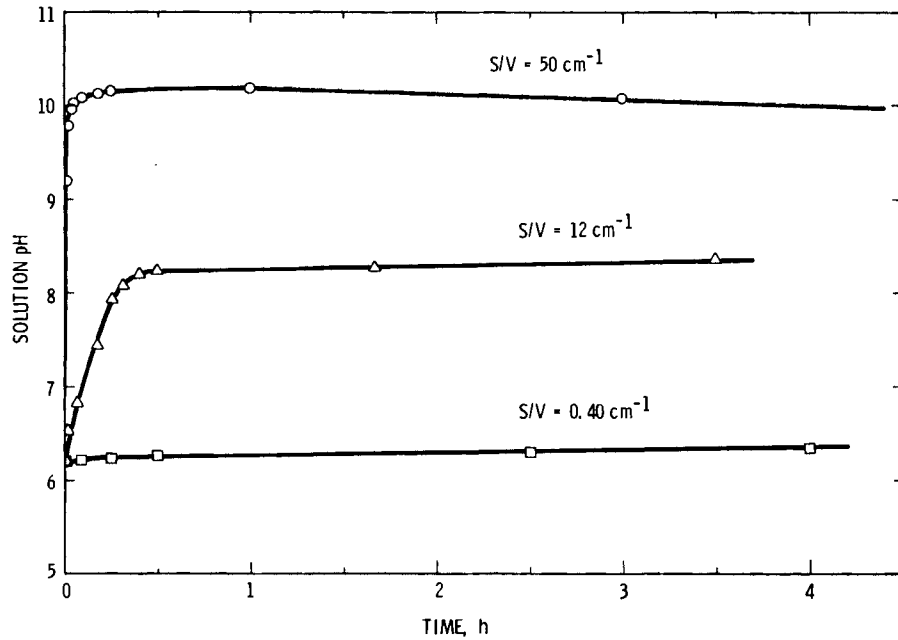


FIGURE 2. The pH as a Function of Time for 76-68 Glass-Demineralized Water Mixtures Held at 23°C--Short-Term Exposure

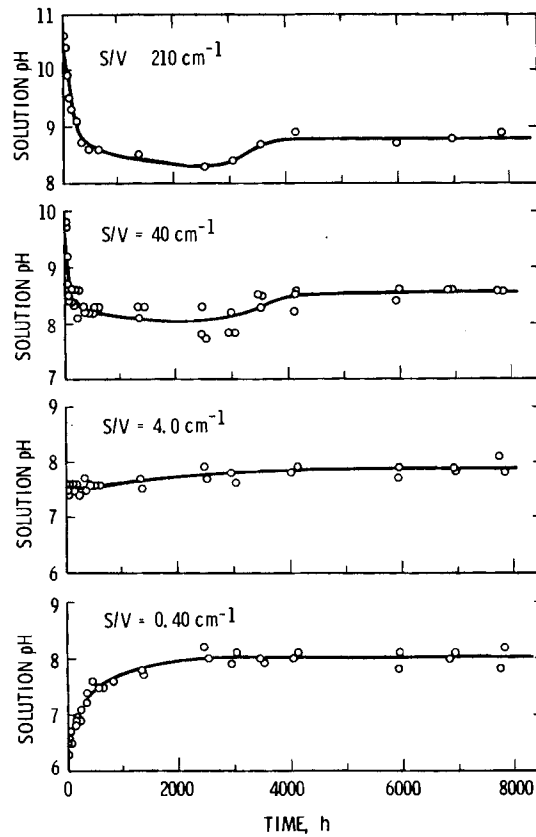


FIGURE 3. The pH as a Function of Time for 76-68 Glass-Demineralized Water Mixtures Held at 23°C--Long-Term Exposure

shown in a subsequent section, the increase in pH after several thousand hours' exposure corresponds to a marked increase in the concentrations of several elements in the solution. It is impossible to predict if longer exposures (>7650 h) for 76-68 glass-water mixtures would lead to further increases in the solution pH.

Tests with 76-68 glass were carried out at S/V values ranging from 0.04 to 210 cm⁻¹. In each case the test was continued for at least 7500 hours, and the pH appeared to reach a constant value. Table 5 shows how the apparent equilibrium pH varied with the S/V value of the 76-68 glass-water mixture.

Tests were carried out to determine if the particle size of the glass would have an effect on the solution pH. Glass-water mixtures having an initial S/V value of 49 cm⁻¹ were prepared using sized fractions of 76-68 glass. The pH of each mixture was monitored as a function of contact time at room temperature (~23°C). The results obtained are presented in Table 6. The data show that the particle size of the glass has very little effect on the pH of the solution, although it does appear that the maximum pH observed initially does decrease slightly with increasing particle size of the glass.

The pH of the glass-water mixtures are also dependent on the type of glass used, although pH variations between the three waste glasses studied were not as great as one might expect. Figure 4 shows the results obtained from long-term exposure of the three waste glasses at 35°C. Although there are minor variations in the shapes of the pH curves for the three glasses, the overall relationships are quite similar. The one significant difference is that only the 76-68 glass exhibits a minimum in the pH curve at high S/V values.

Some short-term tests lasting up to 1080 hours were carried out at 35°C with the 79-339 glass. The pHs of the 79-339 glass-water mixtures were much lower than those of the other glass-water mixtures at corresponding S/V values, as can be seen in Figure 5.

TABLE 5. Apparent Equilibrium pH as a Function of S/V for 76-68 Glass-Demineralized Water Mixtures Held at Room Temperature (≈23°C)

<u>S/V, cm⁻¹</u>	<u>Apparent Equilibrium pH</u>
0.04	8.0
0.4	8.0
2	7.9
4	7.9
12	8.2
20	8.4
40	8.6
41	8.5
49	8.5
50	8.6
88	8.6
210	8.8

TABLE 6. Effect of Glass Particle Size on the pH of 76-68 Glass-Demineralized Water Mixtures Having Initial S/V Values of 49 cm^{-1} (Temperature $\cong 23^\circ\text{C}$)

Time, h	Solution pH								Average
	Glass Sieve Size ^(a) -20 + 40	Glass Sieve Size -40 + 70	Glass Sieve Size -70 + 100	Glass Sieve Size -100 + 140	Glass Sieve Size -140 + 200	Glass Sieve Size -200 + 230	Glass Sieve Size -230 + 325	Glass Sieve Size -325	
0.02	9.1	9.3	9.1	8.9	9.4	9.3	8.9	8.9	9.1
0.25	9.0	9.4	9.5	9.3	9.6	9.7	9.6	9.6	9.5
4	9.1	9.3	9.2	9.5	9.4	9.3	9.3	9.1	9.3
24	7.9	7.9	8.1	8.2	7.9	8.1	8.1	8.0	8.0
96	8.0	8.0	8.1	8.1	7.9	8.1	8.1	8.1	8.1
168	8.0	8.1	8.1	8.1	7.9	8.1	8.1	8.1	8.1
264	8.1	8.1	7.9	8.1	7.8	8.0	8.1	8.1	8.0
912	8.2	8.3	8.3	8.3	8.1	8.3	8.3	8.3	8.3
1560	8.1	8.1	8.1	8.1	8.0	8.1	8.1	8.1	8.1
2064	8.1	8.2	8.2	8.3	7.7	8.1	8.1	8.0	8.1
2568	8.1	8.2	8.1	8.4	8.1	8.3	8.1	8.3	8.2
3096	8.3	8.3	8.2	8.4	8.2	8.3	8.3	8.4	8.3
3720	8.2	8.5	8.3	8.6	8.3	8.4	8.4	8.6	8.4
5568	8.5	8.6	8.5	8.6	8.3	8.6	8.6	8.5	8.5
7440	8.5	8.6	8.5	8.6	8.4	8.6	8.5	8.5	8.5

(a) U.S. Standard Sieve Series

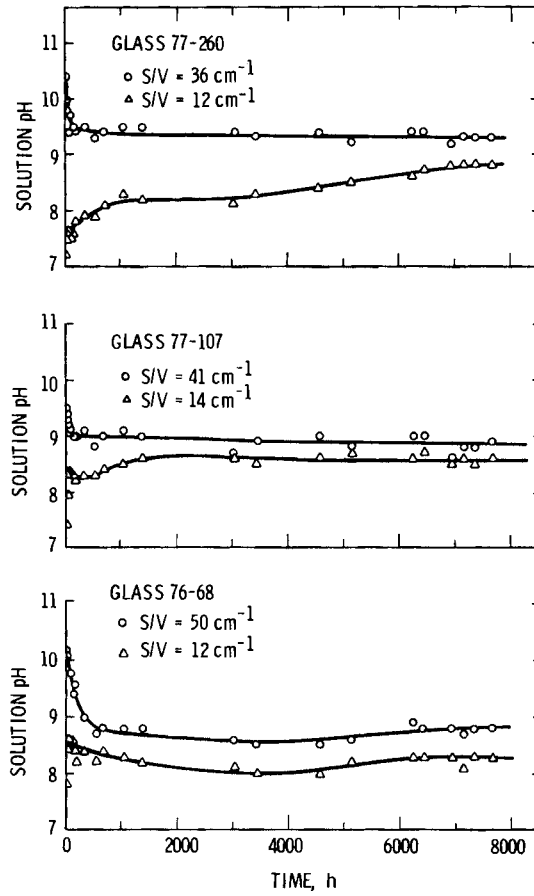


FIGURE 4. The pH as a Function of Time for Different Glass-Demineralized Water Mixtures Held at 35°C

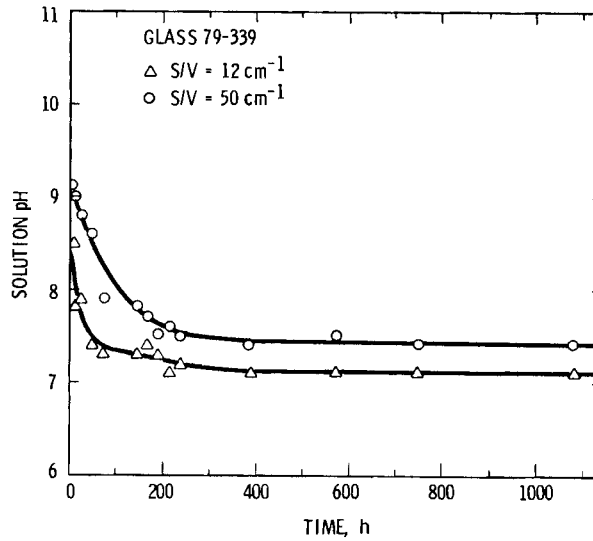


FIGURE 5. The pH as a Function of Time for 79-339 Glass-Demineralized Water Mixtures Held at 35°C

The tests show that the apparent equilibrium pH of glass-water mixtures having the same initial S/V value increases with the solution temperature. Table 7 shows the results obtained with the three waste glasses over a temperature range of 23°C to 150°C. The tests lasted for up to 7650 hours, and in each case it appeared that the pH of the solution had reached a constant value. It was difficult to obtain stable pH readings at 95°C; therefore, the 95°C values given in Table 7 are at best only approximations. No attempt was made to measure solution pH at 150°C. Instead samples of the solutions were cooled and the pH was determined at room temperature. One factor observed in all of the tests was that the time required for the pH to reach a constant value decreased as the solution temperature increased. The general shapes of the pH curves obtained at the higher temperatures with the various glasses were very similar to those obtained at 35°C (Figure 4) except that the curves were displaced to higher pH levels and compressed on the time frame.

TABLE 7. Apparent Equilibrium pH Values for Glass-Demineralized Water Mixtures Held at Various Temperatures

<u>Glass</u>	<u>Temperature, °C</u>	<u>S/V, cm⁻¹</u>	<u>Apparent Equilibrium pH</u>
76-68	23	12	8.2
		50	8.6
	35	12	8.3 (8.4)(a)
		50	8.8 (8.9)
	65	12	8.6 (8.8)
		50	9.3 (9.7)
	95	12	8.8 (9.2)
		50	9.6 (10.1)
	150	2	(9.7)
	77-107	35	14
41			8.9 (9.0)
65		14	8.7 (8.8)
		41	9.1 (9.4)
95		14	9.0 (9.2)
		41	9.7 (10.2)
77-260	35	12	8.8 (8.9)
		36	9.3 (9.4)
	65	12	9.0 (9.4)
		36	9.4 (9.8)
	95	12	9.2
		36	9.9

(a) Values in parentheses are values measured at room temperature.

When the solution pH reached an equilibrium value in the elevated-temperature tests, samples of the solutions were taken and their pH measured at various temperatures. The values shown in parentheses in Table 7 are the pH values of the solutions at room temperature. Figure 6 shows how the pH varied with temperature for solution samples taken from 76-68 glass-water mixtures that were held at 35°C until the solution pH reached a constant value. The effect of temperature on the pH of demineralized water is also shown in Figure 6, as are values reported in the literature for ultra-high-purity water (Dorsey 1940). The results show that the pH of the solutions decrease about 0.5 to 1.0 pH units as the temperature increases from 24°C to 95°C. Samples taken from the other glass-water systems gave similar results.

In the supersaturation tests where glass-water mixtures were equilibrated at higher temperatures (80°C to 100°C), evaporated to a small volume, and then cooled and held at 35°C, the pH of the resulting solution at 35°C was much higher than the apparent equilibrium pH values obtained in the constant-temperature tests at 35°C. Even systems with low initial S/V values gave high pH values after concentration. Typically, with 76-68 glass the pH of the concentrated solutions at 35°C ranged from 10 to 11, as compared to a maximum of 9 for glass-water mixtures equilibrated at 35°C. The final pH of the concentrated solution depends on the S/V ratio of the system, the length of time the glass-water mixture is held at the higher temperature, and the degree of concentration. Replicate experiments produced somewhat different results, indicating that an uncontrolled variable(s) was affecting the results. Evaporating a system that had been equilibrated at 35°C also resulted in a higher solution pH but not as high as that produced by evaporating the solution at a higher temperature. As will be shown in the following section, the concentrations of dissolved species were much higher in the evaporated solutions at 35°C than in the solutions equilibrated at 35°C.

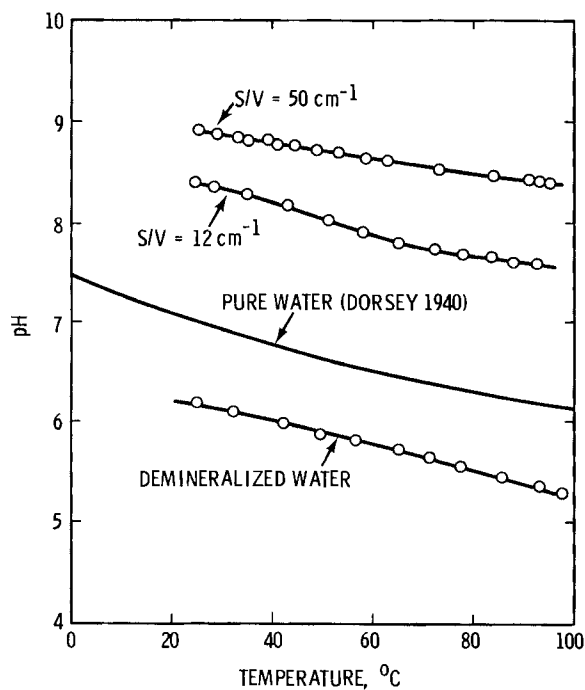


FIGURE 6. The Effect of Temperature on the pH of the Solutions Produced When 76-68 Glass is Equilibrated with Demineralized Water at 35°C

3.2 DISSOLUTION BEHAVIOR AND SOLUBILITY LIMITS

The waste glasses studied contain many components. The system that results when a waste glass is contacted with demineralized water is complex. In such systems a number of variables can affect the solubilities of the individual elements in the solution produced as the glass dissolves. The possibility of complex interactions between the large number of dissolved species complicates the problem of determining the solubility limits of the individual elements. It was beyond the scope of this work to analyze the various glass-water systems to determine the species present in the solution or the solid phases present. Therefore, it was impossible to identify the chemical compounds that determine the solubility limits of individual elements in the different systems. The best that could be achieved was an elemental analysis of each of the solutions to determine the concentrations of individual elements.

As described in Section 2.2, two methods were used to try to determine the solubility limits of the glass components in demineralized water. In the first method equilibrium was approached from subsaturation by contacting the glass and water at a constant temperature and determining the composition of the solution as a function of time. In the second method, equilibrium was approached from supersaturation. These two methods work very well in determining solubility relationships in simple systems. As will be shown in subsequent sections, applications of the two methods to the glass-water systems gave very different results. This difference is probably not too surprising, considering the complexity of the systems and the many variables involved that made it impossible to ensure that the data from the two methods were obtained under identical conditions.

The subsaturation method gave relatively low solution concentrations for the various elements. The data indicate that many of the elements appeared to reach a maximum concentration in a relatively short time, and remained essentially constant thereafter, suggesting that saturation had been attained. The second method, in which equilibrium was approached from supersaturation, yielded solution concentrations for the various elements that were, in general, several times greater than those obtained with the first method. Without additional information on the compositions of the various systems with regard to the species present in solution and the solid phases present, it is difficult to explain why the two methods gave such different results. Additional discussion on probable reasons for these differences is given in Section 3.2.3.

When a waste glass is contacted with demineralized water at a constant temperature the dissolution behavior of the individual glass components can be divided into four general categories:

1. the elements that dissolve to an appreciable level and even after prolonged contact may not have reached an equilibrium concentration in the solution; (Elements in this group include sodium, potassium, silicon, boron, and molybdenum.)
2. those elements that dissolve to an intermediate level and appear to reach equilibrium concentrations in relatively short periods of time;

3. those elements that are present in solution below the detection limits of the analytical procedures used, making it impossible to determine if the elements have reached saturation in the solution;
4. those elements that exhibit erratic behavior and whose concentrations in solution fluctuate over wide ranges with time but appear to reach saturation after prolonged exposure. (Zinc, calcium, barium, and strontium are typical of this group.)

No attempt was made to determine the solubility limits for several elements present in the waste glasses. The elements not considered were rubidium, silver, and the rare earths, yttrium, samarium, and praseodymium. Rubidium, which is present in the waste glasses in low concentrations, can be expected to dissolve in a manner similar to the other alkali metals. Similarly, yttrium, samarium and praseodymium can be expected to behave in a manner analogous to the other rare earths.

3.2.1 Soluble Species

Sodium, potassium, silicon, boron and molybdenum, assuming they are present in a glass in appreciable concentrations, represent the bulk of the material that dissolves when the waste glass is contacted with demineralized water. In most of the constant-temperature tests the concentrations of the five elements in solution were continuing to increase at a slow rate after contact times as long as 7650 hours. Table 8 gives the maximum solution concentrations for the five elements that were measured in the various tests where a glass was contacted with demineralized water at a constant temperature. The effect of temperature and system S/V on the dissolution of the soluble species is readily apparent. In some of the tests, especially those using 77-260 glass, it appeared that the concentrations of some elements may have reached saturation (underlined values in Table 8), but insufficient data were available to ensure that saturation had been reached.

Much higher sodium, potassium, silicon, boron, and molybdenum concentrations were attained in those tests in which equilibrium was approached from supersaturation. Typically, in these tests the glass-water mixtures were held at a high temperature (80°C to 150°C) for several hundred hours, evaporated to a small liquid volume and/or cooled and held at a constant 35°C for several days. The solutions were then sampled and analyzed for dissolved species. Tests of this type were carried out under a wide variety of conditions, but in every test the final solution temperature was 35°C. Some typical results are shown in Table 9. In every test the concentrations of the soluble species in solution were several times greater than concentrations obtained in the constant-temperature tests at 35°C. (See Table 8.)

The solution concentrations in the supersaturation experiments appear to depend on several factors including the initial S/V ratio of the glass-water system, the time the system is held at the higher temperature, and, most importantly, the extent of evaporation of the solution. Replicate experiments gave significantly different results, however, indicating that at least one uncontrolled variable was affecting the results. The concentration values given in Table 9 are typical values and there is no evidence to indicate that changes in the test conditions would not produce even higher concentrations of the five elements at 35°C.

TABLE 8. Maximum Concentrations Measured When Glasses Were Contacted with Demineralized Water at a Constant Temperature for Extended Periods of Time

Glass	Temp., °C	S/V, cm ⁻¹	Apparent Equilibrium pH	Contact Time, h	Maximum Concentration Measured, ppm					
					Na	K	Si	B	Mo	
76-68	35	0.075	7.1	2332	1.7		3.6	0.6	0.2	
		10.5	8.2	7320	43		29	12	6	
		12	8.3	7650	53		33	15	7	
		50	8.8	7650	78		25	19	8	
	65	10.5	8.5	6980	87		53 ^(a)	24	11	
		12	8.6	7320	96		<u>46</u>	25	<u>11</u>	
		50	9.3	7320	240		<u>59</u>	56	<u>23</u>	
	95	12	8.8	1892	177		98	58	24	
		50	9.6	1882	424		123	132	56	
	150	~2 ^(b)	9.7 ^(c)	768	202		220	75	34	
	77-107	35	14	8.6	7650	61	56	43	48	19
			41	8.9	7650	108	<u>70</u>	47	91	31
		65	14	8.7	7320	310	166	87	249	99
			41	9.1	7320	302	<u>191</u>	<u>64</u>	236	79
		95	14	9.0	1892	283	198	95	218	151
41			9.7	1892	784	<u>397</u>	<u>107</u>	699	239	
77-260		35	10	8.7	7320	40	20	21	10	7
			12	8.8	7650	<u>44</u>	25	24	11	9
			36	9.3	7650	<u>86</u>	31	<u>25</u>	20	14
	65	10	8.9	6980	83	27	37	20	14	
		12	9.0	7320	<u>96</u>	40	40	21	15	
		36	9.4	7320	<u>209</u>	35	56	44	29	
	95	12	9.2	1892	<u>521</u>	60	56	107	85	
		36	9.9	1892	<u>981</u>	90	<u>106</u>	188	145	
	77-339	35	12	7.1	1080	5		4	0.9	
			50	7.4	1080	17		9	3	

(a) Values underlined are those cases in which the solution concentration appeared to reach saturation.

(b) S/V value calculated using the geometric surface areas of the large glass pieces used in the tests.

(c) pH at room temperature.

TABLE 9. Concentrations of Soluble Species Obtained in Tests Where Equilibrium Was Approached from Supersaturation

Glass	Initial S/V, cm ⁻¹	Initial Contact Temp., °C	Initial Contact Time, h	Final Contact Temp., °C	Final Contact Time, h	Concentration Factor ^(a)	Solution pH ^(b)	Concentration in Solution, ^(c) ppm				
								B	K	Mo	Na	Si
76-68	1.4	95	650	35	96	55	9.6	124		55	385	300
	2.0	95	650	35	96	71	10.0	370		180	1090	420
	2.7	95	650	35	96	90	10.0	430		180	1170	209
	3.4	95	650	35	96	44	10.4	156		72	442	180
	4.0	95	650	35	96	54	10.0	510		260	1400	314
76-68	1.1	85	984	35	72	85	10.3	555		250	1860	840
	2.2	85	984	35	72	88	10.4	660		288	3040	1070
	3.3	85	984	35	72	77	10.4	470		230	1380	490
76-68	20.0	85	720	35	96	12	10.2	310		284	720	313
	40.0	85	720	35	96	15	10.3	492		296	954	429
76-68	186	150	165	35	144	1	9.9	113		41	278	38
	310	150	165	35	144	1	10.0	195		65	462	57
77-107	0.33	85	984	35	72	103	10.4	146	118	64	198	146
	156	150	165	35	144	1	10.1	301	143	60	323	190
77-260	0.30	85	984	35	72	72	10.7	252	150	135	960	690
	160	150	165	35	144	1	10.2	88	24	50	393	120

(a) Concentration factor is the initial solution volume divided by the final solution volume after evaporation.

(b) pH of the solution at 35°C after evaporation.

(c) Concentration in the solution at 35°C after evaporation.

If one plots the concentrations of the soluble species as a function of contact time for those tests where the glass-water mixtures were equilibrated at a constant temperature, irregularly shaped curves are obtained. Some typical concentration curves are shown in the following sections. It is difficult to explain the shape of the curves with the limited data available. While it is possible that the irregularities were due to problems inherent with the test procedures and analytical instruments used in the study, all of the available data indicate that this was not the case. It appears that the irregular shapes of the concentration curves shown in the following sections are real, even though it is difficult to explain why the concentrations vary as they do.

In the following section sodium dissolution behavior is discussed in some detail. The dissolution behavior of the other soluble species is quite similar to that of sodium, and only a few typical concentration plots of the other elements are shown.

3.2.1.1 Sodium

Figures 7 and 8 show sodium concentration curves for 76-68 glass-water mixtures held at 35°C or 65°C for up to 7650 hours. There is no indication in any of the figures that the sodium concentrations had reached saturation. The data do show the marked effect the S/V ratio of the system has on sodium dissolution. The apparent minimums in the sodium concentration curves at high S/V values after 3000 to 4000 hours of contact appear to be real and correspond to the minimums in the pH curves (Figure 3). The increase in the sodium concentration after 4000 to 5000 hours corresponds to similar increases in solution pH. The tests carried out at S/V values of 10.5 and 12 cm⁻¹ used sized glass fractions whose surface areas varied by about a factor of ten so that the actual quantities of glass initially present varied by about a factor of nine. This variation in the amount of glass present appeared to have little effect on the results obtained. In all of the tests, sufficient excess glass was present to ensure that only a small fraction of the sodium in the glass was dissolved.

Figure 9 shows how sodium dissolution varied with temperature for 76-68 glass-water mixtures having about the same S/V ratio. There was no indication in any of the tests that the sodium concentration had reached saturation, although the spread in data obtained during the latter stages of the 150°C tests makes it difficult to determine how the sodium concentration was changing. Because of the experimental procedure used, the tests at 150°C could only be carried out at low S/V ratios (~2 cm⁻¹). The S/V ratios for the 150°C tests were calculated on the basis of the geometric surface areas of the solid glass sections used, however, and the effective surface areas of the glass sections may have been significantly greater than their geometric surface areas. Unfortunately, because of experimental difficulties and scheduling problems the tests at 95°C and 150°C lasted only 1892 hours and 768 hours, respectively, as compared to more than 6900 hours for the tests at 35°C and 65°C.

Figure 10 shows sodium concentration curves for 77-107 glass-water mixtures held at 35°C. Similar curves were obtained at 65°C and 95°C, except that the sodium concentrations were correspondingly higher. In none of the tests was there an indication that the sodium concentration had reached saturation. Irregularities in the shape of the sodium concentration curves cannot

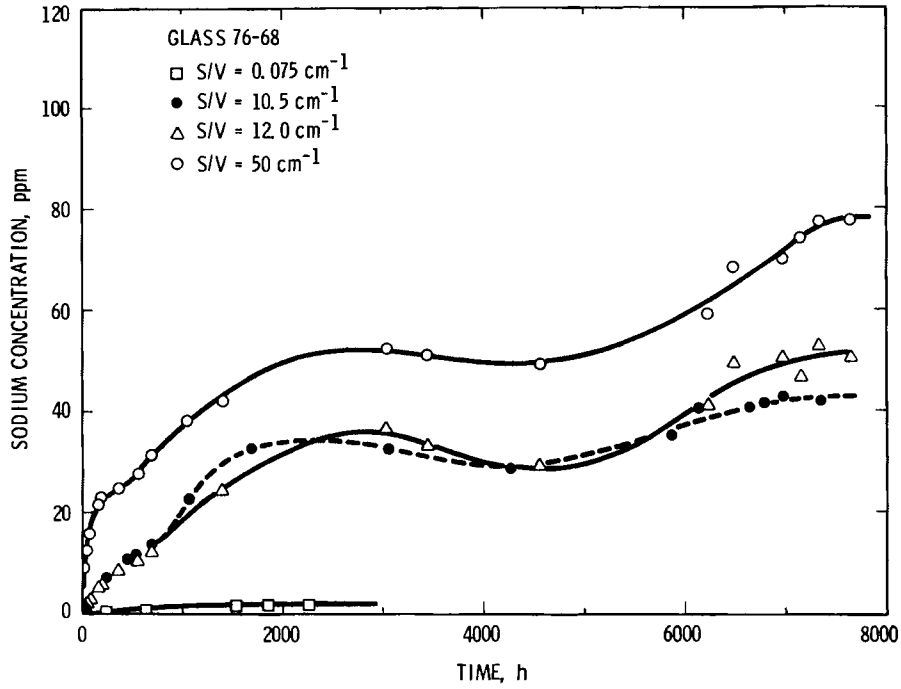


FIGURE 7. Sodium Concentration Versus Time for 76-68 Glass-Demineralized Water Mixtures Held at 35°C

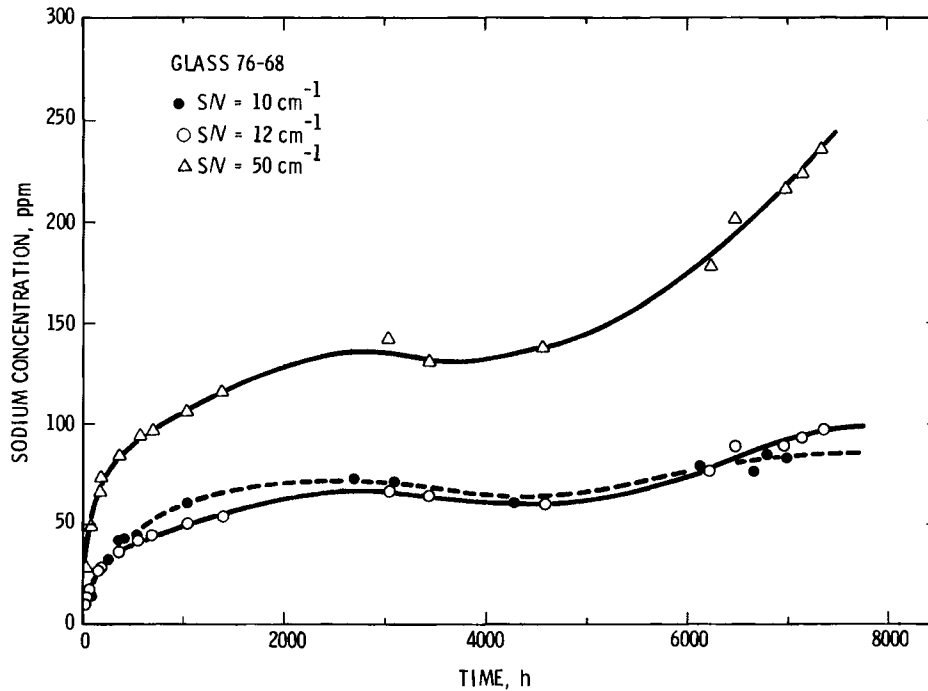


FIGURE 8. Sodium Concentration Versus Time for 76-68 Glass-Demineralized Water Mixtures Held at 65°C

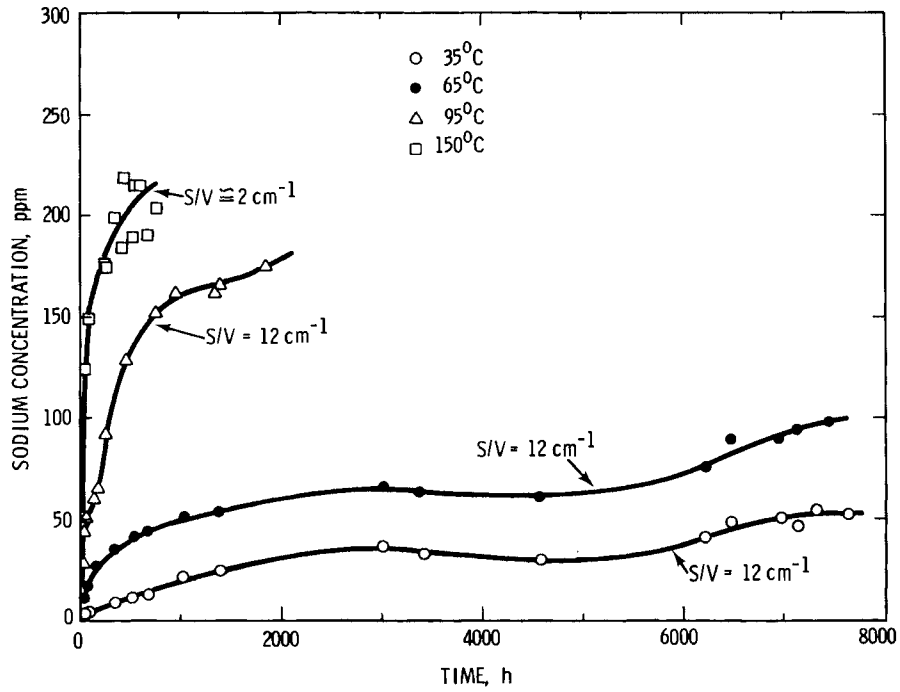


FIGURE 9. The Effect of Temperature on the Dissolution of Sodium From 76-68 Glass in Demineralized Water

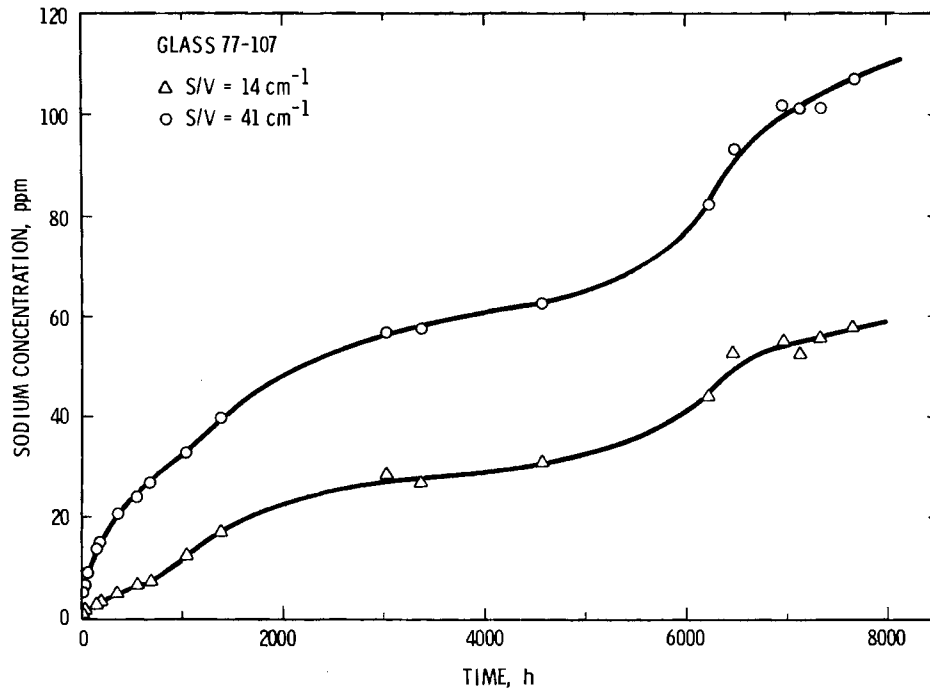


FIGURE 10. Sodium Concentration Versus Time for 77-107 Glass-Demineralized Water Mixtures Held at 35°C

be attributed to pH variations because the data indicate that the pH of 77-107 glass-water mixtures reach a constant value in a relatively short period of time (Figure 5).

Figure 11 shows sodium concentration curves obtained with 77-260 glass at 35°C. The data indicate that the sodium concentrations may have reached saturation after several thousand hours' contact. The surprising factor is the large difference in the apparent sodium saturation values for systems having different S/V ratios. It is possible that differences in solution pH could account for the variation in the apparent sodium saturation values with S/V, but this appears unlikely. Tests at 65°C and 95°C gave sodium concentration curves similar to those obtained at 35°C, except that the sodium concentrations were much higher.

Figure 12 shows the results obtained with glass 79-339 at 35°C. Unfortunately, the tests had to be terminated after 1080 hours of contact. The short-term results show that sodium dissolved from the 79-339 glass at a slower rate than from the other glasses tested, and there was no indication that the sodium concentration had reached saturation.

3.2.1.2 Silicon

The dissolution behavior of silicon in the waste glasses was quite similar to that of sodium. Figures 13 through 15 show silicon concentration curves obtained with the three glasses at 35°C. The data indicate that the silicon concentrations reached equilibrium levels after about 6000 hours. The spread in the data is so great, however, that it is impossible to tell if saturation was actually reached in any of the tests. One unexpected result was that increasing the S/V ratio to a high value with 76-68 glass appeared to reduce silicon dissolution.

Silicon dissolution behavior at the higher temperatures was similar to that at 35°C, except that the time required to reach apparent equilibrium was much shorter at the higher temperature and the spread in the data was much greater. As was the case at 35°C, the spread in the data was so great that it was impossible to tell if the silicon concentrations had actually reached equilibrium.

A great amount of work has been done on the solubility of amorphous silica and the various quartz phases in aqueous solutions. A comparison of the literature data with the results obtained in this work is presented in Section 3.3.

3.2.1.3 Other Soluble Species

The dissolution behavior of potassium, boron, and molybdenum was similar to that of sodium. Figures 16 through 18 show typical concentration curves for the three elements at 35°C. The general shape of the concentration curves for the three elements was very similar in all of the tests with the four glasses. There was little indication in most of the tests that the concentrations of the three elements had reached saturation. Exceptions were the 77-107 glass-water systems where the potassium concentration appeared to reach a constant value.

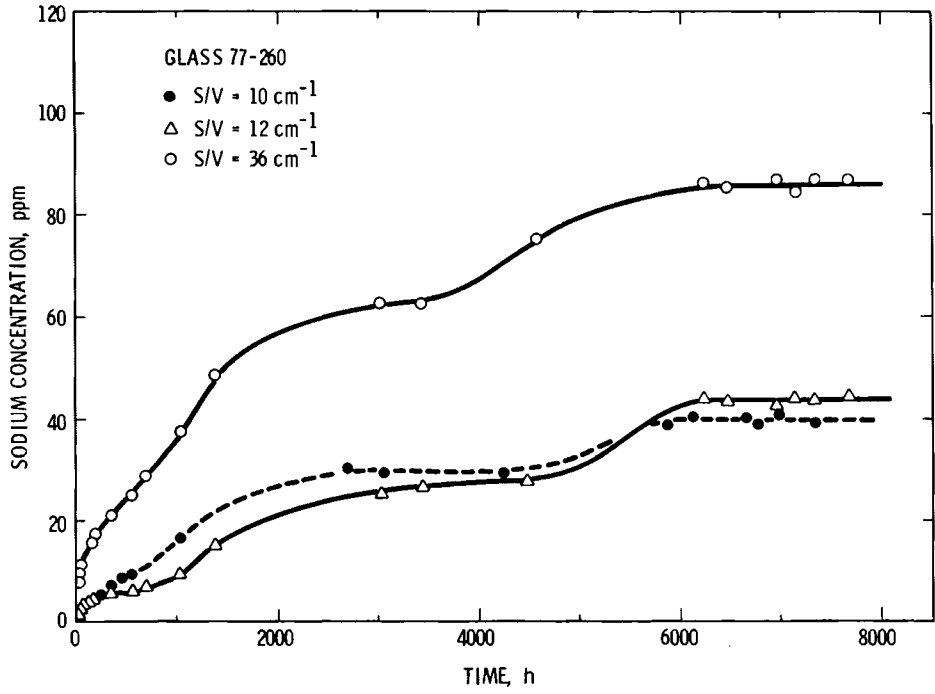


FIGURE 11. Sodium Concentration Versus Time for 77-260 Glass-Demineralized Water Mixtures Held at 35°C

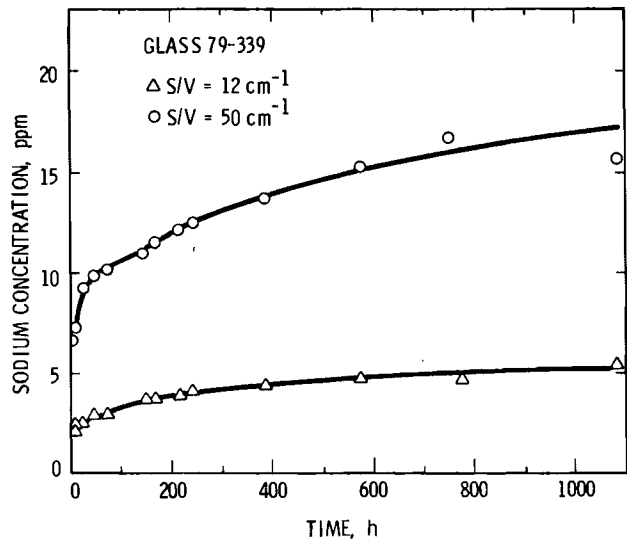


FIGURE 12. Dissolution of Sodium From 79-339 Glass in Demineralized Water at 35°C

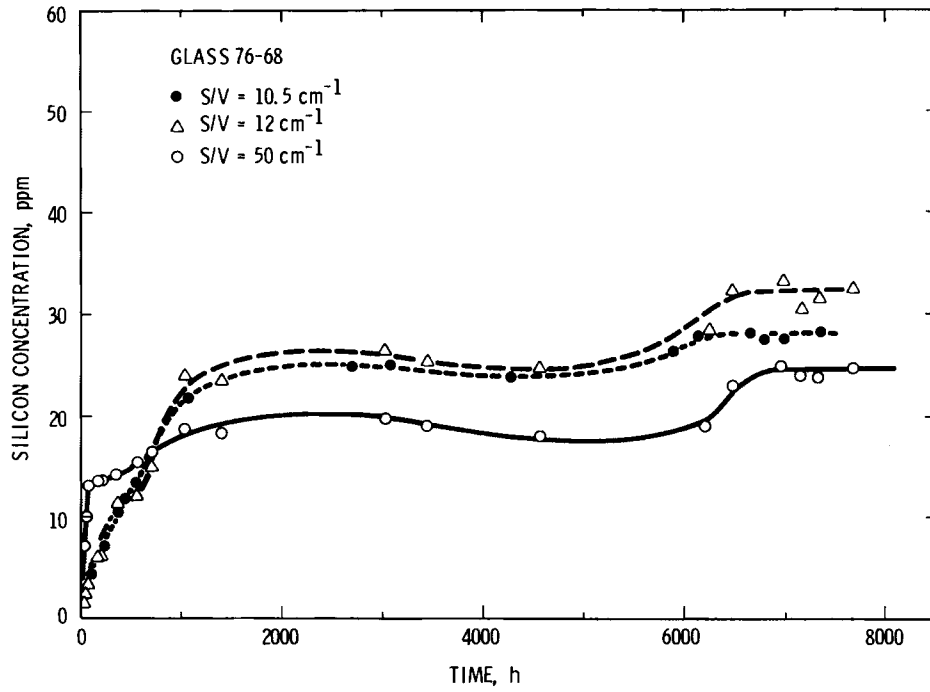


FIGURE 13. Silicon Concentration Versus Time for 76-68 Glass-Demineralized Water Mixtures Held at 35°C

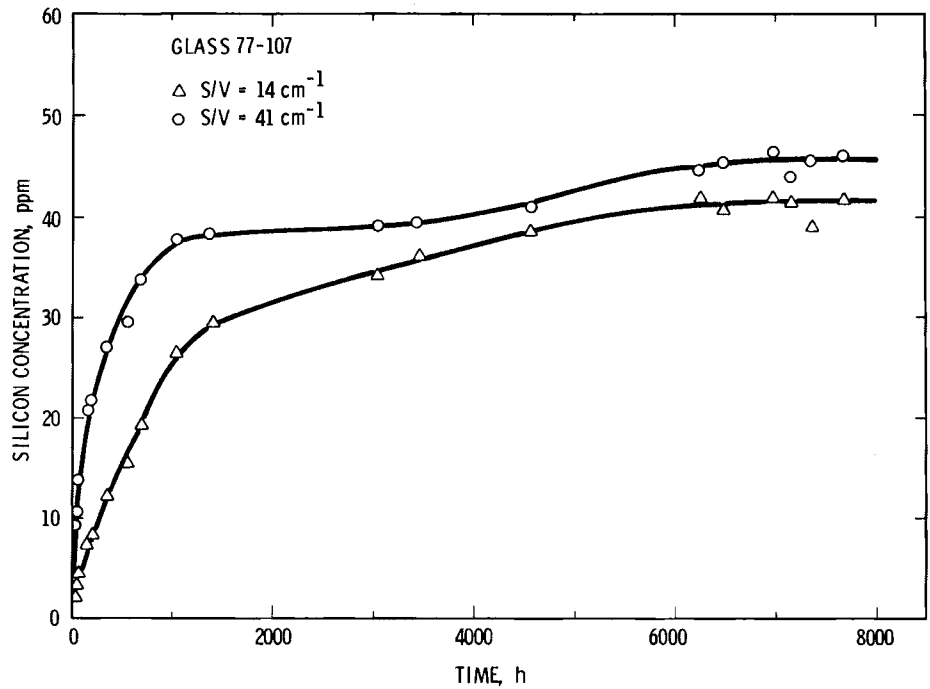


FIGURE 14. Silicon Concentration Versus Time for 77-107 Glass-Demineralized Water Mixtures Held at 35°C

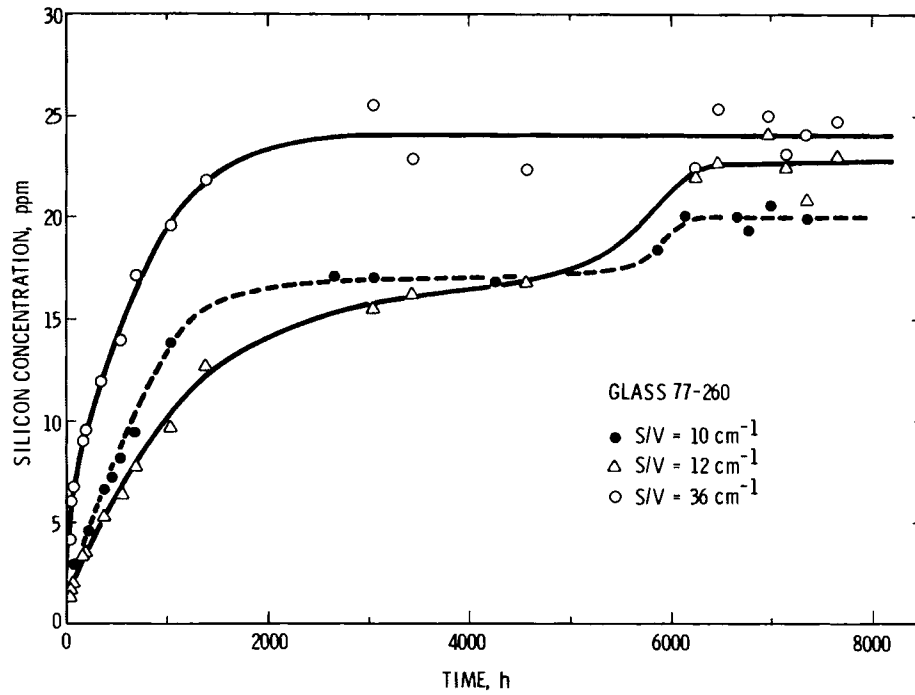


FIGURE 15. Silicon Concentration Versus Time for 77-260 Glass-Demineralized Water Mixtures Held at 35°C

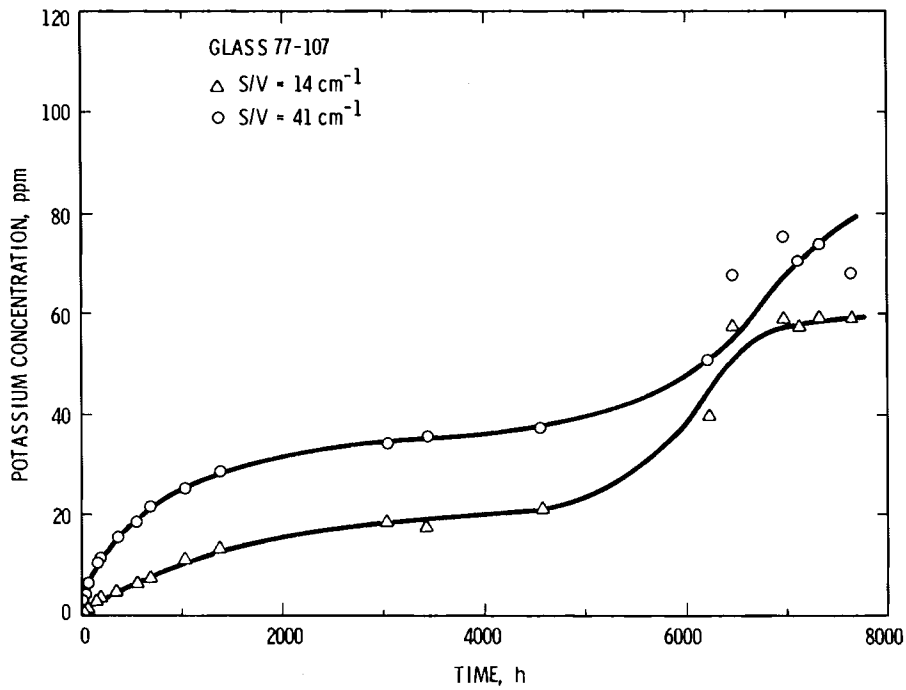


FIGURE 16. Potassium Concentration Versus Time for 77-107 Glass-Demineralized Water Mixtures Held at 35°C

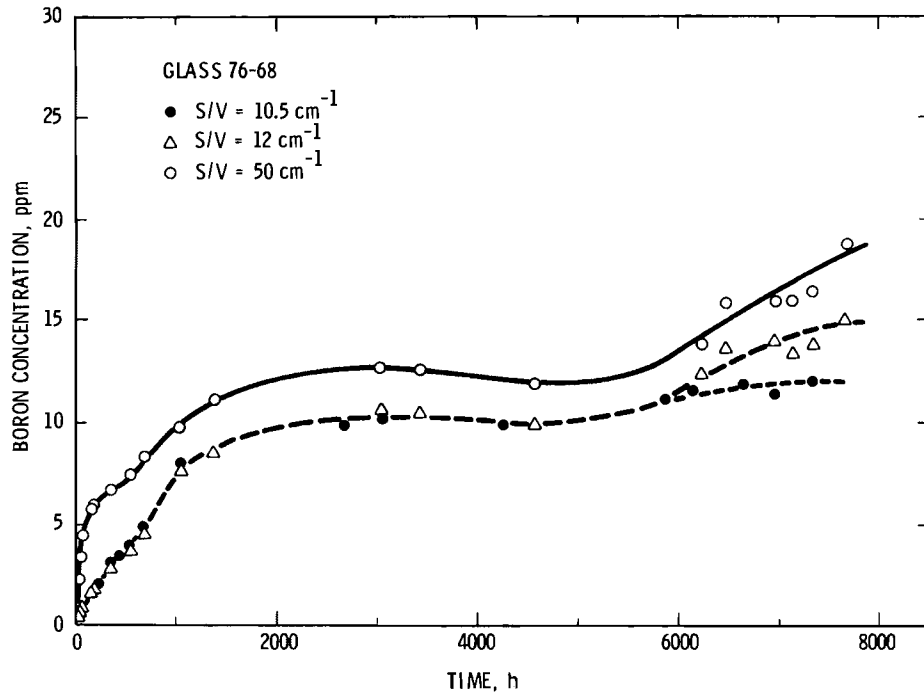


FIGURE 17. Boron Concentration Versus Time for 76-68 Glass-Demineralized Water Mixtures Held at 35°C

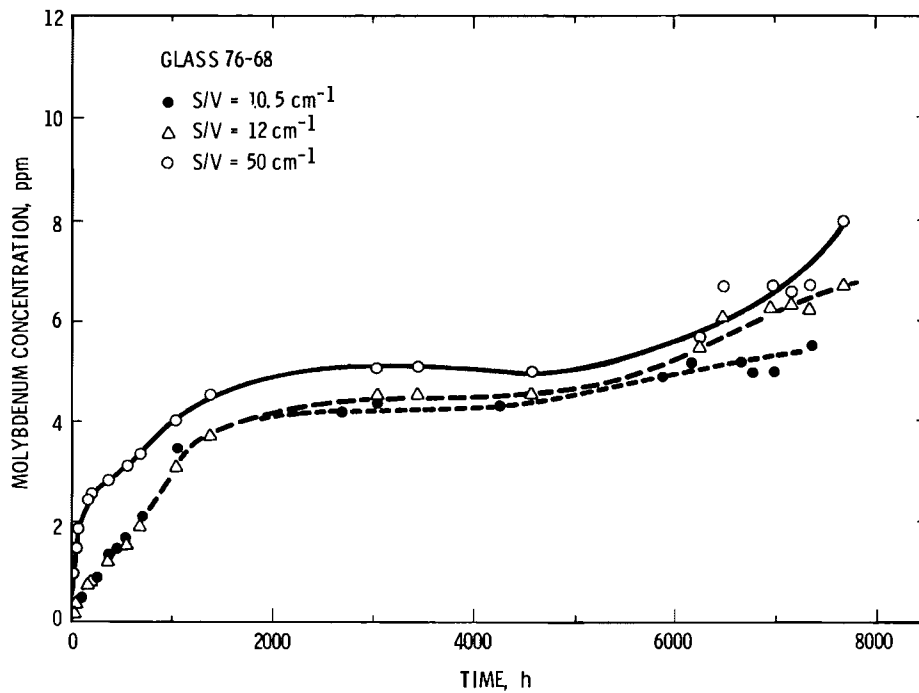


FIGURE 18. Molybdenum Concentration Versus Time for 76-68 Glass-Demineralized Water Mixtures Held at 35°C

3.2.2 Less Soluble Species

When a waste glass was contacted with demineralized water at a constant temperature for an extended period of time many of the less soluble elements appeared to reach equilibrium concentrations in the solution. Other elements, however, were present in the solution at concentrations below the detection limits for the ICP. This made it impossible to determine if the concentrations of these elements had reached equilibrium levels in the solution. Still other elements exhibited erratic behavior.

Some of the elements reached the apparent saturation concentrations in a relatively short period of time (<100 hours at 35°C). Other elements exhibited erratic behavior during the initial contact, with the concentrations fluctuating over wide ranges, but appeared to reach equilibrium concentrations after prolonged contact (>5000 hours at 35°C). Figure 19 shows the calcium and chromium concentration curves obtained with 77-107 glass at 65°C. The plots are typical of the concentration curves for the less soluble species that were obtained with the waste glasses over the temperature ranges studied. The curve for chromium is typical for those less soluble elements that reached apparent saturation concentrations in relatively short periods of time. The large fluctuations in the calcium concentration during the early contact were observed in all of the tests with the waste glasses but were not evident in the tests with 79-339 glass. Other elements exhibiting erratic behavior similar to that of calcium include barium, strontium, uranium and zinc. In many of the tests, zinc did not appear to reach an equilibrium concentration but continued to fluctuate over wide ranges. Several other elements exhibited erratic behavior in some but not all of the tests; elements in this group included iron, nickel and phosphorus.

A number of the Millipore filters that were used in obtaining the solution samples were analyzed to see if the erratic behavior of some elements could be attributed to the filter discs. No evidence was obtained to show that the filter discs were affecting the analytical results in any way. Similarly, the examination of the filter holders, syringes and vials used in obtaining the samples gave no evidence that they affected the analytical results obtained.

The results of the constant-temperature tests with the four glasses are presented in Tables 10 through 20. The large standard deviations assigned to many of the values given in the tables indicate the considerable spread in the analytical data. This spread made it difficult to assume that some of the less soluble species had actually attained saturation concentration in the solutions.

After evaluating the data presented in Tables 10 through 20, it is apparent that most of the less soluble elements exhibited the expected behavior. The apparent equilibrium concentrations for many of the elements vary with solution temperature and pH in a normal manner. Several of the less soluble species exhibited anomalous behavior, however, which cannot be explained by normal chemical considerations. The data indicate that the solubilities of at least some of the cations are controlled by solid phases other than simple oxides or hydroxides.

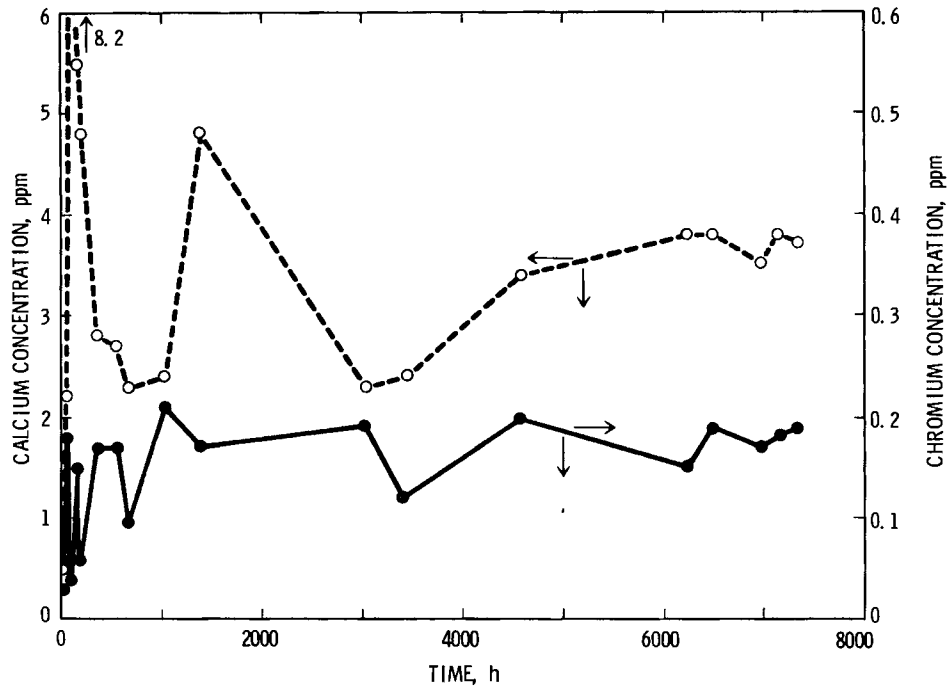


FIGURE 19. Calcium and Chromium Concentrations Versus Time for a 77-107 Glass-Demineralized Water Mixture Held at 65°C--S/V = 41 cm⁻¹

TABLE 10. Equilibrium Concentrations of Various Elements in 76-68 Glass-Demineralized Water Mixtures Held at 35°C

Element	Equilibrium Test Conditions			
	Mixture S/V Solution pH ^(a) Contact Time	10.5 cm ⁻¹ 8.2 6980 h	12 cm ⁻¹ 8.3 7650 h	50 cm ⁻¹ 8.8 7650 h
Al ^(b)		0.037 ± 0.016	0.053 ± 0.020	0.066 ± 0.022
B		(c)	(c)	(c)
Ba		0.007 ± 0.002	0.045 ± 0.024	0.11 ± 0.042
Ca		0.64 ± 0.21	2.2 ± 0.6	3.5 ± 0.3
Cd		(<0.004) ^(d)	(<0.004)	(<0.004)
Ce		(<0.04)	(<0.04)	(<0.04)
Co		(<0.01)	(<0.01)	(<0.01)
Cr		0.19 ± 0.04	0.24 ± 0.008	0.26 ± 0.018
Cs		2.0	3.0	6.0
Eu		(<0.002)	(<0.002)	(<0.002)
Fe		0.035 ± 0.021	0.041 ± 0.012	0.047 ± 0.021
Gd		(<0.01)	(<0.01)	(<0.01)
La		(<0.008)	(<0.008)	(<0.008)
Mo		(c)	(c)	(c)
Na		(c)	(c)	(c)
Nd		(<0.02)	(<0.02)	(<0.02)
Ni		(<0.02)	0.024 ± 0.008	0.037 ± 0.014
P		0.58 ± 0.20	0.27 ± 0.008	0.20 ± 0.12
Ru		(<0.05)	(<0.05)	(<0.05)
Si		(c)	(c)	(c)
Sr		0.041 ± 0.008	0.23 ± 0.07	0.51 ± 0.12
Te		(<0.06)	(<0.06)	(<0.06)
Ti		(<0.002)	(<0.002)	0.002
U		0.8	1.3	1.7
Zn		0.12	---	---
Zr		(<0.008)	(<0.008)	(<0.008)

(a) Apparent equilibrium pH at 35°C.

(b) Aluminum was an impurity resulting from ball-milling of the glass.

(c) Concentration still increasing--see Section 3.2.1.

(d) Value in parentheses indicates the concentration is below the detection limit of the analytical procedure used--the element may or may not be at the equilibrium concentration.

TABLE 11. Equilibrium Concentrations of Various Elements in 76-68 Glass-Demineralized Water Mixtures Held at 65°C

Element	Equilibrium Test Conditions		
	Mixture S/V Solution pH ^(a) Contact Time	10.5 cm ⁻¹ 8.5 6980 h	12 cm ⁻¹ 8.6 7320 h
	Equilibrium Concentration, ppm		
Al ^(b)	0.082 ± 0.008	0.086 ± 0.019	0.17 ± 0.02
B	(c)	(c)	(c)
Ba	0.029 ± 0.017	0.045 ± 0.017	0.031 ± 0.007
Ca	0.54 ± 0.22	1.2 ± 0.4	0.86 ± 0.38
Cd	0.004 ± 0.002	0.005 ± 0.002	0.006 ± 0.003
Ce	(<0.04) ^(d)	0.073 ± 0.010	0.051 ± 0.014
Co	(<0.01)	0.017 ± 0.006	0.034 ± 0.006
Cr	0.40 ± 0.008	0.42 ± 0.020	0.85 ± 0.04
Cs	2.6 ± 0.5	3.2 ± 0.3	4.7 ± 0.4
Eu	(<0.002)	(<0.002)	(<0.002)
Fe	0.14 ± 0.04	0.52 ± 0.19	0.81 ± 0.07
Gd	(<0.01)	(<0.01)	(<0.01)
La		0.10 ± 0.03	0.040 ± 0.002
Mo	10.6 ± 0.2	10.8 ± 0.5	22.5 ± 0.6
Na	(c)	(c)	(c)
Nd	(<0.02)	0.060 ± 0.011	(<0.02)
Ni	0.023 ± 0.007	0.039 ± 0.016	0.084 ± 0.006
P	1.3 ± 0.12	0.66 ± 0.10	2.5 ± 0.05
Ru	(<0.05)	(<0.05)	(<0.05)
Si	52.7 ± 1.5	45.5 ± 0.7	59.3 ± 1.4
Sr	0.014 ± 0.006	0.096 ± 0.010	0.037 ± 0.008
Te	(<0.06)	(<0.06)	0.078 ± 0.012
Ti	0.0022 ± 0.0008	0.092 ± 0.031	0.082 ± 0.011
U	0.7 ± 0.3	0.65 ± 0.25	1.4 ± 0.2
Zn		1.3 ± 0.6	1.6 ± 0.7
Zr	(<0.008)	0.092 ± 0.036	0.061 ± 0.022

(a) Apparent equilibrium pH at 65°C.

(b) Aluminum was an impurity resulting from ball-milling of the glass.

(c) Concentration still increasing--see Section 3.2.1.

(d) Value in parentheses indicates the concentration is below the detection limit of the analytical procedure used--the element may or may not be at the equilibrium concentration.

TABLE 12. Equilibrium Concentrations of Various Elements in 76-68 Glass-Demineralized Water Mixtures Held at 95°C

Mixture S/Y	Equilibrium Test Conditions	
	12 cm ⁻¹	50 cm ⁻¹
Solution pH ^(a)	8.8	9.6
Contact Time	1892 h	1892 h
Element	Equilibrium Concentration, ppm	
Al ^(b)	0.44 ± 0.04	0.73 ± 0.08
B	(c)	(c)
Ba	0.31 ± 0.17	0.33 ± 0.09
Ca	0.74 ± 0.51	0.37 ± 0.065
Cd	0.0071 ± 0.0036	0.047 ± 0.034
Ce	(<0.04) ^(d)	(<0.04)
Co	0.023 ± 0.012	0.018 ± 0.005
Cr	0.82 ± 0.09	1.1 ± 0.24
Cs	3.4 ± 0.4	6.5 ± 0.9
Eu	0.0029 ± 0.0017	0.0026 ± 0.0009
Fe	1.2 ± 0.1	1.9 ± 0.1
Gd	0.031 ± 0.015	0.089 ± 0.043
La	0.013 ± 0.006	0.024 ± 0.011
Mo	(c)	(c)
Na	(c)	(c)
Nd	(<0.02)	0.022 ± 0.008
Ni	0.041 ± 0.013	0.029 ± 0.005
P	2.3 ± 0.2	6.9 ± 0.1
Ru	(<0.05)	(<0.05)
Si	(c)	(c)
Sr	0.038 ± 0.018	0.027 ± 0.014
Te	0.16 ± 0.03	0.43 ± 0.10
Ti	0.022 ± 0.011	0.019 ± 0.010
U	3.5 ± 0.8	1.8 ± 0.3
Zn	1.7 ± 0.4	0.80 ± 0.42
Zr	0.029 ± 0.016	0.029 ± 0.008

(a) Apparent equilibrium pH at 65°C.

(b) Aluminum was an impurity resulting from ball-milling of the glass.

(c) Concentration still increasing--see Section 3.2.1.

(d) Value in parentheses indicates the concentration is below the detection limit of the analytical procedure used--the element may or may not be at the equilibrium concentration.

TABLE 13. Equilibrium Concentrations of Various Elements in 76-68 Glass-Demineralized Water Mixtures Held at 150°C

Element	Equilibrium Test Conditions	
	Mixture S/V ^(a)	Solution pH ^(b)
	2 cm ⁻¹	9.7
		768 h
Element	Equilibrium Concentration, ppm	
Al ^(c)	0.69 ± 0.14	
B	(d)	
Ba	(e)	
Ca	(e)	
Cd	0.033 ± 0.019	
Ce	(<0.04) ^(f)	
Co	0.11 ± 0.06	
Cr	1.3 ± 0.3	
Cs	9.7 ± 0.8	
Eu	(<0.002)	
Fe	(e)	
Gd	(<0.01)	
La	0.077 ± 0.012	
Mo	(c)	
Na	(c)	
Nd	(<0.02)	
Ni	0.010 ± 0.02	
P	3.8 ± 0.7	
Ru	0.078 ± 0.023	
Si	(c)	
Sr	0.051 ± 0.009	
Te	0.63 ± 0.27	
Ti	(e)	
U	(e)	
Zn	4.2 ± 2.1	
Zr	(e)	

- (a) Based on geometric surface area of solid glass sample.
 (b) Apparent equilibrium pH measured at room temperature.
 (c) Aluminum was an impurity resulting from ball-milling of the glass.
 (d) Concentration still increasing--see Section 3.2.1.
 (e) Concentrations fluctuated with time--equilibrium was not established.
 (f) Value in parentheses indicates concentration was below the detection limit--could not determine if equilibrium was reached.

TABLE 14. Equilibrium Concentrations of Various Elements in 77-107 Glass-Demineralized Water Mixtures Held at 35°C

Mixture S/Y	Equilibrium Test Conditions	
	14 cm ⁻¹	41 cm ⁻¹
Solution pH ^(a)	8.6	8.9
Contact Time	7650 h	7650 h
Element	Equilibrium Concentration, ppm	
Al ^(b)	0.11 ± 0.05	0.24 ± 0.05
B	(c)	(c)
Ba	0.18 ± 0.05	0.18 ± 0.03
Ca	4.4 ± 0.9	4.6 ± 0.4
Cd	(<0.004) ^(d)	(<0.004)
Ce	(<0.04)	(<0.04)
Co	(<0.01)	(<0.01)
Cr	0.040 ± 0.017	0.078 ± 0.014
Cs	14 ± 3	21 ± 4
Eu	(<0.002)	(<0.002)
Fe	0.049 ± 0.028	0.041 ± 0.013
Gd	(<0.01)	(<0.01)
K	56 ± 3	70 ± 5
La	(<0.008)	(<0.008)
Mo	(c)	(c)
Na	(c)	(c)
Nd	(<0.02)	(<0.02)
Ni	(<0.02)	(<0.02)
P	0.35 ± 0.20	0.36 ± 0.19
Ru	(<0.05)	(<0.05)
Si	(c)	(c)
Sn	0.83 ± 0.25	0.96 ± 0.04
Te	(<0.06)	(<0.06)
Ti	(<0.002)	(<0.002)
U	1.4 ± 0.4	2.5 ± 0.3
Zn	(e)	(e)
Zr	(<0.008)	0.018 ± 0.005

(a) Apparent equilibrium pH at 35°C.

(b) Aluminum was an impurity resulting from ball-milling of the glass.

(c) Concentration still increasing--see Section 3.2.1.

(d) Value in parentheses indicates the concentration is below the detection limit for the analytical procedure--cannot determine if the element is at equilibrium in the solution.

(e) Concentration fluctuated with time--equilibrium was not established.

TABLE 15. Equilibrium Concentrations of Various Elements in 77-107 Glass--Demineralized Water Mixtures Held at 65°C

Element	Equilibrium Test Conditions	
	14 cm ⁻¹	41 cm ⁻¹
Mixture S/V	14 cm ⁻¹	41 cm ⁻¹
Solution pH ^(a)	8.7	9.1
Contact Time	7320 h	7320 h
Element	Equilibrium Concentration, ppm	
Al ^(b)	0.59 ± 0.06	0.51 ± 0.02
B	(c)	(c)
Ba	0.11 ± 0.04	0.14 ± 0.03
Ca	2.6 ± 0.4	3.7 ± 0.2
Cd	0.012 ± 0.006	0.0062 ± 0.0020
Ce	(<0.04) ^(d)	(<0.04)
Co	0.029 ± 0.005	0.016 ± 0.005
Cr	0.23 ± 0.02	0.18 ± 0.01
Cs	14 ± 1.2	26 ± 1
Eu	0.003 ± 0.0007	(<0.002)
Fe	0.089 ± 0.004	0.064 ± 0.015
Gd	(<0.01)	(<0.01)
K	166 ± 2	191 ± 6
La	(<0.008)	(<0.008)
Mo	(c)	(c)
Na	(c)	(c)
Nd	(<0.02)	(<0.02)
Ni	0.074 ± 0.021	0.026 ± 0.005
P	0.39 ± 0.14	0.32 ± 0.10
Ru	0.067 ± 0.008	0.061 ± 0.006
Si	87 ± 4	64 ± 5
Sr	0.59 ± 0.06	0.84 ± 0.04
Te	0.61 ± 0.18	0.43 ± 0.08
Ti	0.0046 ± 0.0010	(<0.002)
U	0.4 ± 0.03	0.2 ± 0.03
Zn	1.3 ± 0.6	0.64 ± 0.28
Zr	0.059 ± 0.023	0.056 ± 0.003

(a) Apparent equilibrium pH at 65°C.

(b) Aluminum was an impurity resulting from ball-milling of the glass.

(c) Concentration still increasing--see Section 3.2.1.

(d) Value in parentheses indicates the concentration is below the detection limit for the analytical procedure used--cannot determine if the element is at equilibrium in the solution.

TABLE 16. Equilibrium Concentrations of Various Elements in 77-107 Glass--Demineralized Water Mixtures Held at 95°C

Element	Equilibrium Test Conditions	
	14 cm ⁻¹	41 cm ⁻¹
Mixture S/V	14 cm ⁻¹	41 cm ⁻¹
Solution pH	9.0	9.7
Contact Time	1892 h	1892 h
Element	Equilibrium Concentration, ppm	
Al ^(b)	0.60 ± 0.15	2.7 ± 0.5
B	(c)	(c)
Ba	0.24 ± 0.06	0.28 ± 0.07
Ca	2.0 ± 0.4	1.7 ± 0.3
Cd	0.0055 ± 0.0024	0.0065 ± 0.0019
Ce	(<0.04) ^(d)	(<0.04)
Co	0.011 ± 0.003	0.022 ± 0.009
Cr	0.35 ± 0.11	0.44 ± 0.04
Cs	36 ± 3	60 ± 2
Eu	(<0.002)	(<0.002)
Fe	0.23 ± 0.04	0.17 ± 0.01
Gd	0.024 ± 0.007	0.030 ± 0.014
K	198 ± 7	397 ± 8
La	0.014 ± 0.005	0.030 ± 0.009
Mo	(c)	(c)
Na	(c)	(c)
Nd	0.027 ± 0.007	(<0.02)
Ni	0.033 ± 0.013	0.073 ± 0.014
P	0.79 ± 0.15	1.6 ± 0.2
Ru	(<0.05)	(<0.05)
Si	95 ± 2	107 ± 5
Sr	0.20 ± 0.08	0.19 ± 0.07
Te	0.75 ± 0.05	1.0 ± 0.16
Ti	0.014 ± 0.007	0.004 ± 0.001
U	0.45 ± 0.21	0.80 ± 0.15
Zn	0.74 ± 0.36	1.4 ± 0.7
Zr	0.069 ± 0.007	0.076 ± 0.008

- (a) Apparent equilibrium pH at 95°C.
 (b) Aluminum was an impurity resulting from ball-milling of the glass.
 (c) Concentration still increasing--see Section 3.2.1.
 (d) Value in parentheses indicates the concentration is below the detection limit for the analytical procedure used--cannot determine if the element is at equilibrium in the solution.

TABLE 17. Equilibrium Concentrations of Various Elements in 77-260 Glass--Demineralized Water Mixtures Held at 35°C

Element	Equilibrium Test Conditions			
	Mixture S/V	10 cm ⁻¹	12 cm ⁻¹	36 cm ⁻¹
	Solution pH ^(a)	8.7	8.8	9.3
Contact Time	7320 h	7650 h	7650	
	Equilibrium Concentration, ppm			
Al ^(b)	0.089 ± 0.029	0.066 ± 0.018	0.13 ± 0.03	
B	(b)	(b)	(b)	
Ba	0.014 ± 0.005	0.043 ± 0.021	0.015 ± 0.002	
Ca	0.40 ± 0.14	1.3 ± 0.5	0.73 ± 0.29	
Cd	(<0.004) ^(c)	(<0.004)	(<0.004)	
Ce	(<0.04)	(<0.04)	(<0.04)	
Co	(<0.01)	(<0.01)	(<0.01)	
Cr	(<0.02)	(<0.02)	(<0.02)	
Cs	3.2 ± 1.5	3.9 ± 0.4	5.9 ± 0.7	
Cu	0.021 ± 0.004	0.034 ± 0.019	0.038 ± 0.017	
Eu	(<0.002)	(<0.002)	(<0.002)	
Fe	0.035 ± 0.016	0.0297 ± 0.020	0.029 ± 0.011	
Gd	(<0.01)	(<0.01)	(<0.01)	
K	(b)	(b)	(b)	
La	(<0.008)	(<0.008)	(<0.008)	
Mn	(<0.002)	0.0029 ± 0.0012	(<0.002)	
Mo	(b)	(b)	(b)	
Na	(b)	(b)	(b)	
Nd	(<0.02)	(<0.02)	(<0.02)	
Ni	(<0.02)	0.03 ± 0.011	(<0.02)	
P	0.19 ± 0.03	(<0.1)	0.25 ± 0.10	
Ru	(<0.05)	(<0.05)	(<0.05)	
Si	(b)	(b)	(b)	
Sr	0.033 ± 0.007	0.20 ± 0.08	0.082 ± 0.012	
Te	(<0.06)	(<0.06)	(<0.06)	
Ti	(<0.002)	(<0.002)	(<0.002)	
U	0.7 ± 0.4	1.5 ± 0.4	3.0 ± 6.7	
Zn	--	--	--	
Zr	(<0.008)	(<0.008)	(<0.008)	

(a) Apparent equilibrium pH at 35°C.

(b) Concentration still increasing--see Section 3.2.1.

(c) Value in parentheses indicates the concentration is below the detection limit for the analytical procedure used--cannot determine if the element is at equilibrium in the solution.

(d) Concentration fluctuated with time--equilibrium was not established.

TABLE 18. Equilibrium Concentrations of Various Elements in 77-260 Glass--Demineralized Water Mixtures Held at 65°C

Mixture S/V Solution pH ^(a) Contact Time	Equilibrium Test Conditions		
	10 cm ⁻¹ 8.9 6980 h	12 cm ⁻¹ 9.0 7320 h	36 cm ⁻¹ 9.4 7320
Element	Equilibrium Concentration, ppm		
Al ^(b)	0.25 ± 0.04	0.24 ± 0.06	0.34 ± 0.04
B	(b)	(b)	(b)
Ba	0.020 ± 0.010	0.025 ± 0.015	0.011 ± 0.004
Ca	0.30 ± 0.06	(d)	0.37 ± 0.07
Cd	(<0.004) ^(d)	(<0.004)	(<0.004)
Ce	(<0.04)	(<0.04)	(<0.04)
Co	(<0.01)	(<0.01)	0.014 ± 0.003
Cr	(<0.02)	0.025 ± 0.015	0.044 ± 0.015
Cs	4.2 ± 0.4	5.5 ± 0.8	7.0 ± 0.5
Cu	0.049 ± 0.013	0.054 ± 0.023	0.011 ± 0.003
Eu	(<0.002)	(<0.002)	(<0.002)
Fe	0.041 ± 0.017	0.040 ± 0.016	0.093 ± 0.034
Gd	0.017 ± 0.004	0.025 ± 0.011	0.086 ± 0.036
K	(b)	(b)	(b)
La	(<0.008)	(<0.008)	(<0.008)
Mn	(<0.002)	0.003 ± 0.001	0.004 ± 0.002
Mo	(b)	(b)	(b)
Na	(b)	(b)	(b)
Nd	(<0.02)	(<0.02)	(<0.02)
Ni	(<0.02)	0.0026 ± 0.015	0.037 ± 0.014
P	0.61 ± 0.24	0.34 ± 0.08	1.7 ± 0.6
Ru	(<0.05)	(<0.05)	(<0.05)
Si	(b)	(b)	(b)
Sr	0.016 ± 0.005	0.032 ± 0.010	0.018 ± 0.006
Te	(<0.06)	(<0.06)	(<0.06)
Ti	(<0.002)	(<0.002)	0.031 ± 0.016
U	0.8 ± 0.4	1.0 ± 0.4	2.9 ± 0.5
Zn	--	--	--
Zr	(<0.008)	(<0.008)	0.027 ± 0.012

(a) Apparent equilibrium pH at 35°C.

(b) Concentration still increasing--see Section 3.2.1.

(c) Value in parentheses indicates the concentration was below the detection limit for the analytical procedure used--could not determine if the element had reached equilibrium in the solution.

(d) Concentration fluctuated with time--equilibrium was not established.

TABLE 19. Equilibrium Concentrations of Various Elements in 77-260 Glass--Demineralized Water Mixtures Held at 95°C

Element	Equilibrium Test Conditions	
	12 cm ⁻¹	36 cm ⁻¹
Mixture S/V	12 cm ⁻¹	36 cm ⁻¹
Solution pH ^(a)	9.2	9.9
Contact Time	1892 h	1892 h
Element	Equilibrium Concentration, ppm	
Al ^(b)	1.7 ± 0.3	1.9 ± 0.05
B	(b)	(b)
Ba	0.23 ± 0.08	0.28 ± 0.08
Ca	0.62 ± 0.19	0.47 ± 0.11
Cd	(<0.004) ^(c)	0.0063 ± 0.0025
Ce	(<0.04)	(<0.04)
Co	0.015 ± 0.004	0.035 ± 0.018
Cr	0.068 ± 0.006	0.12 ± 0.02
Cs	13 ± 0.4	25 ± 1
Cu	0.16 ± 0.06	0.46 ± 0.04
Eu	(<0.002)	0.0031 ± 0.0014
Fe	0.24 ± 0.08	0.41 ± 0.12
Gd	0.26 ± 0.06	0.82 ± 0.21
K	(b)	(b)
La	0.022 ± 0.010	0.013 ± 0.04
Mn	0.0095 ± 0.0016	0.031 ± 0.009
Mo	(b)	(b)
Na	(b)	(b)
Nd	(<0.02)	0.047 ± 0.011
Ni	0.10 ± 0.02	0.16 ± 0.06
P	20 ± 0.5	13 ± 2
Ru	(<0.05)	(<0.05)
Si	(b)	(b)
Sr	0.030 ± 0.012	0.040 ± 0.018
Te	0.12 ± 0.04	0.54 ± 0.13
Ti	0.024 ± 0.010	0.039 ± 0.014
U	(d)	(d)
Zn		
Zr	0.026 ± 0.012	0.042 ± 0.012

(a) Apparent equilibrium pH at 95°C.

(b) Concentration still increasing--see Section 3.2.1

(c) Value in parentheses indicates the concentration is below the detection limit for the analytical procedure used--cannot determine if the element is at equilibrium in the solution.

(d) Concentration fluctuated with time--equilibrium was not established.

TABLE 20. Equilibrium Concentrations of Various Elements in 79-339 Glass--
Demineralized Water Mixtures Held at 35°C

Mixture S/V Solution pH ^(a) Contact Time	Equilibrium Test Conditions	
	12 cm ⁻¹ 7.1 1080 h	50 cm ⁻¹ 7.4 1080 h
Element	Equilibrium Concentration, ppm	
Al	0.058 ± 0.030	0.30 ± 0.17
B	(b)	(b)
Ca	0.65 ± 0.18	1.2 ± 0.3
Cs	0.20 ± 0.05	0.30 ± 0.03
Fe	0.035 ± 0.014	0.067 ± 0.12
Mn	(b)	(b)
Na	(b)	(b)
Si	(b)	(b)

(a) Apparent equilibrium pH at 35°C.

(b) Concentration still increasing--see Section 3.2.1

In those tests where equilibrium was approached from supersaturation the concentrations of most of the less-soluble species at 35°C were much higher than the apparent equilibrium values attained in the constant-temperature tests at 35°C. As was the case with the soluble species, the concentrations of the less soluble species attained in the supersaturation tests varied over wide ranges depending on the test conditions. Variables affecting the results included: the glass type, the S/V of the glass-water system, the time the system was held at the higher temperature, and most importantly the extent to which the solution was evaporated before equilibration at 35°C. Replicate experiments gave significantly different results indicating that at least one uncontrolled variable was affecting the results. Some typical results from the supersaturation tests with the three waste glasses are given in Table 21. Other tests carried out under different conditions gave very different results, even though the final temperature in each test was 35°C. When comparing the values given in Table 21 with the 35°C data in Tables 10 through 19, it is obvious that, in general, the concentrations attained in the supersaturation tests are several times greater than the concentrations attained in the constant-temperature tests. The results emphasize that even with the less soluble elements, the solution concentrations attained in waste glass-water systems are highly dependent on the conditions under which the tests are conducted. The data show that it is impossible to define precise solubility limits for elements in glass-water systems without precisely defining the system, particularly with regard to its thermal history.

3.2.3 Factors Affecting Solubility

As was shown in the previous sections, the two methods used to measure the solubilities of glass components in demineralized water gave very different results. Without additional data on the species present in the solution and the solid phases present in the glass-water system, it is impossible to state with certainty why the two methods gave different results. There are, however, several possible explanations for the differences observed.

TABLE 21. Some Typical Solution Concentration Obtained When Equilibrium Was Approached From Supersaturation

Test Condition Parameters and Units	Values for Each Test		
	76-68	77-107	77-260
Glass	76-68	77-107	77-260
System S/V, cm ⁻¹	1.4	0.33	0.30
Initial Contact Temp., °C	95	85	85
Initial Contact Time, h	650	984	984
Final Contact Temp., °C	35	35	35
Final Contact Time, h	96	72	72
Concentration Factor ^(a)	71	103	72
Final Solution pH ^(b)	10.0	10.4	10.7

Elements	Concentration in Solution, ppm		
Al	1.8	0.57	17
B	370	146	252
Ba	0.12	0.32	0.12
Ca	3.9	4.2	3.7
Cd	0.017	0.007	0.016
Ce	0.042	(<0.04)	(<0.04)
Co	0.079	0.035	0.10
Cr	7.0	0.43	0.26
Cs	65	73	47
Cu	--	--	0.49
Eu	0.018	(<0.002)	(<0.002)
Fe	1.8	0.21	0.13
Gd	0.047	(<0.01)	0.39
K	--	118	150
La	0.020	(<0.008)	(<0.008)
Mn	--	--	0.13
Mo	180	64	135
Na	1090	198	960
Nd	0.050	(<0.02)	(<0.02)
Ni	0.15	0.18	0.12
P	20	1.7	14
Ru	0.16	(<0.05)	0.11
Si	420	146	690
Sr	0.39	1.6	0.43
Te	0.69	0.49	0.065
Ti	0.31	(<0.001)	0.010
U	28	17	12
Zn	5.9	0.75	
Zr	0.21	0.039	0.13

(a) Initial solution volume divided by final solution volume after evaporation.
 (b) Solution pH at 35°C.

- The solution concentrations measured by the subsaturation method may be far below the actual saturation limits for the different elements and continued contact of the glass-water systems for very long periods would yield concentration values similar to those of the supersaturation method. The fact that many of the elements appeared to reach saturation in the solutions and that the dissolution rates of others decreased to very low levels can be attributed to reduced diffusion of the individual elements through the residual glass layer and through any solid phases that may have formed on the glass surface.
- Lower solution pH values were attained when equilibrium was approached from subsaturation, as compared to the pH values attained when equilibrium was approached from supersaturation (Section 3.1). This could affect the solubility of the less soluble species, but it is unlikely that pH differences could account for the very large differences observed in the concentrations of the soluble species (with the possible exception of silicon).
- When the glass is contacted with demineralized water at a constant temperature, the solubility of individual elements in the solution will be determined by the solid phases that are initially present or that form with time as the glass dissolves. If the glass is contacted with water at a high temperature for a long time and the solution is then evaporated and/or cooled to a lower temperature, some precipitation of dissolved materials will occur. The solid phases that precipitate may or may not have the same compositions as the solid phases present when the glass is contacted with water at a constant temperature. Therefore, in the two methods used to measure solubilities different solid phases may control the solubility of a given element, resulting in different solubility limits.
- When equilibrium was approached from supersaturation, the solutions may have been supersaturated with respect to some elements when analyzed. This could help account for differences observed between replicate supersaturation experiments.

Each of the first three factors discussed above may be at least partially responsible for the differences in the results obtained with the two procedures.

There are, however, a number of other factors, not previously discussed, that have the potential for affecting the solubilities of glass components in a glass-water system under certain conditions.

- When the glass is contacted with water in the presence of air, absorption of CO_2 may occur and the resulting carbonate-bicarbonate species in solution may affect solution pH and the solubilities of some elements. It is possible, therefore, that the solubility limits of some elements in solution could be quite different in CO_2 -free systems and systems exposed to air. Since the work described here involved systems exposed to air, results obtained with CO_2 -free systems may be quite different from the data given in this report.
- When the glass components dissolve in water, complex anionic species may be formed in solution that serve to control the solubilities of various cations. Typical of

the anions that may form are various silicates, phosphates, molybdates, and borates. Therefore, the solid phases that control the solubilities of the individual glass elements in solution may be quite different from what one might expect.

- When a glass dissolves in water, various solid forms of hydrated silica can form. These hydrated silica species possess some ion-exchange properties and may affect the dissolution behavior and solubilities of some elements.
- Certain anions may be present in a waste glass in small concentrations (i.e., as impurities in the glass formers) and could affect the solubilities of some elements. The presence of these anions, such as sulfate and fluoride, may not be evident from a typical glass analysis.
- The presence of a radiation field may have an effect on the solubility of some species through radiolysis and pH effects.

From the results of this work and considering the great many variables involved, it is clear that a thorough understanding of solubility relationships in a glass-water system will require a great deal of additional experimental work. The most basic requirement is to identify the solid phases that control the solubilities of the individual glass elements in water under various conditions.

3.3 EVALUATION OF THE SOLUBILITY DATA

A great deal of work has been done on the stability and dissolution behavior of waste glasses in aqueous media. Very little data has been published, however, on the solubilities of the individual glass elements in the solutions produced when a waste glass is contacted with an aqueous medium. The solubilities of some glass elements in the aqueous solutions may be controlled simply by solution pH and the corresponding oxide or hydroxide solid phases. The solubilities of other glass constituents may be controlled by more complex solid phases. Solubility data are available for individual oxides and hydroxides in water, but little has been published on solubility relationships in complex glass-water systems.

Work at PNL with 76-68 glass doped with plutonium indicates that the solubility of plutonium in solutions contacting the doped glass appears to be controlled by $\text{PuO}_2(\text{c})$ or some compound of similar solubility (Rai and Strickert 1980). Similar results were observed with neptunium doped 76-68 glass, where the solubility of the neptunium appeared to be controlled by $\text{NpO}_2(\text{c})$ or some compound of similar solubility (Rai and Strickert 1980).

Although experimental evidence is lacking, the solubilities in aqueous solutions of at least some cations in the waste glasses may be controlled by more complex phases than the simple oxides and hydroxides. For example, in some of the constant-temperature tests the cesium concentrations were relatively low and the concentrations appeared to reach equilibrium levels. It is difficult to explain the low cesium concentrations unless a complex solid phase, such as cesium phosphomolybdate, is controlling the cesium solubility. It should be noted, however, that low cesium concentrations were also obtained with the 79-339 glass that contained neither molybdenum or phosphorus.

It is difficult to assess the accuracy and reliability of the solubility data obtained in this work because comparable data are not available in the literature. Solubility results for the individual elements can be compared, however, with published data on the solubilities of individual oxides, hydroxides, or other compounds in aqueous solutions. Considering the complexities of the waste glass-water systems, it is questionable if such comparisons are valid or meaningful. Nonetheless, such comparisons are of interest and two elements--silicon and calcium--are discussed below.

A great amount of work has been done on the silica-water system and considerable data has been published on the solubility of amorphous silica and the various crystalline silica modifications in aqueous solutions. Considerable disagreement exists in the published data on silica solubility, and much remains to be learned of the chemistry of the silica-water system. Figure 20 shows a recently published solubility curve for amorphous silica in water at 0°C to 150°C (Fournier and Rowe 1977), as well as a solubility curve for quartz (Morey, Fournier and Rowe 1962). The solubility data are presented in terms of the silicon concentration of the solution. The silicon solubility data obtained in this study are also included in Figure 20. In every case the maximum silicon concentrations measured in the constant-temperature tests fall between the solubility curves for the amorphous silica and the quartz. With two exceptions, the silicon concentrations obtained in the supersaturation experiments greatly exceeded the reported solubility for amorphous silica at 35°C.

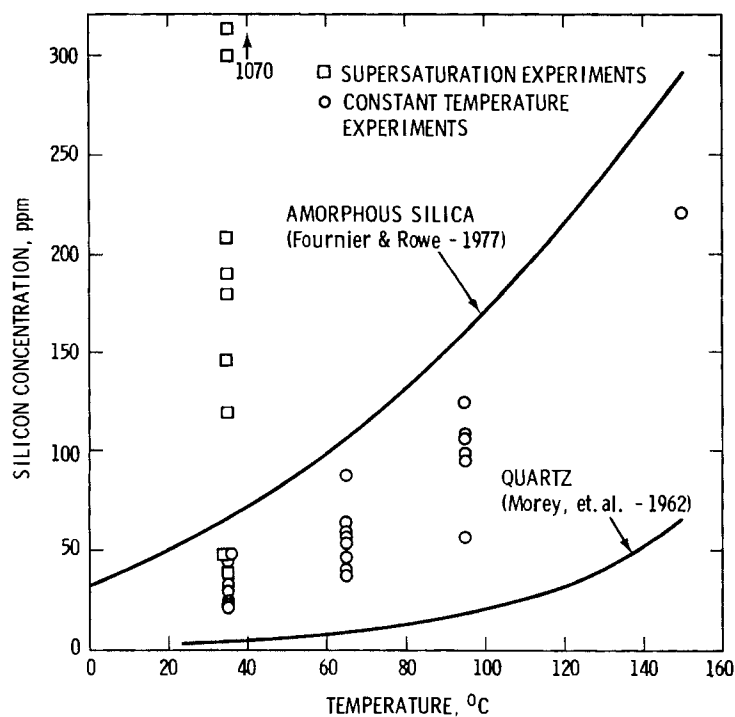


FIGURE 20. Solubility of Amorphous Silica and Quartz in Water As a Function of Temperature--Showing Results Obtained in This Study

The data presented in Figure 20 do not take into account pH effects. Published data show that the pH of the solution has a marked effect on the solubility of amorphous silica, especially at pH levels greater than 9. The pH effect is more pronounced at temperatures below 100°C than at higher temperatures. In both the constant-temperature tests and the supersaturation experiments the final pHs of the test solutions varied over a considerable range depending on the test parameters.

In Figure 21 the silicon concentrations attained at 35°C in the two types of experiments are plotted as a function of the final solution pH. Published data for amorphous silica at 25°C, 50°C and 90°C are also included in the figure (Goto 1955; Alexander, Heston and Iler 1954). The data show that even after allowing for the effects of pH the silicon concentrations attained in the constant-temperature tests at 35°C are considerably lower than the solubility limits for amorphous silica at 35°C.

In the supersaturation experiments the final solution pH was generally about one to two pH units higher than the apparent equilibrium pH levels attained in the constant-temperature experiments at 35°C. Figure 21 shows that when pH effects are considered the silicon concentrations attained in the supersaturation experiments correspond more closely to the published data, but some of the measured concentrations are still much larger than the reported solubility limits for amorphous silica.

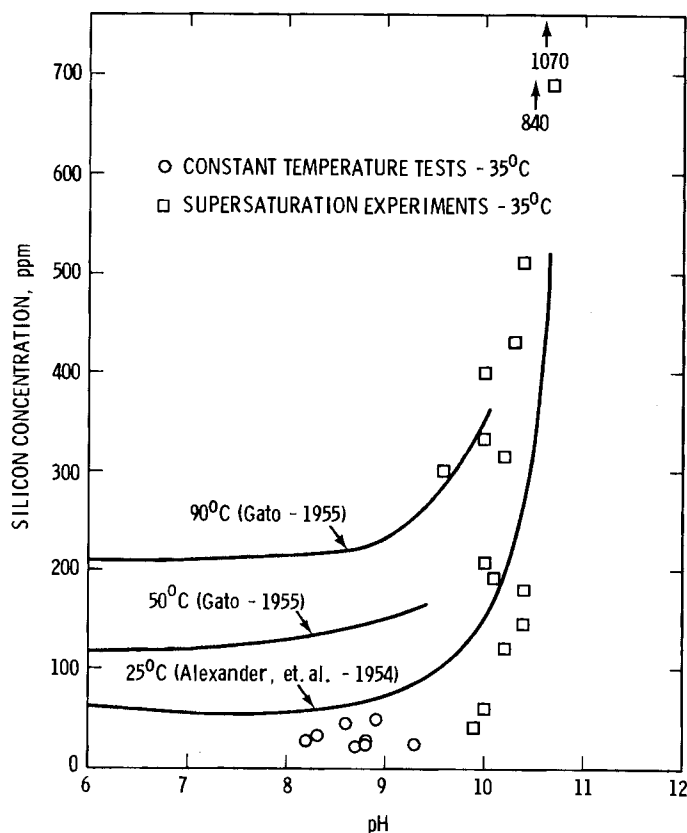


FIGURE 21. Effect of pH on the Solubility of Amorphous Silica in Water

There are several possible explanations for the differences observed between the silicon concentrations in the constant-temperature tests and published data on silica solubility.

- Certain impurities in the solution effectively reduce the solubility of silica (Iler 1979). Aluminum is especially effective in this regard. At 37°C the solubility of amorphous silica was reduced from 170 ppm to 30 ppm to 97 ppm where aluminum oxide was added to the system (Jephcott and Johnson 1950). At 25°C and pH 8.5 the addition of 0.08 ppm of aluminum ion decreased the solubility of quartz from 6 ppm to 3 ppm and 0.3 ppm of aluminum reduced the silica concentration to zero (Baumann 1967). Thus the presence of various dissolved species from the waste glass could effectively reduce the solubility of amorphous silica below the published values for a pure silica-water system.
- In the constant-temperature tests the silicon concentrations had not perhaps reached saturation levels. Although the test data indicated that the silicon concentrations had reached equilibrium levels or were increasing very slowly, very long contact times perhaps would yield silicon concentrations approaching the published solubility limits for amorphous silica.
- Some solid phase other than amorphous silica may be controlling the solubility of the silicon in the solutions.

There are also several possible explanations for the high silicon concentrations in some of the supersaturation experiments.

- Some solid phase(s) other than amorphous silica may have controlled the silicon concentrations of the solutions.
- After cooling to 35°C the solutions may have been supersaturated with respect to dissolved silica.
- The solutions may have contained polymeric or colloidal silica that was not removed by the Millipore filters.

Without additional analytical data on the waste glass-water systems, particularly with regard to the solid phases present and the silicon species in solution, it is impossible to determine why the solution concentrations measured in this work varied from the published silica solubility data.

Calcium appeared to reach equilibrium concentrations in most of the constant-temperature tests. The 77-107 glass produced much higher calcium concentrations than the other three glasses, but even with the 77-107 glass the calcium concentrations in the constant-temperature tests were less than 5 ppm. Even in the supersaturation experiment the calcium concentrations measured at 35°C did not exceed 6 ppm.

Table 22 presents solubility data for a number of slightly soluble calcium compounds. The values are for the pure compounds in water. The effects of solution pH, ionic strength, CO₂ partial pressure (in the case of CaCO₃), impurities, etc., on solubility are not considered. Comparing the results obtained in this work with the data presented in Table 22, the calcium

TABLE 22. Solubility of Calcium Compounds in Water(a)

Compound	Temperature, °C	Ksp(b)	Calcium Concentration, ppm
Ca(OH) ₂	25	9.0 x 10 ⁻⁶	812
	35	7.3 x 10 ⁻⁶	756
	60	4.2 x 10 ⁻⁶	620
	90	1.8 x 10 ⁻⁶	576
	100	1.2 x 10 ⁻⁶	400
CaCO ₃	25	4.8 x 10 ⁻⁹	22
	39	3.8 x 10 ⁻⁹	19
	50		15
	100	4.3 x 10 ⁻¹⁰	8
CaSO ₄	25	9.1 x 10 ⁻⁶	806
	50	5.5 x 10 ⁻⁶	476
	70	3.2 x 10 ⁻⁶	368
	100	1.2 x 10 ⁻⁶	197
Ca ₃ (PO ₄) ₂	20	2.0 x 10 ⁻²⁹	0.04
	30	1.1 x 10 ⁻²⁹	0.03
CaSiO ₃	30	2.5 x 10 ⁻⁸	17
CaF ₂	25	4.0 x 10 ⁻¹¹	9

(a) Data taken from following references: Sillens and Martell 1964; Meites 1963; Stephens and Stephens 1963; Greenburg and Copeland 1960; and Zharkovskii 1951.

(b) Ksp - solubility product

concentrations obtained are obviously much lower than the solubility limits for all of the compounds listed in the table except for Ca₃(PO₄)₂. If Ca₃(PO₄)₂ was controlling the calcium solubility then the calcium content of the test solution should have been much lower. Allowing for the effects of factors such as solution pH, ionic strength, etc., the calcium concentrations in the various test solutions might have been controlled by a CaCO₃ or CaSiO₃ solid phase but not by Ca(OH)₂. Calcium forms a large number of complex compounds that are slightly soluble in water, i.e., aluminates, aluminosilicates, silicophosphates, etc. One or more such compounds could form in the waste glass-water systems and could affect the solubility of calcium in the solutions.

Additional work is needed to identify the solid phase(s) that controls calcium solubility in the waste glass-water systems. Until such data is available it is impossible to assess the accuracy of the calcium solubility data obtained in this work. This also applies to the results obtained with the other glass constituents. While it is not possible to evaluate the accuracy of the data, the results provide an indication of the range of solution concentrations that can be expected in waste glass-water systems under various conditions.

4.0 CONCLUSIONS

When a waste glass is contacted with demineralized water, the system that results is complex because of the many chemical species involved. The dissolution behaviors of the individual glass elements and their solubilities in the aqueous solution are dependent on a number of variables, including: 1) the composition of the glass, 2) the temperature of the solution, 3) the S/V ratio of the glass-water system (which helps determine the pH of the solution), and 4) the thermal history of the glass-water system. The initial composition of the aqueous phase will also affect the dissolution behavior of the glass and the solubilities of the individual glass components in the solution.

Attempts to determine solubility limits for the glass components in the aqueous solution by approaching equilibrium from below saturation and from above saturation gave very different results. In every case the latter technique gave solution concentrations for the individual elements that were, in general, several times greater than the values obtained by the former method. Although the results obtained by the two methods varied greatly, both sets of data appear to be valid. The differences between the data obtained by the two methods can probably be explained by the fact that it was not possible to reach the same steady-state conditions using the two methods.

In evaluating all of the results obtained in this study, one fact becomes obvious. It is not possible to define the solubility limits and dissolution behaviors of glass components in demineralized water without thoroughly describing the glass-water system, particularly with regard to its thermal history. The solubility data in this report represent values obtained under given sets of conditions, and as such they are not directly applicable to glass-water systems in general. The data presented do give an indication of the range of solution concentrations that can be expected in glass-water systems; they also point out some of the variables that effect the dissolution behavior of glass components in aqueous solutions.

One other fact becomes obvious from this work. There is a definite need to expand the solubility work to determine the species present in the aqueous solutions and to identify the solid phases that control the solubilities of the individual glass elements in the solutions under various conditions. The solubilities of some cations appear to be controlled simply by solution pH and the corresponding oxide or hydroxide solid phases. The solubilities of other cations are controlled by more complex solid phases. Until the solid phases controlling the solubilities of the individual components have been identified, it will not be possible to predict precise solubility limits for the individual elements in the waste glass-water systems under various conditions.

The data presented in this report do provide an indication of the range of solution concentrations that can be expected in waste glass-water systems. The results provide additional information on the dissolution behavior of waste glasses in water and are of use in predicting the behavior of radionuclides in a repository environment.



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