

THE BEHAVIOR OF DEFENSE WASTE REFERENCE GLASS
IN A LONG-TERM PULSED-FLOW LEACH TEST

Aa. Barkatt, P. B. Macedo, B. C. Gibson,
R. Mowad, W. Sousanpour, Al. Barkatt,
M. A. Boroomand, M. Adel-Hadadi and V. L. Rogers
The Vitreous State Laboratory
The Catholic University of America
Washington, D.C. 20064

ABSTRACT

The results of 17-month pulsed-flow tests on Defense Waste Reference Glass in de-ionized water and in ground-water confirm and validate mechanistic conclusions and predictions previously proposed on the basis of short-term data. The results show that even at 90°C the dissolution rates of this glass are below 1×10^{-5} yr⁻¹ if the flow rate does not considerably exceed 0.1 m/yr. A simple kinetic model for the mathematical analysis of the dissolution kinetics and steady-state leachate compositions in flowing water, previously used for data obtained with another glass, is found to be applicable for the present results.

INTRODUCTION

A pulsed-flow test method was developed^{1,2} to obtain data on the leach behavior of nuclear waste forms under slow-flow conditions similar to those considered most likely to prevail in geologic repositories. Previously reported data included both short-term and long-term results on Savannah River Laboratory (SRL) TDS-131 defense waste borosilicate glass^{1,2} as well as short-term results on the Materials Characterization Center Defense Waste Reference Glass (DWRG), which is generically similar to SRL TDS-165 glass².

This paper presents results from the long-term use of the pulsed-flow test method on DWRG and discusses their implications in the prediction of release rates from glass exposed to slowly flowing aqueous media.

EXPERIMENTAL METHODS

The partial-exchange pulsed-flow test has been documented elsewhere¹. Briefly, monolithic or powdered samples are leached in a volume of leachant (usually 100 mL) inside a gas-tight polytetrafluoroethylene vessel with a septum cap. A constant fraction (usually 25%) of the leachant is removed at fixed intervals (usually 1, 7 or 28 days) by means of a syringe and replaced with fresh leachant. The test continues until the concentrations of leached species become constant within experimental error. This generally requires the total exchanged volume to reach 3-4 times the leach volume (usually this means at least 12-16 exchanges). Furthermore, in order for the effective release rates of the various glass components to stabilize and for the resulting leachate composition to become independent of time, the total time has to be sufficient for completion of the build-up of the surface layers and for approach to steady-state with respect to the interaction between the surface solid and the aqueous phase. These conditions require total test times of at least 11-15 months at relatively high temperatures (70-90°C) and significantly longer times at lower temperatures, where surface alteration processes are much slower. The tests are carried out at several different surface-to-volume (S/V) ratios (usually between 10-2000 m⁻¹) and the results are scaled to a particular S/V ratio to provide data about leach behavior

over a range of effective contact times or flow rates¹ considered applicable to repository conditions.

In addition to the flow tests described above, a few static tests were carried out on powdered glasses. A modified MCC-3S powder leach test procedure³ was used^{2,4}. Large amounts (5-10 g) of powdered glass of a medium fine mesh size (usually -60 + 120 mesh) were leached in small volumes of aqueous leachant (14-40 mL) inside polytetrafluoroethylene vessels smaller than but otherwise similar to those employed in the flow tests. Leachate samples were removed for analysis at long intervals (3-12 months), but in this case fresh leachant was not added.

Both the flow tests and the static powder tests were carried out using de-ionized water and synthetic basalt ground-water^{2,5} as leachants. Rectangular slices of ductile iron² were added in several flow tests. The tests were carried out at temperatures of 70°C and, in most cases, 90°C. Each test was carried out in duplicate or in triplicate.

RESULTS

The results of leachate analyses from flow tests carried out with various S/V ratios at 90°C on Defense Waste Reference Glass in de-ionized water and in ground-water are shown in Tables I and II, respectively. The sampling and leachant exchange interval is 28 days, corresponding to an experimental contact time, $(T_r)_{exp}$, of 112 days since the fraction of leachate exchanged at the end of each sampling interval is 0.25 of the total volume of 100 mL. The total time of exposure has now reached 17 months. Tables I and II complement the short-term data given in Tables 1.10 and 1.11 of Ref. 2.

The results shown in Table I indicate that in de-ionized water an increase in contact time from 28 days to 112 days results in a very mild increase in leachate concentrations. Furthermore, the pH levels no longer rise. The increase in leachate concentrations resulting from the increase in contact time by a factor of 4 does not exceed 50% even in the cases of the most leachable species (Na, Li, B). The increase is even smaller in the cases of less soluble elements (Si, U) and an actual decrease in leachate

TABLE I

Results of Long-term Dynamic Leach Tests on DWRG in De-ionized Water at 90°C

S/V m ⁻¹	T _r days	Block/ Powder	pH	Si	B	Leachate Concentration, mg/L							
						Na	Li	Cs	Sr	Ca	Al	Fe	U
10.7	4	B	9.04	3.67	0.40	1.25	0.38	0.14	0.031	0.12	0.36	0.05	0.05
30.4	8	B	9.40	11.3	1.48	4.45	1.44	0.35	0.057	0.27	1.26	0.02	0.11
80.9	4	B	9.67	20.7	2.77	8.37	2.24	0.69	0.048	0.22	2.19	0.11	0.29
88.0 ^a	4	B	9.84	19.6	3.16	9.57	2.78	0.84	0.035	0.14	1.59	0.17	0.09
157	4	B ^b	9.46	18.0	2.45	11.6	2.20	0.79	0.031	0.13	1.72	0.12	0.13
266	4	B	9.87	31.2	4.63	13.8	4.14	1.12	0.039	0.17	3.39	0.29	0.81
291	4	P	9.77	22.8	3.14	9.82	2.82	0.76	0.047	0.20	2.52	0.23	0.73
970	4	P	9.83	28.4	4.12	13.8	3.86	0.87	0.048	0.19	3.09	0.36	0.67
1940	4	P	9.91	30.6	4.63	14.6	4.38	0.93	0.051	0.20	3.33	0.46	0.86
10.7	28	B	9.05	12.1	1.28	3.38	1.26	0.25	0.11	0.46	0.79	0.06	0.21
80.9	28	B	9.70	29.4	3.64	8.68	3.43	0.67	0.065	0.32	2.25	0.15	0.52
88.0 ^a	28	B	10.4	28.7	6.94	16.1	6.19	0.77	0.032	0.14	1.96	0.17	0.69
157	28	B ^b	9.58	33.1	4.25	11.6	7.75	0.46	0.73	0.35	2.42	0.48	0.83
266	28	B	10.0	50.1	6.90	15.3	6.22	0.78	0.072	0.27	4.05	0.39	0.88
291	28	P	10.0	48.0	6.74	15.2	6.16	0.82	0.084	0.29	3.87	0.37	1.02
970	28	P	10.3	67.2	11.5	24.5	9.73	0.80	0.059	0.21	4.64	0.25	1.23
1940	28	P	10.3	72.0	12.9	29.7	11.9	0.87	0.061	0.25	4.69	0.66	1.45
10.7	112	B	8.10	14.5	1.53	4.22	1.44	0.33	0.29	0.97	0.62	0.88	0.59
80.9	112	B	9.18	30.2	4.05	12.1	3.89	0.82	0.077	0.34	1.92	0.09	0.61
88.0 ^a	112	B	10.2	44.6	11.4	36.1	10.3	0.92	0.034	0.14	3.30	0.30	1.27
157	112	B ^b	8.97	41.5	6.03	16.4	5.34	0.65	0.16	0.57	2.06	2.16	0.48
266	112	B	9.68	49.7	8.07	23.3	8.18	0.70	0.020	0.11	3.08	0.06	1.04
291	112	P	9.80	51.9	8.33	24.2	8.12	0.78	0.037	0.11	3.31	0.10	0.98
970	112	P	10.1	70.8	13.1	38.5	13.1	0.69	0.004	0.04	4.16	0.20	1.32
1940	112	P	10.1	77.6	15.4	46.0	16.1	0.77	0.019	0.09	4.11	0.33	1.70

^aIron present; S_{Fe}/S_{glass} = 1.79^bHighly polished (3200-grit equivalent; in all other cases, 360- to 600-grit equivalent)

TABLE II

Results of Long-term Dynamic Leach Tests on DWRG in Ground-water at 90°C^a

S/V m ⁻¹	T _r days	S _{Fe} / S _{glass}	pH	Si	B	Leachate Concentration, mg/L							
						Na	Li	Cs	Sr	Ca	Al	Fe	U
0.0 ^b			9.71	35.0	-0.01	324	0.01	-0.03	-0.005	3.72	0.01	-0.02	0.00
10.5	112	0.00	8.77	40.4	0.55	382	0.48	-0.09	0.120	4.60	0.47	0.06	0.65
10.3	112	2.55	11.1	24.6	7.51	375	6.23	1.42	0.043	0.69	2.36	0.40	0.19
91.3	112	0.00	8.80	39.4	0.89	339	1.01	0.16	0.219	4.12	0.46	-0.01	0.55
92.0	112	1.71	11.2	88.8	41.0	430	33.7	1.41	0.642	3.02	3.96	9.23	1.14
224	112	0.00	8.89	42.4	1.49	360	1.95	0.30	0.323	4.27	0.57	0.01	1.04

^aBlock samples^bPure synthetic ground-water prepared according to Ref. 5

concentrations with increasing contact time is observed in the cases of Cs, Al, Ca and Sr. Only in tests carried out at the lowest S/V ratios (corresponding to the highest equivalent flow rates) is a significant increase in the concentrations of all leached species observed upon increasing the contact time from 28 days to 112 days.

The results observed in ground-water in the absence of iron indicate that increases in leachate concentrations with increasing contact time are generally smaller than the corresponding increases in de-ionized water (except in the cases of U and Sr) and are significant only for the smallest S/V values. On the other hand, in the presence of ductile iron, leachate concentrations with respect to the soluble species continue to rise by a factor of approximately 3 when the contact time is increased by a factor of 4. Accordingly, the effect of ductile iron in raising the leachate concentrations and the corresponding leach rates increases with increasing contact time. For instance, when the S/V ratio is 10.4 m^{-1} and $(T_r)_{\text{exp}}$ is 4 days (corresponding to an equivalent flow rate, f , of 317 m/yr according to Ref. 1) the presence of ductile iron causes an increase by a factor of 2.36 in boron concentration; when S/V is 92 m^{-1} and $(T_r)_{\text{exp}}$ is 112 days ($f = 1.28 \text{ m/yr}$) the presence of iron results in an increase by a factor of 46.1 in boron concentration.

DISCUSSION

The results of the flow tests at long contact times are in complete agreement with the predictions of the model described in Ref. 2, which was based on results obtained at much shorter contact times. Accordingly, the new set of results may be concluded to support and validate this model, at least for time scales which can be studied in laboratory experiments. In more detail, the results obtained in de-ionized water at long contact times show that as the contact time increases, effects of saturation become progressively more significant, the increase in leachate concentrations becomes less pronounced and the effective leach rates decrease. These effects are less marked in the case of DWRG than in the case of the more alkaline TDS-131 glass. This observation agrees with the finding that the appearance of well-defined surface alteration products is more pronounced in the case of TDS-131 under similar conditions of exposure². This is probably due to the higher pH and the higher solute concentrations in the TDS-131 leachates.

In the case of ground-water, the presence of relatively high levels of silica in the leachant itself accelerates the alteration process and the onset of saturation with respect to the alteration products². The additional data now obtained at long contact times are in agreement with this picture since they show that at similar contact time and S/V ratio the leach rates observed in ground-water are much lower than those observed in de-ionized water. For instance, when $(T_r)_{\text{exp}} = 112$ days and $S/V = 266 \text{ m}^{-1}$ (in de-ionized water) or 224 m^{-1} (in ground-water) the concentration of Si observed in the ground-water leachate (42 mg/L) is only slightly below the one observed in de-ionized water (50 mg/L). However, the leachate concentrations of B and Li, which reflect the effective release rates of these soluble species, are lower by factors of 4-5 in ground-water. This is presumably due to the formation of an altered surface layer which restricts the migration of even highly soluble glass components into the aqueous phase². The long-contact-time data provide a further indication in support of a model

assuming the build-up of a dense, relatively insoluble altered layer when leachate concentrations reach high levels. While the absolute concentrations of most glass components in the leachate increase with increasing contact time or S/V ratio and finally level off, the concentration of Al sharply falls off. For instance, at an S/V ratio of 224 m^{-1} , the steady-state Al concentration decreases from a value of 1.51 mg/L when $(T_r)_{\text{exp}} = 4$ days to 1.17 mg/L at 28 days and to 0.57 mg/L at 112 days (see Table II and Ref. 2). This decrease in Al concentrations, together with a corresponding slight decrease in Si levels, indicates that aluminosilicate species have a significant contribution to the composition of the altered layer, in agreement with previous findings based on solution chemistry as well as surface analysis².

The present data confirm the conclusion that the leach rate of U relative to that of the soluble glass components is much higher in ground-water than in de-ionized water, probably due to the presence of complexing anions (chloride, fluoride, sulfate, carbonate). A similar trend is observed at long contact times and high S/V ratios in the case of Sr, where both the presence of the anions mentioned above and the moderating effect of ground-water on the pH rise may contribute to higher levels of Sr in ground-water leachates.

The present results also confirm the observation that the presence of ductile iron causes a large increase in leach rates due to the reaction of iron with dissolved silica and a steep rise in pH.² The effect of iron is largest under conditions which otherwise promote saturation, i.e. in ground-water and at long contact times.

Grambow⁶ has recently suggested that leach rates do not continue to decrease indefinitely as contact times increase. Instead, the interaction between the glass and the leachant becomes characterized by a constant dissolution rate. Si, Al, Fe, etc., re-precipitate as well-defined solid phases, while the concentrations of soluble species such as boron and the alkalis continue to grow at a constant rate. Grambow⁶ has combined the flow test data and the static test data reported for TDS-131 glass leached in de-ionized water at 70°C as reported in Refs. 2 and 4 and shown that the concentration of boron in the leachate appeared to increase linearly with the product of contact time and S/V between the data point obtained in the slowest flow test [$(T_r)_{\text{exp}} \cdot S/V = 4 \times 10^5 \text{ days} \cdot \text{m}^{-1}$, $f = 0.030 \text{ m/yr}$] and the data point obtained in the static powder test [$(T_r)_{\text{exp}} \cdot S/V$ of the order of $1 \times 10^7 \text{ days} \cdot \text{m}^{-1}$, equivalent flow rate of approximately $1 \times 10^{-3} \text{ m/yr}$]. The combination of flow test data and static powder test data may be somewhat inaccurate because static test leachates retain leach products (in particular, alkalis) dissolved during the earliest stages of exposure, and the resulting high pH level and large extent of leaching can persist for long periods of time². In any case, static powder tests have now been run on the less alkaline DWRG. The results at 70°C are given in Refs. 2 and 4. The test at 90°C has been conducted with an S/V ratio of 3500 m^{-1} and a contact time of 377 days. Under these conditions, the leachate is found to contain 37.1 mg/L B, 83.6 mg/L Si, 82.5 mg/L Na, 44.6 mg/L Li, 1.84 mg/L Cs, 4.30 mg/L Al, 5.60 mg/L U and 0.24 mg/L Sr. The results of all flow tests and static powder tests carried out so far on DWRG in de-ionized water at 70°C and at 90°C are shown in Fig. 1. It can be seen that in this case the leach rates continue to decrease even at the highest ranges of contact time \times S/V covered in both types of tests. The difference

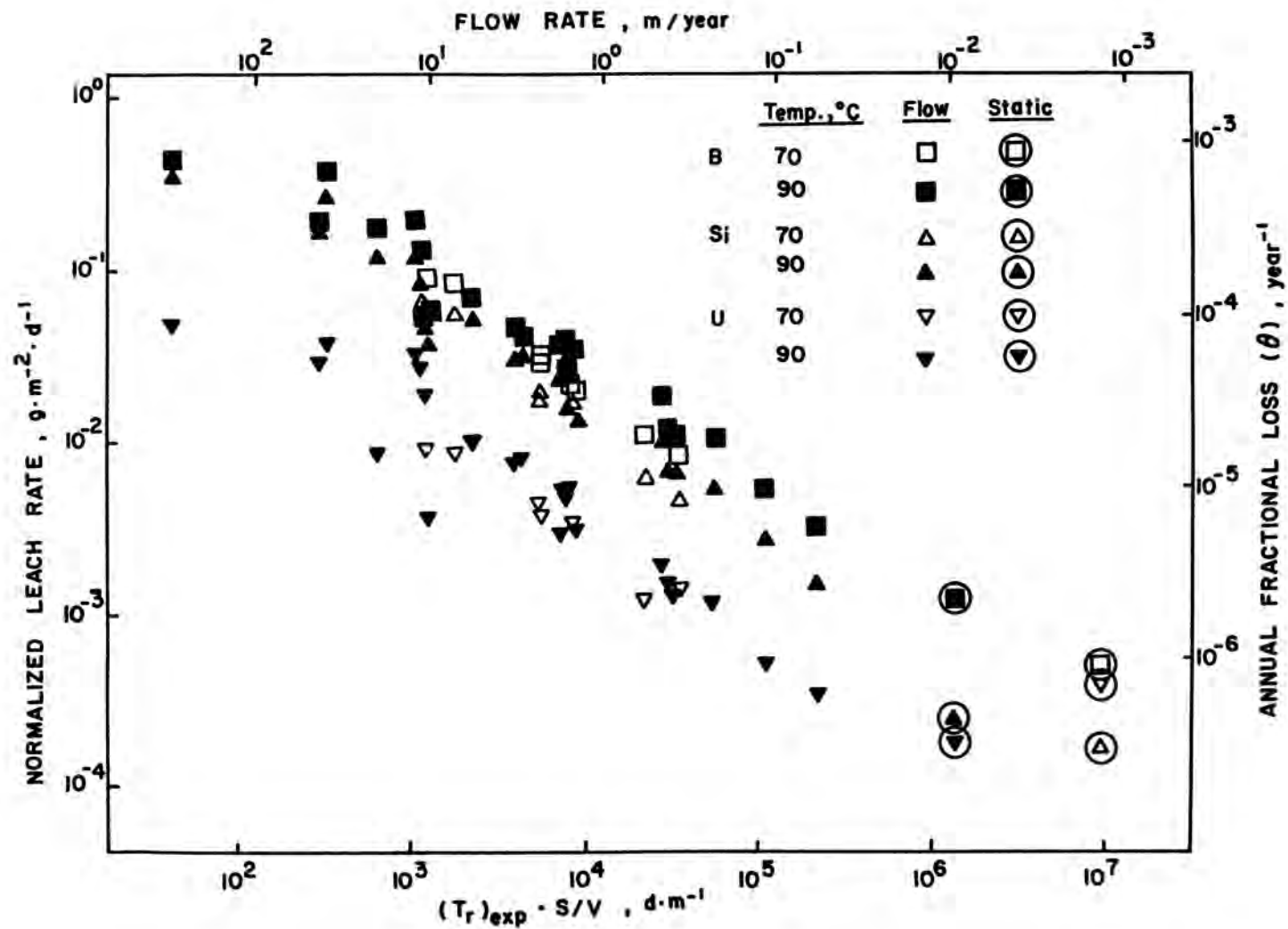


Fig. 1. Normalized leach rates and annual fractional losses based on B, Si and U as a function of generalized contact time or equivalent flow rate. DWRG, de-ionized water, 90°C and 70°C.

in behavior between the two glasses can be attributed to the lower alkalinity of DWRG and to the much lower extent of pH rise in its leachates. This prevents solubilities, which control slow-flow release rates, from continuing to rise with increasing pH.

As mentioned above, based on the conversion of $(T_r)_{exp} \cdot S/V$ to flow rates according to Ref. 1 and the data shown in Refs. 2 and 6, levelling off of the leach rates may occur only at flow rates below 0.03 m/yr in the case of TDS-131 and below 0.001 m/yr in the case of DWRG. Such extremely low flow rates may not be very realistic in the case of water-saturated repositories (e.g., basalt), where mass diffusion is likely to have an equivalent velocity of approximately 0.01 m/yr.² At the low flow rate limit, the annual fractional release rate for the most leachable component of TDS-131 (boron) at 70°C based on the geometric parameters given in Ref. 1, is 3×10^{-5} year⁻¹ at an equivalent flow rate of 0.03 m/yr. As detailed above, the leach rate may stabilize at this level and not fall below the benchmark value¹ of 1×10^{-5} year⁻¹. However, in the case of DWRG, the flow test data shown in Fig. 1 indicate that the release rate based on boron at 90°C reaches 1×10^{-5} yr⁻¹ at an equivalent rate of about 0.1 m/yr and drops further to 6×10^{-6} yr⁻¹ at a flow rate of 0.06 m/yr. Release rates at 70°C are slightly lower. If static test data are taken into consideration, it can be concluded that the release rates drop below 1×10^{-6} yr⁻¹ at flow rates lower than 0.001 m/yr, which can be relevant to the case of repository formations not saturated with respect to water (e.g., tuff).

A simple kinetic model has recently been proposed⁷ for the dissolution of glass in flowing water. According to this model, silica concentrations in the leachate follow the expressions:

$$C = k_1 \cdot (k_3 + F)^{-1} \text{ and } C = k_2 \cdot (k_3 + F)^{-1}$$

The dissolution rate, k_1 , of the original glass surface, controls the leaching at high flow rates; the dissolution rate of the altered surface, k_2 , predominates at moderate and slow flow rates; k_3 is the re-precipitation rate; and F is a linear flow parameter, equal to the reciprocal of $(T_r)_{exp} \cdot S/V$. The re-precipitation rate, k_3 , is assumed to increase exponentially from zero to a final value which characterizes the steady-state conditions, and this exponential rise is assigned a rate constant, k_6 . Based on this model and on the dependence of steady-state leachate concentrations on flow rate, it was possible to obtain fairly good agreement between calculated values and experimental data for the evolution of leachate composition as a function of exposure time in the case of TDS-131 glass at 70°C.¹ The parameters used in that case were $k_1 = 0.066 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, $k_2 = 0.025 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, $k_3 = 8.8 \times 10^{-5} \text{ m} \cdot \text{d}^{-1}$. The same model has now been applied to the results obtained with DWRG at 90°C based on the dependence of steady-state leachate concentrations on flow rate as given in Table I above and in Table 1.10 in Ref. 2. The values of the rate constants derived from this dependence are $k_1 = 0.084 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, $k_2 = 0.044 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $k_3 = 8.2 \times 10^{-4} \text{ m} \cdot \text{d}^{-1}$. The values of k_1 and k_2 are slightly higher than those obtained for TDS-131 at 70°C (see above). This reflects the similarity of the behavior of the two glasses under high-flow, near-neutral conditions and the higher temperature used in the case of DWRG. The value of k_3 is higher by an order of magnitude in the case of DWRG. This can be readily interpreted in terms of the high alkalinity of TDS-131, which gives rise to

high leachate pH values under conditions of near-saturation and so lowers the effective value of k_3 , since in high-pH media much of the silica is dissociated into soluble silicate ions which do not take part in the re-precipitation process. The use of the parameters given above for DWRG, based on the steady-state results, gives a good fit with the time-dependent data, as shown in Fig. 2.

ACKNOWLEDGMENT

This work was supported in part by Savannah River Laboratories under Contract No. AX0-654-764.

REFERENCES

1. Aa. BARKATT, P. B. MACEDO, W. SOUSANPOUR, Al. BARKATT, M. A. BOROOMAND, C. F. FISHER, J. J. SHIRRON, P. SZOKE and V. L. ROGERS, "The Use of a Flow Test and a Flow Model in Evaluating the Durability of Various Nuclear Waste-form Materials." Nucl. Chem. Waste Manage. 4:153-169 (1983).
2. J. E. MENDEL, ed., Final Report of the Defense High-Level Waste Leaching Mechanisms Program. PNL-5157, Pacific Northwest Laboratory, Richland, Washington (1984).
3. MATERIALS CHARACTERIZATION CENTER, "MCC-3S Agitated Powder Leach Test Method." In Test Methods Submitted for Nuclear Waste Materials Handbook. PNL-3390, Pacific Northwest Laboratory, Richland, Washington (1984).
4. Aa. BARKATT, P. B. MACEDO, W. SOUSANPOUR, Al. BARKATT, M. A. BOROOMAND, V. L. ROGERS, A. NAZARI, G. PIMENOV and J. J. SHIRRON, "Leach Mechanisms of Borosilicate Glass Defense Waste Forms -- Effects of Composition." In Waste Management '84, Vol. 1, ed. R. G. Post, pp. 627-631. Arizona Board of Regents, Tucson, Arizona (1984).
5. T. E. JONES, Reference Material Chemistry -- Synthetic Ground Water Formulation. RHO-BW-ST-37P, Rockwell Hanford Operations, Richland, Washington (1982).
6. B. GRAMBOW, "A General Rate Equation for Nuclear Waste Glass Corrosion." In Scientific Basis for Nuclear Waste Management, Vol. VIII, eds. C. M. Jantzen, J. A. Stone and R. C. Ewing. North-Holland, New York. To be published.
7. Aa. BARKATT, B. C. GIBSON and M. BRANDYS, "A Kinetic Model of Nuclear Waste Glass Dissolution in Flowing Water Environments." In Scientific Basis for Nuclear Waste Management, Vol. VIII, eds. C. M. Jantzen, J. A. Stone and R. C. Ewing. North-Holland, New York. To be published.

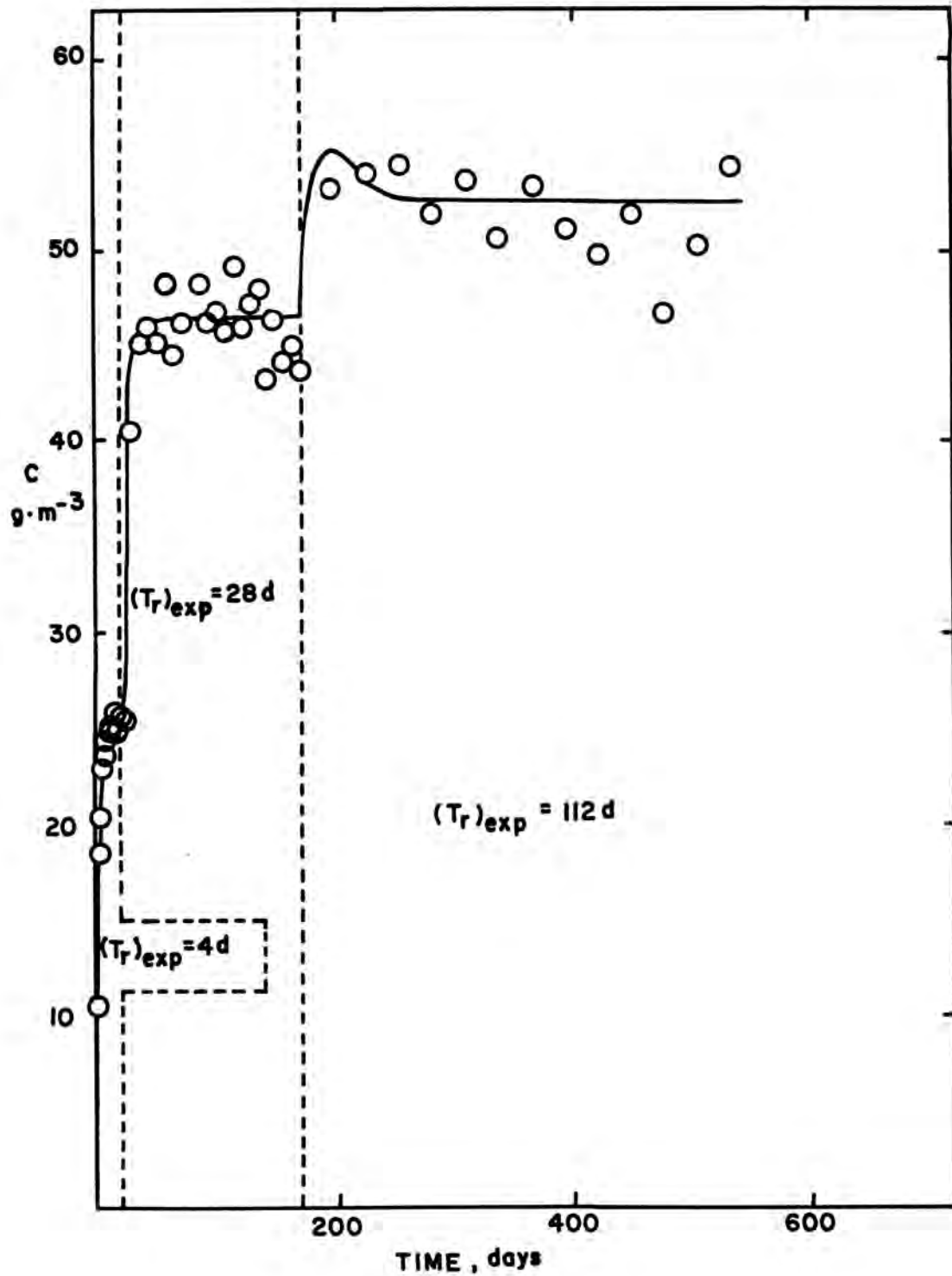


Fig. 2. Dependence of Si concentration in the leachate on exposure time. DWRG, de-ionized water, 90°C , $S/V = 291\text{ m}^{-1}$, $k_1 = 0.084\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, $k_2 = 0.044\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, $k_3 = 0.00082\text{ m}\cdot\text{d}^{-1}$, and $k_6 = 0.115\text{ d}^{-1}$.