This document was prepared in conjunction with work accomplished under Contract No.
DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-81-693
ACC. NO. 139701

CC: F. E. Kruesi, Wilmington
    H. F. Ring
    S. Mirshak, SRL
    J. L. Crandall
    J. D. Spencer
    J. F. Ortaldo
    C. E. Coffey-T. H. Gould
    W. E. Stewart
    M. J. Plodinec
    R. B. Ferguson
    J. A. Stone
    N. E. Bibler
    P. D. Soper
    WMQ File
    TIS File Copy (2)

December 7, 1981

MEMORANDUM

TO: J. A. KELLEY/L. M. PAPOUCHADO

FROM: G. G. WICKS/R. M. WALLACE

GLASS DISSOLUTION MECHANISMS - PART I
MCC-1 STATIC LEACHABILITY DATA

INTRODUCTION

The leachability of glass has been studied by many different techniques. Most of the theoretical work has focused only on very simple glass systems.[1] This work has lead to the identification of two main stages of glass corrosion: (1) interdiffusion and (2) matrix dissolution. These corrosion modes alone are inadequate to fully describe leaching of the more complicated waste glass systems.

Recent work at SRL has identified a further stage of corrosion for waste glass compositions, (3) surface layer formation.[2] The formation and stability of protective surface layers are believed to be the most important factors affecting long term performance of waste glass products during permanent storage.

The primary objective of this report was to analyze a growing body of leachability data[3,4,5,6] to determine if existing concepts and models describing leachabilities of simple glasses apply to the more complex waste glass systems. Since the leachability behavior of waste glass forms failed to conform to existing models, a new model was developed based on diffusion of soluble components through the developing surface layers. While this model, called the SRL Leachability Model, does not yet completely describe all aspects of the leachability of SRP waste glasses quantitatively, it does represent the data more accurately than other existing models. This model will be improved as more data becomes available.

SUMMARY

Examination of the ratios of the concentrations of various elements in leachates and in the original four different glasses revealed that the ratios were virtually independent of time within the period from three days to twenty-eight days. However, the absolute values of elemental ratios in solution differed from the corresponding ratios in the original glasses. These observations lead to the following conclusions:

(1) The interdiffusion and matrix dissolution processes go to steady state quite rapidly at 90°C and diffusion through a surface layer is the dominant process, even in the first three days of leaching.

(2) Glasses investigated in this study corrode congruently but only part of each component enters the solution; the remainder, primarily components from the waste, precipitate and become part of the surface layer. Different fractions of the various elements originally in the glass enter the leachate and the surface layer, hence the appearance of incongruent dissolution. The surface layer may also adsorb trace components also giving rise to the appearance of incongruent dissolution.

An SRL leachability model was developed which assumes that glass corrodes congruently and the rate of corrosion is controlled by the diffusion of soluble silicates through an insoluble layer at the interface between the glass and the bulk solution. The thickness of the insoluble layer is proportional to the amount of glass that has dissolved from the start of the experiment. The silicate concentration gradient at the surface is equal to the difference between the solubility of amorphous silicate at the pH of the experiments and the concentration of silicates in the bulk leachate divided by the thickness of the layer.

The model predicts that the slope of a log concentration vs. log time plot should be 0.5 initially and theoretically approach zero as the leachate becomes saturated with silicates. A similar model for the case of matrix dissolution involving diffusion of silicates across a film of fixed thickness predicts a slope that starts at 1.0 for dilute solutions that ideally approaches zero as the solution becomes saturated.

Experimental values of the slopes in the four MCC-1 tests varied between 0.5 and 0.25. This provides a relative measurement of the reaction rate exponents. The estimated fractional saturation of silicates in these tests was only sufficient to account for slopes from 0.94 to 0.76 for the matrix dissolution model and from 0.48 to 0.41 for the surface layer model. The SRL simple surface layer model is therefore superior to the matrix dissolution model in describing these experiments, but it is still not able to account for some of the very small slopes observed.

The pH of the leachate solutions was nearly the same after three days of leaching as after twenty-eight days. This was attributed to the buffering action of silicates and borates in solution. Values of the pH calculated from the composition of the leachates and equilibrium constants found in the literature agree reasonably well with the values measured at 25°C. Values of the pH were also calculated for the 90°C case and were used together with solubility data to estimate the degree of silica saturation at that temperature.

EVALUATION OF LEACHING RESULTS

Four different waste glasses were subjected to the MCC-1 standard leach test at 90°C in distilled water with a surface area to volume of leachant ratio of $0.1cm^{-1}$. The compositions of these glasses are shown in Table 1 and the concentration of selected elements in the leachates after 3, 7, 14, and 28 days of leaching at 90°C are shown in Tables 2 through 5. Temperature dependence was also examined and will be discussed in a later report. These tables contain the raw data upon which subsequent arguments will be based.

pH of Leachates

One of the most striking features about these leaching data is that the pH of the leachates seems to have stabilized within the first three days and changed very little thereafter. If interdiffusion were the predominant process, we would expect the pH to increase in the early stages due to the increased concentration of alkali hydroxides in the leachate. This process seems to have been completed within the first three days and the

interdiffusion and matrix corrosion processes have gone to steady
state within that period.

The pH does not reach higher values because of the buffering
action of silicate and borate in the leachate. To demonstrate
this point the pH of each of the solutions at 25°C was calculated
from the composition of the solutions using methods described in
Appendix III and values of the equilibrium constants found in the
literature. These pH values, shown in Table 6, agree fairly well
with the experimental values also shown.

The values of pH in solution were not measured at 90°C, the
temperature of the leaching experiments. To evaluate the leaching
models it was necessary to know the degree of saturation of silica
in solution at the pH and temperature of the experiments. The
values of pH at 90°C for the leachate solutions were calculated
from values of the equilibrium constants found in the literature.
The silicate solubilities were then calculated from these values
of the pH and literature values of the solubility of amorphous
silica in water, using the methods described in Appendix III.
These values are also shown in Table 6.

Ratios of Elements in Leachates

Further insight into leaching mechanisms was obtained by tak-
ing the ratios of the concentrations of the various components in
the leachates. These are shown in Table 7 together with the cor-
responding ratios in the original glasses. It was surprising that
these ratios were virtually constant. If an interdiffusion and
matrix dissolution process were in operation one would expect an
initially high ratio of network modifiers (Na, K, Li) to network
formers (Si) followed by a gradual decrease in the ratio as steady
state is approached. There appears to be a slight trend of this
sort with the NBS glass but one in the reverse direction with
76-68 glass. In neither case is the variation greater than 20%.

The variations of the ratios with time are not nearly as
large as the difference between the ratio in solution and that in
the original glass, as can be seen in Table 8. Here the average
over time of each ratio is given together with the corresponding
ratios in the original glass and the quotient of the ratio in
solution divided by the ratio in the glass. A value of this
quotient greater than one implies a relative enrichment in
solution of the component in the numerator over that in the
denominator; a value less than one implies relative depletion.
Thus, in all solutions, boron and the alkali elements (Li, Na, K)
are enriched relative to silicon. With the glasses containing
waste (76-68, SRL-1 and SRL-2), the alkali elements are slightly
enriched in the leachate relative to boron while in the NBS glass

potassium was depleted relative to boron; aluminum was also depleted relative to boron in the two cases examined. Other elements such as iron and strontium were also probably depleted relative to boron and the alkali elements in the waste glasses because only very small quantities of these elements were found in the leachate. These elements, however, were not studied in detail. The quotients were nearly the same from one glass to the next among those containing waste but some of the quotients for NBS glass were significantly different from the others.

The preceeding observations are consistent with the following picture of the glass corrosion process. The process of inter-diffusion and matrix dissolution have come to steady state at 90°C long before the end of the first three day leaching period and the predominant mode of leaching involves congruent corrosion of the glass followed by diffusion of soluble components through the surface layer. As the glass reacts with water, a certain fraction of each element will enter solution and another fraction will react with other components in the system to precipitate and form an addition to the surface layer. Thus some silica will enter solution as sodium silicate while another fraction will precipitate as calcium silicate or form an alumino silicate gel. Since alkali ions and borates are less likely to form insoluble compounds than silicon, these elements will tend to be enriched relative to silicon in the leachate. This picture of the leaching process accounts for constant ratios of elements in the leachates that are markedly different from those in the original glass.

SRL Leachability Model

The preceeding observations indicate that for most of the period covered by the MCC-1 tests at 90°C, glass corrodes congruently and that insoluble surface layers are formed. It remains to be shown how these surface layers can affect the rate of leaching. We have developed a model based on simple physical principles to show one way the surface layer might affect leach rates. We realize this model is a gross oversimplification and that other factors will have to be considered later. Details of the model are given in Appendix 2; a brief description follows:

The model assumes that glass corrodes congruently and that the rate of corrosion is controlled by diffusion of soluble silicates through the insoluble layer. The thickness of the insoluble layer is proportional to the amount of glass that has corroded and hence to the total amount of dissolved silica. The silicate in solution within the layer next to the glass-layer interface is in equilibrium with amorphous silica formed on the freshly corroded glass and the rate of diffusion of the dissolved silicates away from that interface is proportional to the concentration gradient of dissolved silicates across the layer. This gradient is equal

to the difference between the equilibrium solubility of amorphous silica (Si_o) and the concentration of silica in the bulk solution (Si) divided by the thickness, ΔX, of the layer. The total amount of silica entering the solution, M_{Si}, per unit time, t, is given by the equation

$$\frac{dM_{Si}}{dt} = AD\left[\frac{(Si_o) - (Si)}{\Delta X}\right] \tag{1}$$

where A is the surface area of the glass and D is the diffusion coefficient of soluble silicates within the layer.

If the system is closed (i.e., all of the dissolved silica remains in the system) the layer thickness is proportional to the concentration of silica in solution and equation (1) reduces to

$$\frac{dy}{dt} = K\frac{(1-y)}{y} \tag{2}$$

where K is a constant and $y = (Si)/(Si_o)$.

If the initial silicate concentration is zero, equation (2) integrates to

$$\ln(1-y) + y = -Kt \tag{3}$$

One way of testing the validity of such an equation is to plot the log of the concentration in solution versus the log of the time and determine if the slope of the experimental curve agrees with that predicted by theory. The slope of the log-log plot for equation (3) is

$$\frac{d \log y}{d \log t} = \frac{t}{y}\frac{dy}{dt} = -\frac{(\ln(1-y) + y)(1-y)}{y^2} \tag{4}$$

The slope is seen only to be a function of y and is equal to 1/2 when y is zero but approaches zero as y approaches one.

Similarly, it can be shown that for simple matrix dissolution without layer formation but with saturation effects considered, the corresponding equations are

$$\frac{dy}{dt} = K(1-y) \tag{5}$$

$$\ln(1-y) = -Kt \tag{6}$$

and

$$\frac{d \log y}{d \log t} = -\frac{(\ln(1-y)(1-y)}{y} \tag{7}$$

In this case the slope of the log -log plot should be one when y is equal to zero and again approach zero as y approaches one.

Values of the slopes for both models as a function of y are given in Table 9.

Comparison of Experimental Slopes of Log-Log Plots with Theory

Table 10 contains the slopes, S, of the lines obtained when a function of the form

$$\log (C_i) = A + S \; \text{Log} \; (t)$$

was fit by least squares to the experimental leaching data in Tables 2-5. Here C_i is the concentration of the i'th component in solution, t is the time in days from the beginning of the experiment and A is a constant. Also shown are the correlation coefficients, R, which show how well the data were fit by the equation.

All of the slopes are less than 0.5 and far less than the value of 1.0 one would expect for a simple matrix dissolution model. To see how well these slopes correspond to those predicted by the layer the matrix dissolution model, the average values of the slopes for those elements for which the correlation coefficient were 0.95 or greater was taken for each glass. These are shown in Table 11 together with the maximum degree of saturation calculated for each of the glasses as described in the previous section. The average slopes are to be compared with those predicted by the two models at that value of the saturation.

Table 11 shows that the surface layer model gives a better representation of the data than the matrix dissolution model, a model that severely overpredicts dissolution of waste glass systems. However, the agreement with experiment is far from perfect. It is possible that the equilibrium constants used for the calculation of silica saturation at 90°C are in error. This is now being assessed. It is more likely that the simple surface layer model needs refinement before it can adequately describe quantitative leaching behavior.

REFERENCES

1. D. E. Clark, C. G. Pantino and L. L. Hench, <u>Corrosion of Glass</u>, Books for the Glass Industry (1979).

2. G. G. Wicks, W. C. Mosley, P. G. Whitkop and K. A. Saturday, "Durability of Simulated Waste Glass - Effects of Pressure and Formation of Surface Layers," DP-MS-81-25, presented at the 6th University Series on Glass Science, University Park, Pennsylvania, July 29-31, 1981. To be published in Journal of Non-Crystalline Solids.

3. G. G. Wicks, Round Robin Leachability Tests of NBS and 76-68 Glasses Using MCC-1, submitted to J. E. Mendel of Battelle Pacific Northwest Laboratory, February, 1981.

4. G. G. Wicks, MCC-1 Static Leach Tests of High Silica SRL Waste Glass, for the Hench Peer Review Meeting Assessing Alternative Waste Forms, May, 1981.

5. G. G. Wicks, MCC-1 and MCC-2 Static Leach Tests of Doped SRL TDS/131 Waste Glass, submitted to D. E. Gordon for the IWG Assessment of Alternative Waste Forms, July, 1981.

6. G. G. Wicks, "Leachability of Simulated SRP Waste Glass, MCC-1 and MCC-2 Static Leach Tests - Part I," DPST-81-653, September, 1981.

7. "Stability Constants," p. 145, Chemical Society, London, 1964, Special Publication No. 17.

8. Ibid, p.105.

9. H. S. Harned and B. B. Owen, " The Physical Chemistry of Electrolytic Solutions," p. 645, Reinhold, New York, 1958.

10. Link-Seidel, "Solubility of Inorganic and Metal Organic".

TABLE 1

Glass and Waste Glass Compositions Used in MCC-1 Static Leach Tests

Compound	Glass System			
	NBS[a]	76-68[b]	SRL-1[c]	SRL-2[d]
Rb_2O		0.13		
SrO		.40	.02	0.1
Y_2O_3		.23		
ZrO_2		1.88	ND	ND
MoO_3		2.42		
CdO		.04		
Cs_2O		1.09	.04	0.3
BaO		0.49		
La_2O_3		.56		
CeO_2		1.26		0.1
Pr_6O_{11}		.56		
Nd_2O_3		4.56	ND	0.7
Sm_2O_3		0.35		
Eu_2O_3		.10		
Gd_2O_3		.05		
Fe_2O_3		10.34	12.6	13.8
Cr_2O_3		0.44		
NiO		.21	1.43	
P_2O_5		.51		
CaO		2.00	1.06	
ZnO		4.97		
TiO_2		2.97	ND	ND

TABLE 1 (Continued)

Compound	Glass System			
	NBS [a]	76-68 [b]	SRL-1 [c]	SRL-2 [d]
Na_2O	1.0	12.80	12.3	13.5
SiO_2	70.0	39.80	52.8	44.8
B_2O_3	17.0	9.47	10.4	9.9
K_2O	8.0			
Li_2O_3	1.0		3.79	ND
Al_2O_3	3.0		5.91	2.6
MnO_2			3.29	4.3
MgO			0.38	ND
La_2O_3			0.4	ND
U_3O_8				0.6

[a] NBS glass contains no waste - analyses supplied by vendor.

[b] 76-68 is commercial waste glass - analyses from batch makeup by PNL.

[c] SRL-1 is high silica S. R. defense waste - analyses of solidified product by AA and IC.

[d] SRL-2 is actinide doped S. R. defense waste - analyses of solidified product by ICP, AA and IC.

TABLE 2

Concentration of Selected Elements in Leachate at 90°C
(MCC-1 Standard Leach Tests)

Leach Time Days		NBS Glass (No Waste) Si	B	Na	K	Al	pH
3	mg/l	44.6	16.7	2.66	15.3	1.29	8.50
	M	1.59E-3	1.54E-3	1.66E-4	3.90E-4	4.77E-5	
7	mg/l	48.5	17.1	2.16	16.2	2.21	8.45
	M	1.73E-3	1.58E-3	9.39E-5	4.14E-4	8.19E-5	
14	mg/l	73.0	24.7	2.12	21.9	2.02	8.46
	M	2.60E-3	2.29E-3	9.21E-5	5.60E-4	7.48E-5	
28	mg/l	80.9	28.2	3.28	24.1	1.85	8.64
	M	2.80E-3	2.61E-3	1.42E-4	6.17E-4	6.85E-5	

TABLE 3

Concentration of Selected Elements in Leachate at 90°C
(MCC-1 Standard Leach Tests)

Leach Time Days		76-68 Waste Glass Si	B	Na	Cs	pH
3	mg/l	24.6	4.90	17.3	.33	9.23
	M	8.76E-4	4.53E-4	7.52E-4		
7	mg/l	36.8	7.53	28.1	.24	9.29
	M	1.31E-3	6.96E-4	1.22E-3		
14	mg/l	46.5	10.3	36.8	.43	9.39
	M	1.65E-3	9.53E-4	1.60E-3		
28	mg/l	61.5	14.3	53.9	.63	9.56
	M	2.19E-3	1.32E-3	2.34E-3		

TABLE 4

Concentration of Selected Elements in Leachate at 90°C
(MCC-1 Standard Leach Tests)

Leach Time Days		SRL-1 Waste Glass Si	B	Na	Li	Al	pH
3	mg/l	21.7	4.12	13.1	2.52	2.32	9.38
	M	7.73E-4	3.81E-4	5.69E-4	3.63E-4	8.59E-5	
7	mg/l	29.3	5.65	16.9	3.27	2.89	9.49
	M	1.04E-3	5.23E-4	7.34E-4	4.71E-4	1.07E-4	
14	mg/l	36.8	7.23	21.9	4.35	3.09	9.54
	M	1.31E-3	6.69E-4	9.53E-4	6.27E-4	1.44E-4	
28	mg/l	40.2	7.70	24.5	(4.85)*	4.52	9.61
	M	1.43E-3	7.12E-4	1.06E-3	(6.99E-4)*	1.67E-4	

*Estimated.

TABLE 5

Concentration of Selected Elements in Leachate at 90°C
(MCC-1 Standard Leach Tests)

Leach Time Days		SRL-2 Waste Glass Si	B	Na	Cs	pH
3	mg/l	26.6	5.18	22.8	.54	10.52
	M	9.48E-4	4.79E-4	9.90E-4		
7	mg/l	31.4	6.26	22.6	.59	9.87
	M	1.12E-3	5.79E-3	9.84E-4		
14	mg/l	45.4	9.46	36.7	.55	10.01
	M	1.62E-3	8.75E-4	1.59E-3		
28	mg/l	56.3	12.4	38.3	.59	10.10
	M	2.00E-3	1.15E-3	1.66E-3		

TABLE 6

pH & Solubility in Leachate Solutions

Time Days	pH 25°C[a] obs	pH 25°C calc	pH 90°C calc	(Si_o) 90°C[b] calc M	$(Si)/(Si_o)$ 90°C[c]
			NBS Glass		
3	8.50	8.63	8.09	.0072	.22
7	8.45	8.61	8.07	.0071	.24
14	8.46	8.55	8.01	.0071	.37
28	8.64	8.57	8.01	.0071	.41
			76-68 Waste Glass		
3	9.23	9.48	8.72	.0095	.092
7	9.29	9.57	8.82	.0103	.13
14	9.39	9.58	8.86	.0108	.15
28	9.56	9.68	8.85	.0107	.20
			SRL-1 Waste Glass		
3	9.36	9.89	8.91	.0113	.068
7	9.49	9.84	8.94	.0117	.089
14	9.54	9.90	9.00	.0126	.10
28	9.61	9.95	9.04	.0132	.11
			SRL-2 Waste Glass		
3	10.52	9.70	8.85	.0106	.089
7	9.87	9.51	8.77	.0099	.113
14	10.01	9.62	8.88	.0110	.147
28	10.10	9.43	8.77	.0099	.20

---

[a] All pH measurements of leachates taken after solutions cooled from 90°C to 25°C.

[b] (Si_o)(90°C) denotes saturation of amorphous silica in solution of given pH.

[c] Denotes ratio of silicon in leachate to saturated silica solution for given pH.

TABLE 7

Observed Elemental Ratios in Leachates and Original Glasses

Atomic Ratios

Leach Time Days	(Na,K)/B	(Na,K)/Si	B/Si	Al/B	Na/Li
		NBS Glass			
Original Glass	.348 (K)	.146 (K)	.419	1.20	
3	.253	.245	.969	.0310	
7	.262	.241	.919	.0518	
14	.245	.210	.881	.0327	
28	.236	.214	.906	.0262	
		76-68 Waste Glass			
Original Glass	1.52 (Na)	.624 (Na)	.411		
3	1.66	.858	.517		
7	1.75	.931	.531		
14	1.67	.970	.578		
28	1.77	1.068	.603		
		SRL-1 Waste Glass			
Original Glass	1.33 (Na)	.452 (Na)	.340	.388	1.56
3	1.49	.736	.492	.225	1.57
7	1.40	.706	.503	.205	1.55
14	1.42	.727	.511	.215	1.52
28	1.49	.741	.499	.235	--
		SRL-2 Waste Glass			
Original Glass	1.53 (Na)	.583 (Na)	.381		
3	2.06	1.04	.505		
7	1.70	0.88	.517		
14	1.82	0.98	.540		
28	1.44	0.83	.575		

TABLE 8

Summary of Elemental Ratios

	NBS Glass	76-68 Waste Glass	SRL-1 Waste Glass	SRL-2 Waste Glass
[(K,Na)/B] L	.249 ± .011 (K)	1.71 ± .056 (Na)	1.45 ± .047 (Na)	1.76 ± .26 (Na)
[(K,Na)/B] G	.348	1.52	1.33	1.53
L/G	.714	1.13	1.09	1.15
[(K,Na)/Si] L	.228 ± .018 (K)	.957 ± .087 (Na)	.728 ± .015 (Na)	.933 ± .095 (Na)
[(K,Na)/Si] G	.146	.624	.452	.583
L/G	1.56	1.53	1.61	1.60
[B/Si] L	.919 ± .037	.557 ± .040	.502 ± .007	.545 ± .024
[B/Si] G	.419	.411	.340	.381
L/G	2.19	1.35	1.48	1.43
[Na/Li] L			1.55 ± .02	
[Na/Li] G			1.56	
L/G			1.00	
[Al/B] L	.0354 ± .011		.220 ± .013	
[Al/B] G	.120		.388	
L/G	.295		.763	

L = Leachate
G = Glass

TABLE 9

Slopes of Log y Vs. Log t Plot as a Function of y

| y* | dlny/dlnt** | |
	Surface Layer	Matrix Dissolution
0	0.50	1.0
0.1	0.48	.94
0.2	0.46	.89
0.3	0.44	.83
0.4	0.42	.77
0.5	0.39	.69
0.6	0.35	.61
0.7	0.31	.51
0.8	0.25	.40
0.9	0.17	.26
1.0	0.00	0.00

---

*y represents the degree of silica saturation in solution
(Si/S_{io}).

**$\frac{dlny}{dlnt}$ represents a reaction rate parameter for a Stage 3
corrosion process (Surface Layer Formation) and for a Stage
2 process (Matrix Dissolution).

TABLE 10

Slopes of Log Concentration Vs. Log Time Plots

	Si	B	Na	K or Li	Al	Cs
			NBS Glass			
S	0.294	0.258	0.074	0.223 (K)	0.144	--
R	0.953	0.939	0.345	0.955	0.585	--
			76-68 Waste Glass			
S	0.405	0.477	0.499			0.327
R	0.997	0.999	0.997			0.765
			SRL-1 Waste Glass			
S	0.283	0.290	0.290	0.305 (Li)	0.278	
R	0.983	0.975	0.991	0.989	0.958	
			SRL-2 Waste Glass			
S	0.351	0.407	0.272			0.027
R	0.984	0.985	0.896			0.565

S = Slope.
R = Correlation coefficient.

TABLE 11

Comparison of Experimental Slopes With Those Predicted by Models

| Glass | $y = Si/Si_o$ | Slope Observed | Calculated Slope | |
			Layer Model	Matrix Dissolution
NBS Glass	.41	.26	.41	.76
76-68 Waste Glass	.20	.46	.46	.89
SRL-1 Waste Glass	.11	.29	.48	.94
SRL-2 Waste Glass	.20	.38	.46	.89

STAGES OF CORROSION OF WASTE GLASS FORMS

The leachability of SRP waste glass forms can be described in three stage processes; interdiffusion, matrix dissolution and surface layer formation.

Stage 1 - Interdiffusion

Interdiffusional processes dominate the early stages of glass corrosion. Network modifiers such as sodium and potassium, diffuse out of the glass during leaching into solution while water from the leachant diffuses into the glass at the same time. This results in a modifier deficient or silica enriched surface layer. Mathematical analysis of this process leads to the conclusion that the concentration of diffusing species in the leachate should increase as the square root of the time, a conclusion verified experimentally for simple glass. During this time period the pH of the leachant increases due to formation of alkali hydroxides in solution.

Stage 2 - Matrix Dissolution

This process is expected to dominate at intermediate leaching times. The dissolution rate is governed by the pH of the leachate which determines the solubility of amorphous silica. The glass dissolution rate may be controlled simply by the rate at which the silica in a saturated solution near the surface can diffuse away from the glass into the bulk solution; it is possible, however, that hydroxide ions might directly affect the rate of reaction between silica and water. If the composition of the solution were to remain constant, the rate of dissolution of the matrix would also be expected to remain constant and the concentration of network formers in solution, such as silicon, would increase linearly with the first power of the time. This dependence has been observed in simple glass systems. In a closed system, where the products of leaching are allowed to accumulate, the dissolution rate is expected to increase as the pH increases but slow down later as the solution becomes saturated with silicates. After a sufficiently long time, the rate of the diffusional processes should be equal to the rate of dissolution (steady state) and congruent dissolution should result if only the two processes are involved.

Stage 3 - Surface Layer Formation

During intermediate and long time periods surface layers can form on waste glass forms[2] resulting from the precipitation of insoluble compounds on the glass surface. These layers may contain compounds such as ferric hydroxide, manganese dioxide or calcium silicate. The existence of similar layers on the surface of even simple glasses has been conjectured[1] to affect the leachability of glass but no detailed formulation of how these layers should affect the leach rate has yet been made.

APPENDIX II

PROPOSED KINETIC MODEL FOR DISSOLUTION OF SRP WASTE GLASS

SRL Leachability Model - First Cut

Assumptions

The following assumptions were made in developing a model to explain leaching of SRP waste glass forms:

(1) Steady state has been attained with respect to the first two processes so that glass corrodes congruently at the beginning of this process.

(2) The surface of the glass at the start consists principally of amorphous silica that is in equilibria with dissolved silica at the interface.

(3) The rate of corrosion of the glass is controlled by the rate at which dissolved silica can diffuse through a layer of insoluble material precipitated on the surface between the glass and the bulk solution.

(4) The amount of materials in the surface layer and hence its thickness will depend on the amount of glass that has corroded from the start of the experiment up to any arbitrary time t.

Derivation of Diffusion of Soluble Species Through Surface Layers of SRP Waste Glass Forms - Stage 3 Corrosion

Schematic Representation of Leaching of SRP Waste Glass Forms
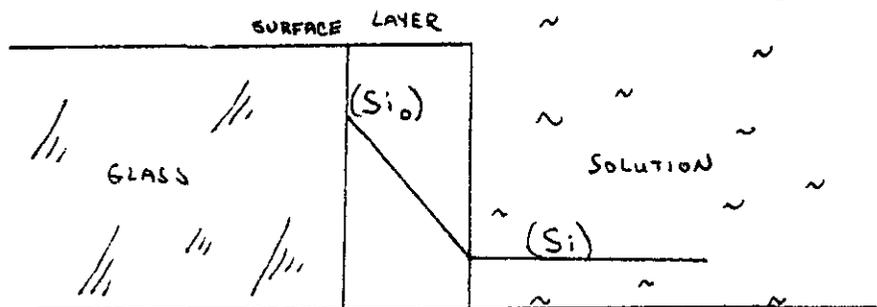
The above diagram shows a developing surface layer of thickness ΔX between the uncorroded glass and the bulk solution. The concentration of silica in solution at the interface of the glass and the surface layer is (S_{io}), the solubility of silica in the aqueous medium. (S_i) is the concentration of silica dissolved in the aqueous medium at time t. The rate at which silica diffuses through the layer is given by

$$\frac{dM_{Si}}{dt} = \frac{AD[(S_{io}) - (S_i)]}{\Delta X} \tag{1A}$$

where D is the diffusion coefficient of dissolved silica within the layer, A is the surface area, and M_{Si} is the amount of silica in solution at time, t.

If G is the amount of glass that has corroded in a given period of time and M_{Si} is the amount of silica to enter solution in the same period

$$M_{Si} = f_{Si}G \qquad (2A)$$

where f_{Si} is a fraction of silica in the glass that ultimately resides in the aqueous medium. This may be less than the fraction of silica in the glass because some of the silica may precipitate onto or within the surface layer. If M_I is the amount of insoluble material generated in the same time period, then:

$$M_I = f_I G \qquad (3A)$$

$$M_I = \frac{f_I}{f_{Si}} M_{Si} \qquad (4A)$$

where f_I is the fraction of the glass that will produce insoluble matter.

If A is the area of the surface layer and ρ is its density and Q is a factor to account for the increased mass of the insoluble components after reacting with water, then

$$M_I = A\rho Q(\Delta X) \qquad (5A)$$

Combining equations (4A) and (5A) and solving for X

$$\Delta X = \frac{f_I}{f_{Si}} \frac{M_{Si}}{A\rho Q} = \frac{f_I}{f_{Si}} \frac{V}{A\rho Q} (S_i) \qquad (6A)$$

where V is the volume of the leachate.

Substitution of equation (6) into equation (1A) yields

$$d\frac{(Si)}{dt} = \left(\frac{A}{V}\right)^2 \frac{f_{Si}}{f_I} \rho QD \frac{[(S_{io}) - (S_i)]}{(S_i)} \qquad (7A)$$

Let $K \equiv \left(\frac{A}{V}\right)^2 \frac{f_{Si}}{f_I} \frac{\rho QD}{(S_{io})}$ and $y \quad \frac{(S_i)}{(S_{io})}$

then

$$\frac{dy}{dt} = \frac{K(1-y)}{y} \qquad (8A)$$

which if $y = 0$ when $t = 0$ intergrates to

$$-\ln(1-y) - y = Kt \tag{9A}$$

for small values of y equation (9A) behaves as

$$y^2/2 = Kt$$

$$\text{or } y = (2Kt)^{1/2}$$

and as y approaches 1 the rate of dissolution approaches zero.

It is often convenient to represent leach data by plotting the log of the amount of material leached versus the log of the time. Thus, if the amount of material leached can be represented by the general function $y = Kt^{\alpha}$ the slope of such a plot will be α. For a simple Stage 1 diffusion this will be 1/2 and for a simple Stage 2 process α will be 1. The slope of such a plot for the process represented by equation (9A) can be derived as follows and represents the Stage 3 process:

$$\text{Since } \frac{d\ln y}{d\ln t} = \frac{dy}{dt} \frac{d\ln y}{dy} \bigg/ \frac{d\ln t}{dt} = \frac{t}{y} \frac{dy}{dt}$$

$$\frac{d\ln y}{d\ln t} = \frac{(-\ln(1-y)-y)(1-y)}{y^2} \tag{10A}$$

The slope of the plot is a function only of y, the degree of saturation, and varies between 1/2 and 0.

Matrix Dissolution - Stage 2 Corrosion

It is also possible to treat in a similar manner the dissolution of the matrix in process 2 by considering diffusion through a surface film in solution but here the thickness of the surface layer does not grow with time. The differential equation has the form

$$\frac{dy}{dt} = K(1-y) \tag{11A}$$

With the solution

$$\ln(1-y) = -Kt \tag{12A}$$

$$\text{and } \frac{d\ln y}{d\ln t} = \frac{[-\ln(1-y)](1-y)}{y} \tag{13A}$$

This function is 1 when y is zero and approaches 0 as y approaches 1.

Values of the slopes of these plots for both the surface layer model (equation 10A) and the matrix dissolution model (equation 13A) are shown in Table 9.

## CALCULATION OF LEACHATE pH VALUES AND SILICA SOLUBILITY OF SRP WASTE GLASS FORMS

The following equilibria were considered in estimating the pH and equilibrium solubility of silica in leachate solutions from their chemical composition:
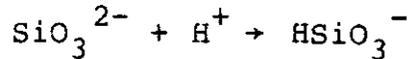
$$SiO_3^{2-} + H^+ \rightarrow HSiO_3^-$$

$$K_{1S} = \frac{(HSiO_3^-)}{(SiO_3^{2-})(H^+)} \tag{14A}$$

$$SiO_3^{2-} + 2H^+ \rightarrow H_2SiO_3$$

$$\beta_{2S} = \frac{(H_2SiO_3)}{(SiO_3^{2-})(H^+)^2} \tag{15A}$$

$$SiO_2 \text{ (amorphous)} + H_2O \rightarrow H_2SiO_3$$

$$K_{Sol} = (H_2SiO_3) \tag{16A}$$

$$B(OH)_4^- + H^+ \rightarrow B(OH)_3 + H_2O$$

$$K_B = \frac{(B(OH)_3)}{(B(OH)_4^-)(H^+)} \tag{17A}$$

$$H_2O \rightarrow H^+ + OH^-$$
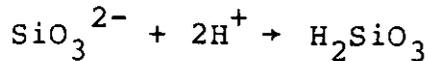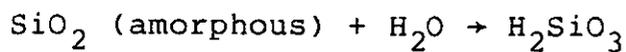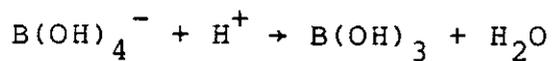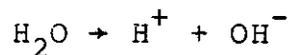
$$K_W = (H^+)(OH^-) \tag{18A}$$

Mass balance on silicate species yields

$$(Si_t) = (SiO_3^{2-}) + (HSiO_3^-) + (H_2SiO_3) \tag{19A}$$

where (Si_t) is the total silicate concentration in solution.

Combining equations (14A) and 15A) with (19A)

$$(Si_t) = (SiO_3^{2-})[1 + K_{1S}(H^+) + \beta_{2S}(H)^2] \tag{20A}$$

Let $Q_S \equiv [1 + K_{1S}(H) + \beta_{2S}(H)^2]$

then $(SiO_3^{2-}) = \dfrac{(Si_t)}{Q_S}$ (21A)

$$(HSiO_3^-) = \dfrac{K_{1S}(H)(Si_t)}{Q_S} \tag{22A}$$

$$(H_2SiO_3) = \dfrac{\beta_{2S}(H)^2(Si_t)}{Q_S} \tag{23A}$$

Mass balance on boron species

$$(B_t) = (B(OH)_3) + (B(OH)_4^-) \tag{24A}$$

$$(B_t) = (B(OH)_4^-)[1 + K_B(H)] \tag{25A}$$

Let $Q_B \equiv [1 + K_B(H)]$

then $(B(OH)_4^-) = \dfrac{(B_t)}{Q_B}$ (26A)

$$(B(OH)_3) = \dfrac{K_B(H)(B_t)}{Q_B} \tag{27A}$$

Charge balance in solution yields

$$(H^+) + \Sigma_i C_i Z_i = (B(OH)_4^-) + 2(SiO_3^{2-}) + (HSiO_3^-) + (OH^-) \quad (28A)$$

where C_i is the concentration of the i'th cation in solution and Z_i is its charge combining equations (18A), (21A), (22A), (26A) and (28A)

$$-\left((H) + \sum_i \bar{z}_i C_i Z_i\right) + \frac{(B_t)}{Q_B} + \frac{(S_{it})}{Q_S}(2 + K_{1S}(H)) + \frac{K_W}{(H)} = 0 \quad (29A)$$

the equilibrium pH of the solution will be found by solving equation (29A) for (H). Since it is a fifth order equation in (H) it is most easily solved numerically.

We know at the outset the solution lies somewhere between pH 0 and pH 14. We can then set these values as limits, take the average and substitute the corresponding value (H) into (29A). If the result is a positive number the average pH was too high and may be substituted as a new upper limit; if the result is negative, the pH chosen was too low and may be substituted as a new lower limit. The procedure is then repeated successively until the desired accuracy is obtained. Twelve iterations are sufficient to reduce the error to less than 0.01 pH units.

When the pH is known the equilibrium solubility of silica may be determined by combining equations (16A) and (23A).

$$(S_{it}) = \frac{K_{Sol}Q_S}{\beta_{2S}(H)^2} \quad (30A)$$

Equation (30A) is the basis for theoretically predicting silica saturation as a function of solution pH. The calculated values at 90°C are shown in Table 6. These data become important in determining the degree of saturation of silica in solution during leaching.

The following constants were used to make the numerical calculations:

T	Log K_{1S}	Log β_{2S}	Log K_B	Log K_W	K_{SOL}
25°C	11.77	21.28	9.24	-14.00	0.0012M
90°C	9.90	18.98	8.62	-12.42	0.0065M
Reference	(7)	(7)	(8)	(9)	(10)