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Zeolite Vitrification Demonstration Program: Chacterization of Nonradioactive Demonstration Product

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ZEOLITE VITRIFICATION DEMONSTRATION PROGRAM: CHARACTERIZATION OF NONRADIOACTIVE DEMONSTRATION PRODUCT

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ABSTRACT

An extensive characterization of specimens of the glass produced during Run 4 (ZVDP-4) of the nonradioactive phase of the Three Mile Island (TMI) Zeolite Vitrification Demonstration Program was conducted by the Materials Characterization Center (MCC) at Pacific Northwest Laboratory (PNL). The characteristics of the ZVDP-4 glass were compared with those of MCC's borosilicate reference glass, MCC 76-68. Tests included analyses of composition, density and phases present, the MCC-1P Static Leach Test Method, measurements of tensile strength and impact behavior, and evaluation of high-temperature vaporization.

The characteristics of ZVDP-4 glass generally are similar to those of MCC 76-68 reference glass, but with some important differences. The MCC-1P 28-day leach test data show that the leach rate in deionized water is much lower beyond 14 days than for the MCC 76-68 borosilicate reference glass; behavior is similar to that observed for some other aluminosilicate glasses. Tensile strength of the ZVDP-4 glass is similar to that of MCC 76-68 glass. The impact test on ZVDP-4 glass produced a smaller average particle size and a larger fraction of inhalable particles (<15 μm diameter) than for MCC 76-68 reference glass. High-temperature vaporization test results were similar to those for MCC 76-68 glass. The cations present in the ZVDP-4 account for about 94 wt% of the glass when calculated as simple oxides; no attempt has been made to identify the anions or other components comprising the 6 percent difference.

ACKNOWLEDGMENT

The detailed characterization data reported here resulted from the work of members of several PNL laboratories associated with the MCC program. Major contributors were:

D. M. Strachan and R. O. Lokken -
MCC-1 Static Leach Tests, phase characterization and density measurements;

M. D. Merz and G. B. Dudder -
MCC-10 Impact Tests and MCC-11 Tensile Strength Tests;

W. J. Gray -
MCC-8 High-Temperature Vaporization Tests;

J. E. Coleman -
Scanning electron microscopy and x-ray fluoresence analyses;

F. T. Hara -
Chemical analyses of the solid products and leachates.

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CHARACTERIZATION OF NONRADIOACTIVE
DEMONSTRATION PRODUCT

INTRODUCTION

An important aspect of the Three Mile Island Zeolite Vitrification Demonstration Program (TMI-ZVDP) is the characterization of the glass products. Glass produced during the nonradioactive runs 1, 2, 3 and 4 was characterized to a limited extent by TMI-ZVDP staff personnel.[1] Glass produced during run 4 (ZVDP-4 glass) has been further characterized under the direction of the Materials Characterization Center (MCC) at Pacific Northwest Laboratory (PNL) using procedures developed and published by the MCC specifically for application to nuclear waste containment materials.[2,3] These procedures are being established to standardize the documentation of chemical and physical properties of nuclear waste materials and permit direct comparison with other nuclear waste containment materials. PNL's simulated nuclear waste glass type MCC 76-68 is the interim reference material for MCC, pending development and full characterization of a certified standard reference material. Therefore, the ZVDP-4 glass data reported here are compared with MCC-established data for MCC 76-68 glass.

Characterization tests on ZVDP-4 glass are listed in Table 1. All specimens were provided by TMI-ZVDP staff personnel during the period October 1981 to February 1982.[1] Canister corrosion was evaluated by TMI-ZVDP personnel.

CHARACTERIZATION

ANALYSIS OF SOLID CANISTER PRODUCT

Specimens from top, middle and bottom locations in ZVDP canister 4 were analyzed for chemical composition (Figure 1). The specimens were fused with KOH, and dissolved in dilute HCl for analysis by inductively coupled plasma (ICP) and atomic absorption (AA) spectrometry. Duplicate specimens were

TABLE 1. MCC Characterization Tests on ZVDP-4 Glass

Test	Sampling Location in Canister 4
Chemical analysis of the solid product	Top (T), Middle (M), Bottom (B)
Phase characterization; crystallinity and glass compositions	T, M, B
Density	T, M, B
MCC-1P/Static Leach Test Method, matrix B, deionized water only	T, M, B
MCC-11P/Splitting Tensile Strength Test Method	M
MCC-10S/Brittle Materials Impact Test Method	M
MCC-8S/High-Temperature Vaporization Test Method	M

submitted to the same analytical laboratory independently by TMI-ZVDP staff and MCC for comparison. Results of these analyses are shown in Table 2; the equivalent oxide concentrations shown have been calculated from the cation concentrations determined by ICP or AA. The simple oxide concentrations total about 94 to 97 wt% of the specimen weight. The difference from 100 percent is assumed to be due to different complex oxides, other anions, and/or analytical error.

There is a small difference between the analyses obtained from the ZVDP and MCC samples for some elements, particularly sodium and lithium. These differences, and those between top, middle, and bottom specimens, may be a qualitative indication of the homogeneity of the glass in the canister. However, the relative standard deviation for these analyses is about 5 percent, so the apparent differences do not appear to be significant.

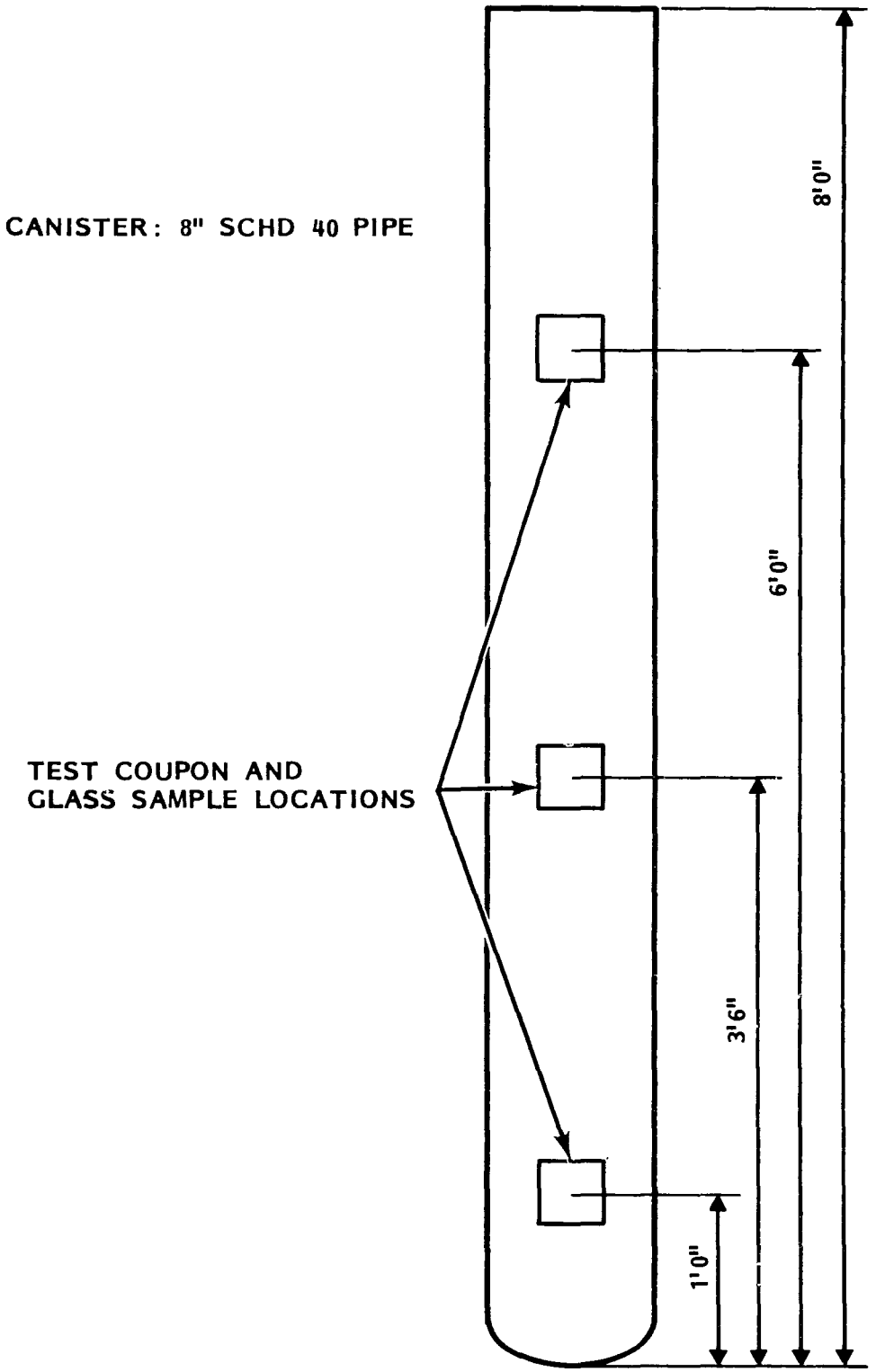

FIGURE 1. Sampling Locations for ZVDP Canisters

TABLE 2. Composition of ZVDP-4 and MCC 76-68 Glass

Oxide[b]	Concentrations[a] of Constituents (wt%) Top MCC	Top TMI[c]	Middle MCC	Middle TMI[c]	Bottom MCC	Bottom TMI[c]	Typical MCC 76-68
Al_2O_3	14.10	14.60	14.2	14.00	14.0	14.30	0.6
B_2O_3	4.93	4.90	4.93	5.30	4.94	4.88	8.8
BaO	0.06		0.06		0.06		0.5
CaO	0.82	0.85	0.84	0.96	0.93	0.94	2.4
Cr_2O_3	0.03		0.03		0.06		0.2
Cs_2O	0.40[d]	0.46[d]	0.37[d]	0.44[d]	0.40[d]	0.46[d]	1.0
CuO	0.03		0.05		0.06		
Fe_2O_3	1.58	1.60	1.59	1.86	1.92	1.82	9.4
Li_2O	5.42[d]		5.38[d]		5.36[d]		
	5.04	4.89	5.08	4.57	5.05	4.64	
MgO	0.31		0.38		0.31		0.2
MnO_2	0.02		0.03		0.05		0.1
Na_2O	13.9[d]		13.9[d]		14.2[d]		
	14.9	16.30	15.1	15.20	15.2	15.90	11.5
SiO_2	45.1	46.90	45.2	44.80	44.9	45.40	40.8
SrO	0.02	0.03	0.02	0.03	0.02	0.03	0.4
TiO_2	7.02	6.95	7.03	7.26	7.04	7.04	3.0
ZnO	0.05		0.05		0.05		4.7
ZrO_2	0.02		0.02		0.02		1.7
Rare earth, others							9.9
Total	93.81[e]	97.47	94.08[e]	94.42	94.32[e]	95.41	95.2

(a) Estimated relative standard deviation = 5%.
(b) Assumed oxides; concentrations calculated from cation analyses.
(c) Analysis of sample submitted to same laboratory by TMI ZVDP staff.(1)
(d) Analyzed by AA; all other analyses by ICP.
(e) Using AA data for Li_2O, Na_2O, and Cs_2O; data used for MCC-1P Static Leach Test Method calculations.

PHASE CHARACTERIZATION

Samples from all three locations in canister ZVDP-4 were examined by x-ray diffraction to determine presence of crystalline phases. All samples were found to be vitreous, with no crystalline phases detectible.

Further examination of the glass phases present was conducted in conjunction with the MCC-1 Static Leach Test Method. Observations are described following the discussion of the leach test results.

DENSITY

The density of the ZVDP-4 glass at top, middle, and bottom canister locations was calculated from size and weight measurements of the pieces used for the leach test, and measured by an immersion density method applied to duplicate specimens. The data (Table 3) show no significant difference between sample locations or measurement methods.

TABLE 3. Density of ZVDP-4 Glass (g/cm^3)

	Immersion Method			Size/Wt Measurements		
Location	Density	Standard Deviation	No. of Samples	Density	Standard Deviation	No. of Samples
Top	2.570	0.007	5	2.562	0.012	6
Middle	2.563	0.006	7	2.571	0.004	6
Bottom	2.554	0.023	14	2.565	0.003	6
Typical MCC 76-68 glass:				2.94	0.01	

THE MCC-1P STATIC LEACH TEST METHOD

The chemical durability of vitrified nuclear waste forms in water is an important measurement of their potential long-term stability. The MCC leach test methods were developed to measure that property. Samples which had been core-drilled from the top, middle, and bottom of ZVPD canister 4 were leach tested according to the MCC-1P Static Leach Test Method.[2] Test matrix B was used with deionized water only; leaching was done at 90°C for 3, 7, 14, and 28 days. Standard leach test specimen wafers were cut using a low-speed, diamond-blade sectioning saw, using water for lubrication and cooling.

Nominal specimen dimensions were 11 by 11 by 3.5 mm, resulting in a geometric surface area of ~400 mm^2. The specimens were ultrasonically cleaned in water, then in ethanol, dried, weighed, and placed in the center of precleaned Teflon® jars, using Teflon® grids for positioning. A volume of deionized water sufficient to produce a specimen surface area-to-leachant volume (SA/V) ratio of 10.00 m^{-1} was added to the jars. The container with lid and contents was weighed and placed in an oven at 90°C. After the required leaching time the leach vessel was removed from the oven, and the specimens removed immediately from the vessel and rinsed in deionized water. The lid was replaced and the solution allowed to cool to room temperature, at which time the pH of a 10-ml aliquot was measured. The remaining solution was replenished with sufficient deionized water to allow for small evaporative losses (<1.5 percent). Then the solution was acidified with concentrated nitric acid equal to 1.0 vol.% of the original volume, minus the aliquot used for pH measurement, to dissolve any species that may have adhered to the container walls. Following an additional 24 hours at 90°C, the acidified solutions were analyzed for dissolved cations by ICP and AA.

Leach Test Results. The leach test results, expressed in normalized grams leached per square meter of specimen surface area, were calculated using the equation:

$$NL_i = \frac{m_i}{f_i \cdot SA}$$

where NL_i = normalized mass of element "i" lost per unit surface area of sample (g/m^2)

m_i = mass of element "i" in solution at the end of the experiment (g)

f_i = mass fraction of element "i" in the sample when the experiment began (dimensionless)

SA = geometric surface area of the sample (m^2)

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Standard deviations were calculated from data of triplicate specimens leached for 28 days. The mass fractions, f_i, were determined from ICP and AA analyses of the duplicate specimens submitted by MCC (Table 1).

Results from leaching of the three samples are listed in Table 4. Figures 2, 3, and 4 show the normalized elemental release from the specimens of the three canister locations as a function of time. Silicon, aluminum, boron, and sodium follow nearly identical leach curves with time in all three samples.

TABLE 4. Results from Leach Tests[a] on ZVDP-4 Glass

Specimen (Canister Sampling Position)	Leach Time (Days)	Normalized Elemental Mass Loss, NL_i							Specimen Wt. Loss (g/m^2)	pH of Leachate[b]
		Al	B	Ca	Cs	Li	Na	Si		
Top	3	5.05	4.67	2.29	7.00	5.63	5.74	4.93	3.65	9.49
	7	9.97	10.52	3.27	11.16	12.44	11.74	9.20	7.96	9.69
	14	13.17	13.92	4.58	19.10	16.89	15.04	12.72	9.63	9.85
	28	13.52	13.56	2.90	20.60	15.98	13.97	13.37	10.03	9.69
	σ[c]	±0.65	±1.28	±0.61	±2.03	±1.30	±0.77	±0.45	±0.61	±0.08
	rel. σ(%)	4.8	9.4	21.0	9.9	8.1	5.5	3.4		
Middle	3	5.68	5.67	2.63	8.31	6.86	6.65	5.59	3.85	9.65
	7	8.76	8.69	3.10	11.66	10.51	10.18	8.52	6.49	9.50[d]
	14	11.37	11.36	2.23	17.19	14.07	12.90	11.27	8.42	9.76
	28	13.87	13.55	3.30	21.29	17.00	14.86	13.73	10.31	9.72
	σ[c]	±0.88	±1.16	±0.79	±1.36	±1.35	±0.97	±0.73	±0.50	±0.09
	rel. σ(%)	6.3	8.6	23.9	6.4	7.9	6.5	5.3		
Bottom	3	6.05	5.83	2.56	7.87	7.02	6.81	5.90	4.10	9.65
	7	9.54	9.06	3.04	12.89	10.93	10.45	9.24	7.49	9.66
	14	12.48	11.99	2.18	20.15	14.95	13.38	12.34	9.90	9.83
	28	14.04	13.56	2.67	21.31	17.03	14.63	14.15	10.78	9.76
	σ[c]	±0.54	±0.64	±0.10	±1.46	±0.74	±0.57	±0.17	±0.60	±0.04
	rel. σ(%)	3.8	4.7	3.7	6.8	4.3	3.9	1.2		

(a) Leach Test: MCC-1P at 90°C in deionized water; surface area of specimens/volume of leachant = 10 m^{-1}; leachate composition analyzed by ICP, except Cs by AA.
(b) pH measured at 23°C; initial pH ~5.5.
(c) σ = one standard deviation from average of three samples leached for 28 days.
(d) Solution spilled before the pH reading had stabilized.

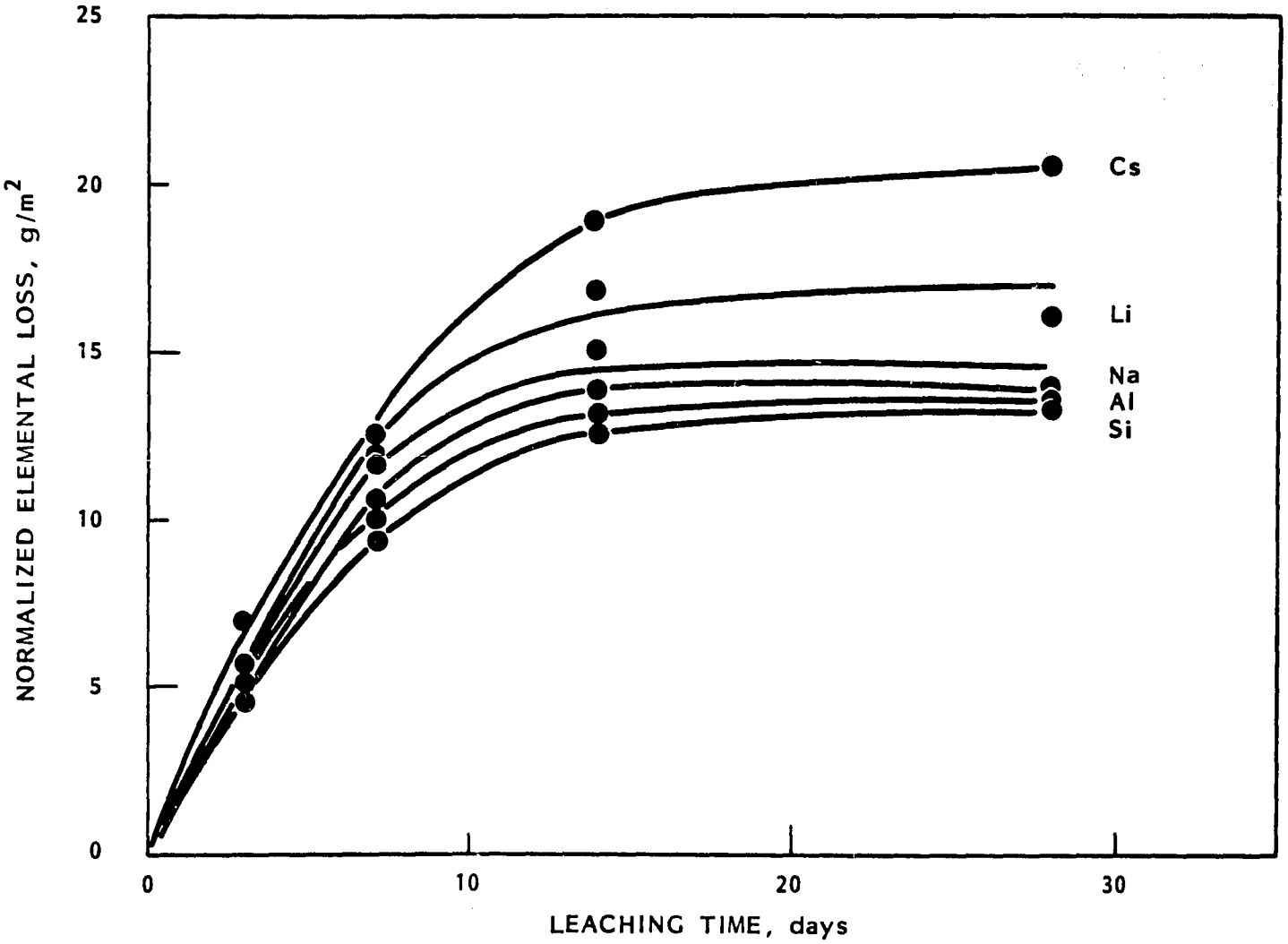


FIGURE 2. Normalized Elemental Losses from ZVDP-4 Glass (Top) as a Function of Leaching Time (90°C, DI Water, SA/V = 10 m^{-1})

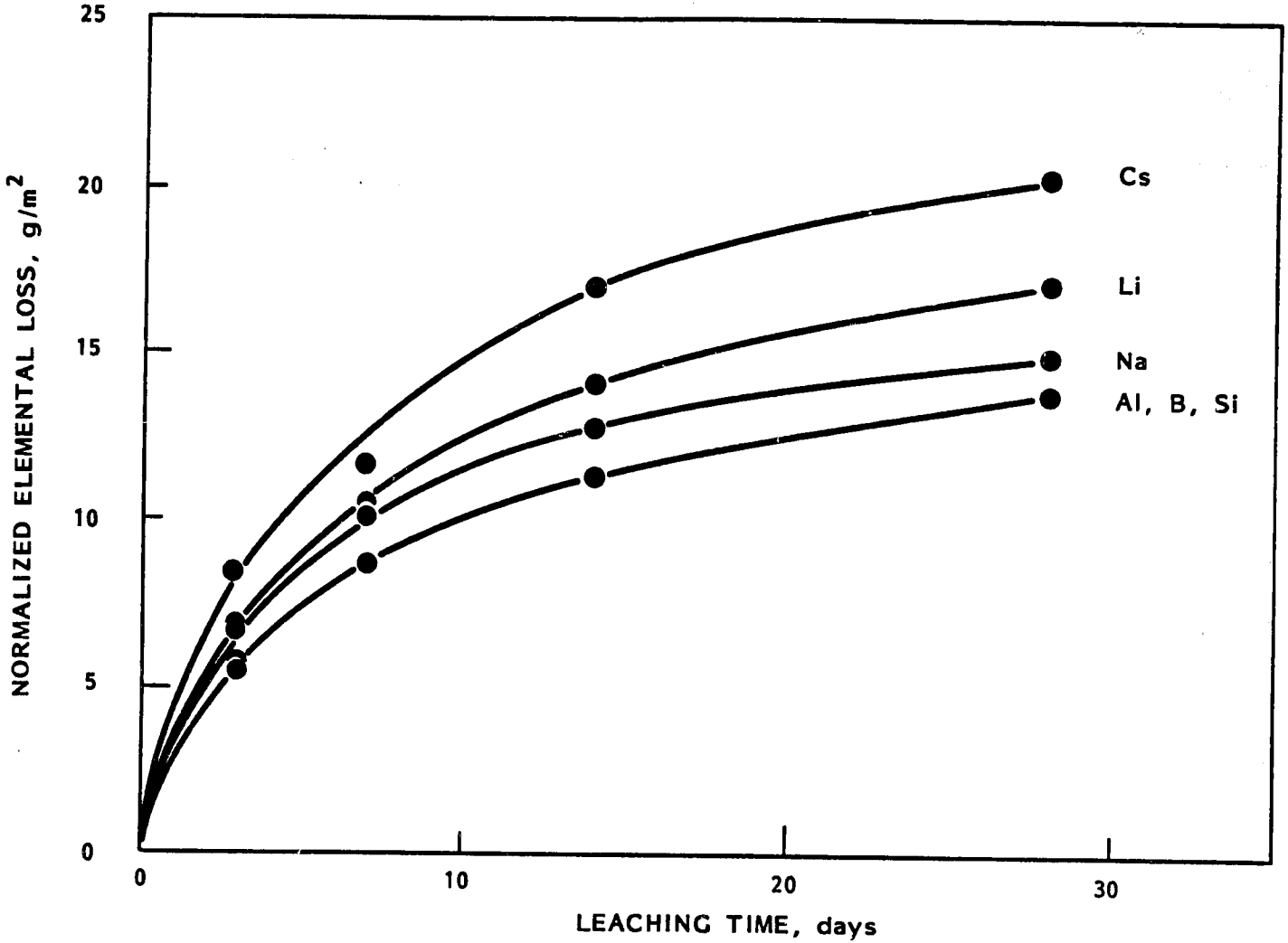


FIGURE 3. Normalized Elemental Losses from ZVDP-4 Glass (Middle) as a Function of Leaching Time (90°C, DI Water, SA/V = 10 m^{-1})

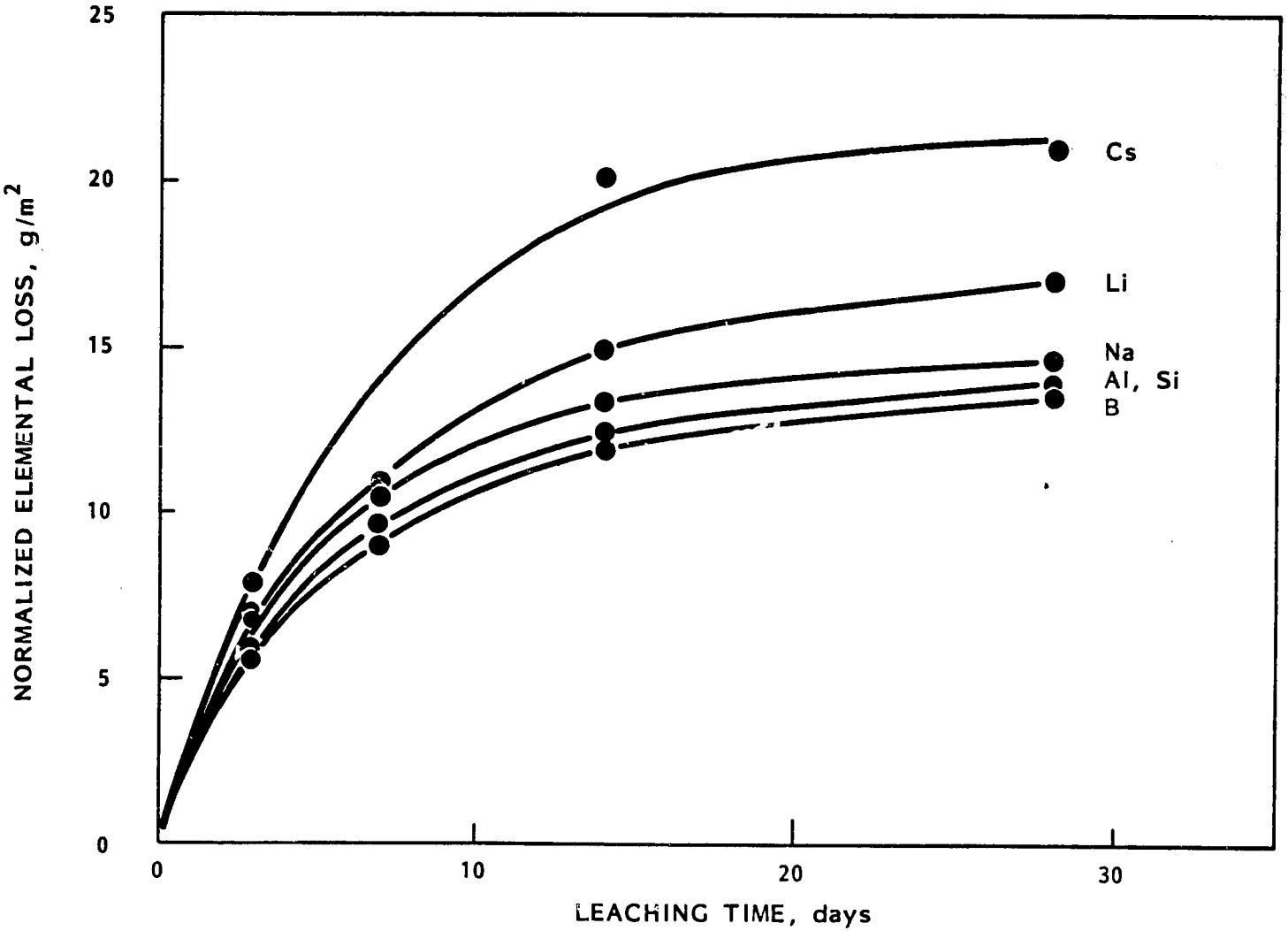


FIGURE 4. Normalized Elemental Losses from ZVDP-4 Glass (Bottom) as a Function of Leaching Time (90°C, DI Water, SA/V = 10 m^{-1})

Lithium and cesium leach consistently faster initially, but follow the same general rate as the other elements after 14 days. The rate of release, i.e., the slope of the curves, is specimen dependent. The rate of release from the canister "top" sample is nearly constant through the first 7 days of leaching, slows down through 14 days, and becomes essentially zero by 28 days of leaching. A more rapid release rate occurs for the first 3 days for the canister "bottom" specimen, followed by progressively slower rates to near zero at 28 days. The "mid-canister" specimen shows a smoothly decreasing leach rate for all elements, with a small positive leach rate still evident at 28 days. Note, however, that the total loss of the respective elements after 28 days is the same (within measurement precision) at all three canister locations; a similar relationship is shown for the total mass loss (Figure 5).

It is particularly informative to compare the total mass loss and elemental loss rates of ZVDP-4 glass with typical curves for the MCC 76-68 borosilicate reference glass (Figures 5 and 6). Whereas the MCC 76-68 reference glass continues to leach at a steadily decreasing rate to a cumulative mass loss of around 35 g/m^2 before leveling off to zero rate at about 180 days, the ZVDP glass specimens appear to level off to a zero leach rate at around 30 days after a weight loss of about 10 g/m^2. It must be remembered that no test data are available for the ZVDP vitreous waste form beyond 28 days.

The leaching behavior of the vitrified products for all four ZVDP nonradioactive canisters can be compared to a limited extent by examining their 7-day leaching behavior, using data obtained by TMI ZVDP personnel (Table 5).[a] It should be emphasized that elemental loss rates this early in the leaching test are highly time dependent, so comparison of 7-day results is less reliable than comparison at longer times. The behavior of ZVDP-1 and -2 glass appears to be similar to that of ZVDP-4, except for the higher aluminum loss.

(a) Memorandum, L. J. Ethridge to G. Bryan, "MCC-1 Matrix A Leach Test on Glass Samples from ZVDP-1, -2, and -3," Nov. 18, 1981.

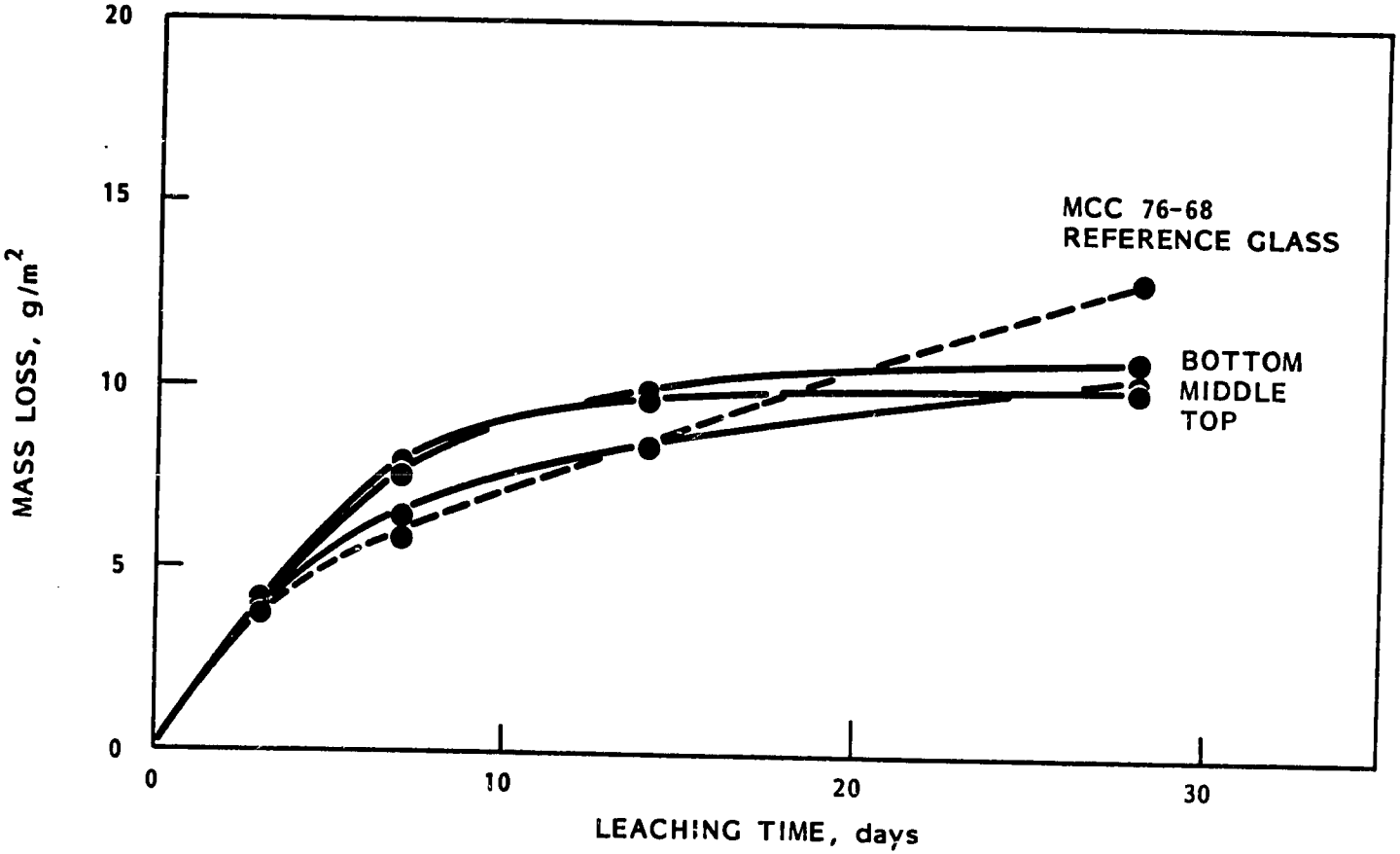


FIGURE 5. Cumulative Mass Loss from ZVDP-4 Glass as a Function of Leaching Time (90°C, DI Water, SA/V = 10 m^{-1})

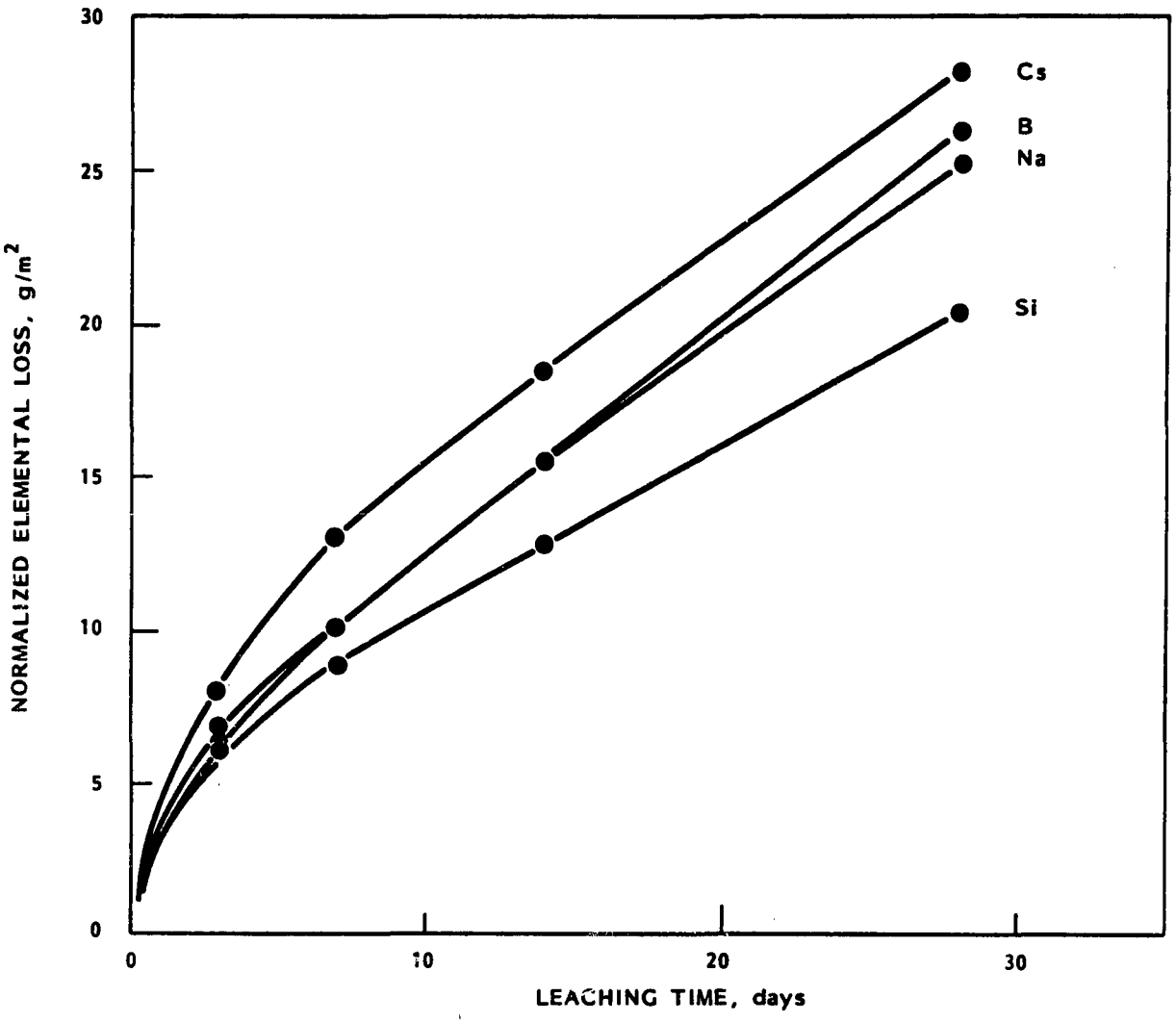


FIGURE 6. Normalized Elemental Losses for Reference Waste Glass MCC 76-68 as a Function of Leaching Time (90°C, DI Water, SA/V = 10 m^{-1})

TABLE 5. Comparison of Elemental Loss from Leaching of Glass from ZVDP-1, -2, -3, and -4[a] (Test: MCC-1P, 7 days, 90°C, deionized water)

Canister/ Sampling Location	Normalized Elemental Loss (g/m^2)							
	Al	B	Ca	Cs	Li	Na	Si	Sr
1[b]	6.15	9.45	na	12.65	11.41	11.77	9.91	na
2[b]	5.83	8.86	na	11.38	10.31	10.58	9.22	na
3/Top[b]	4.72	6.86	na	6.99	8.29	7.58	7.45	0.39
3/Middle[c]	4.58	6.39	na	6.40	7.35	6.90	7.28	0
3/Bottom[c]	2.98	4.29	na	4.64	5.13	4.92	5.07	1.77
4/Top[d]	9.97	10.52	3.27	11.16	12.44	11.74	9.20	na
4/Middle[d]	8.76	8.69	3.10	11.66	10.51	10.18	8.52	na
4/Bottom[d]	9.54	9.06	3.04	12.89	10.93	10.45	9.24	na

na = not analyzed.
(a) Canisters 1, 2, and 3 tested by TMI-ZVDP staff using MCC-1P matrix A.[3]
(b) Average of 3 samples.
(c) Average of 2 samples.
(d) 1 sample.

Elemental losses reported for ZVDP-3 glass are only ~40 to 80 percent of those for ZVDP-4 glass; large differences in leaching occurred in glass at top and bottom of ZVDP-3. In every case, the data indicate that elemental losses for any of the four nonradioactive canisters would not exceed that reported in detail here for ZVDP-4.

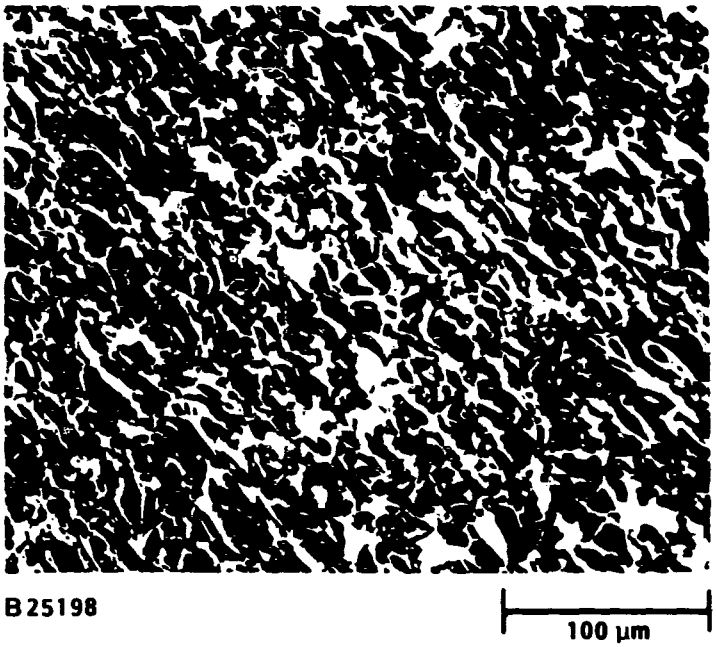
The pH of the leachates from ZVDP-4 glass specimens increased during leaching, rapidly for 1 to 3 days, and more slowly up to 28 days. All leachates increased similarly from an initial value of ~5.5 to ~9.7 after 28 days.

Phase Characterization. Detailed phase characterization of the vitreous products of ZVDP was conducted on specimens from the middle of the canister. Specimens were examined by scanning electron microscopy (SEM) and energy dispersive x-ray fluorescence analysis (EDX), both in the as-prepared condition and after leaching for 28 days. After examination of the exposed surfaces,

the samples were sectioned and polished. Photomicrographs of the as-cut surface before leaching (Figure 7) show that the surface morphology is typical of glasses cut with a diamond blade. Comparison of Figures 7 and 8 shows the effect of 28 days of leaching. The sharp, angular pitted original surface is changed to the grainy texture of the leach layer. The cracks on the surface of the leached specimen probably are due to drying of the specimen. Figure 9 illustrates the changes in surface composition after leaching. The top EDX trace shows the relative intensities of the various elements in the original material; the lower trace is from the same sample after leaching for 28 days. The surface appears to be enriched in titanium and iron (elements which were below detection limit concentrations in the leachate), and calcium, which demonstrated a low normalized release (~3.3 g/m^2) after 28 days. Figure 10 shows a typical small region enriched in titanium on the leached surface, resulting from the low Ti leach rate of the glass.

The profiles obtained from polished sections of the same materials (Figure 11) confirm that the jagged edge, which corresponds to the sharp angular surface seen in Figure 7 (the initial cut surface of the specimen) is eliminated during leaching. The most prominent features seen in the leached sample (Figure 12) are the typical leach layer with an average thickness of 2 μm and darker finger-shaped areas about 4 μm wide intruding into the sample. Similar "fingers" frequently occur during leaching of as-cut glass specimens. These two areas have nearly the same composition, as shown by their respective EDX traces (1 and 2, Figure 13). The areas are depleted in sodium, aluminum and silicon, and appear to be enriched in calcium, titanium and iron. The remaining traces in Figure 13 are from the areas indicated in Figure 12, progressively deeper into the bulk of the sample. The area immediately adjacent to the leach layer is only slightly different from the interior bulk composition (compare locations 3 and 6).

The EDX is not capable of analysis of lithium and boron. The cesium concentration in the sample is near the EDX detection limit.



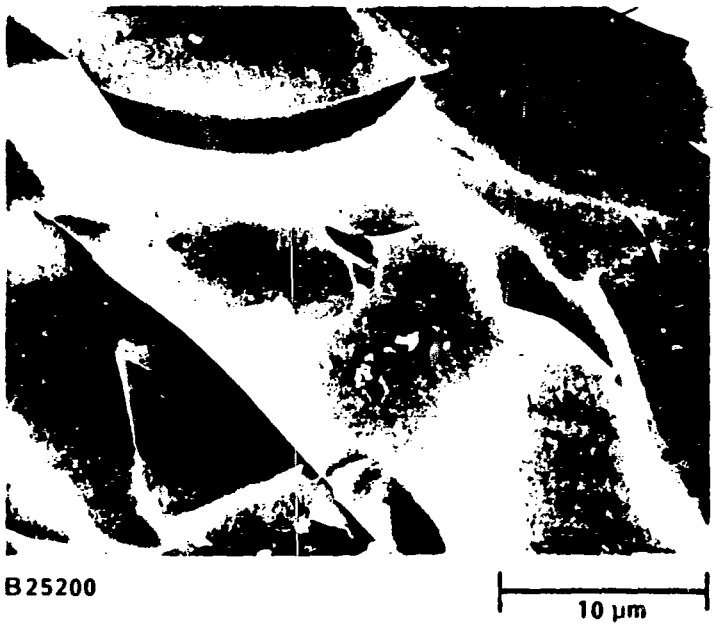
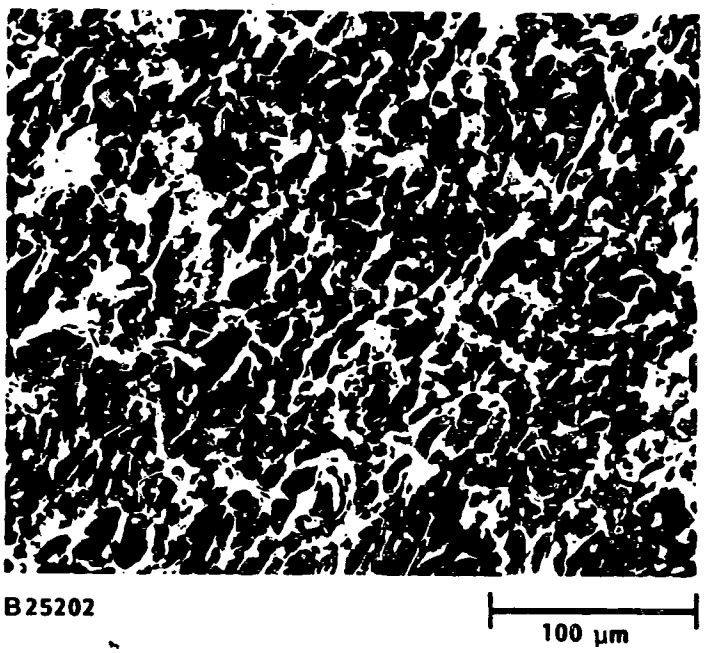


FIGURE 7. SEM Micrographs of the As-Cut Surface of a Specimen of ZVDP-4 Glass (Middle) Before Leaching



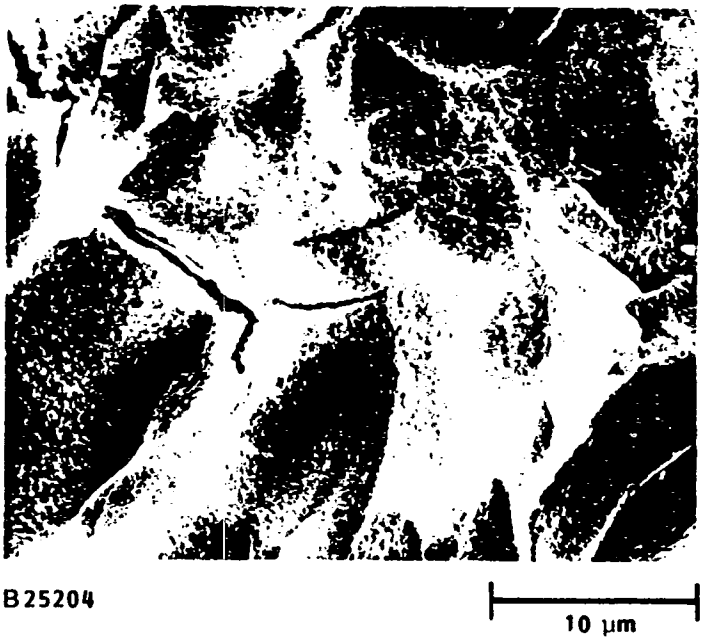


FIGURE 8. SEM Micrographs of the Surface of a Cut Specimen of ZVDP-4 Glass (Middle) After Leaching for 28 Days

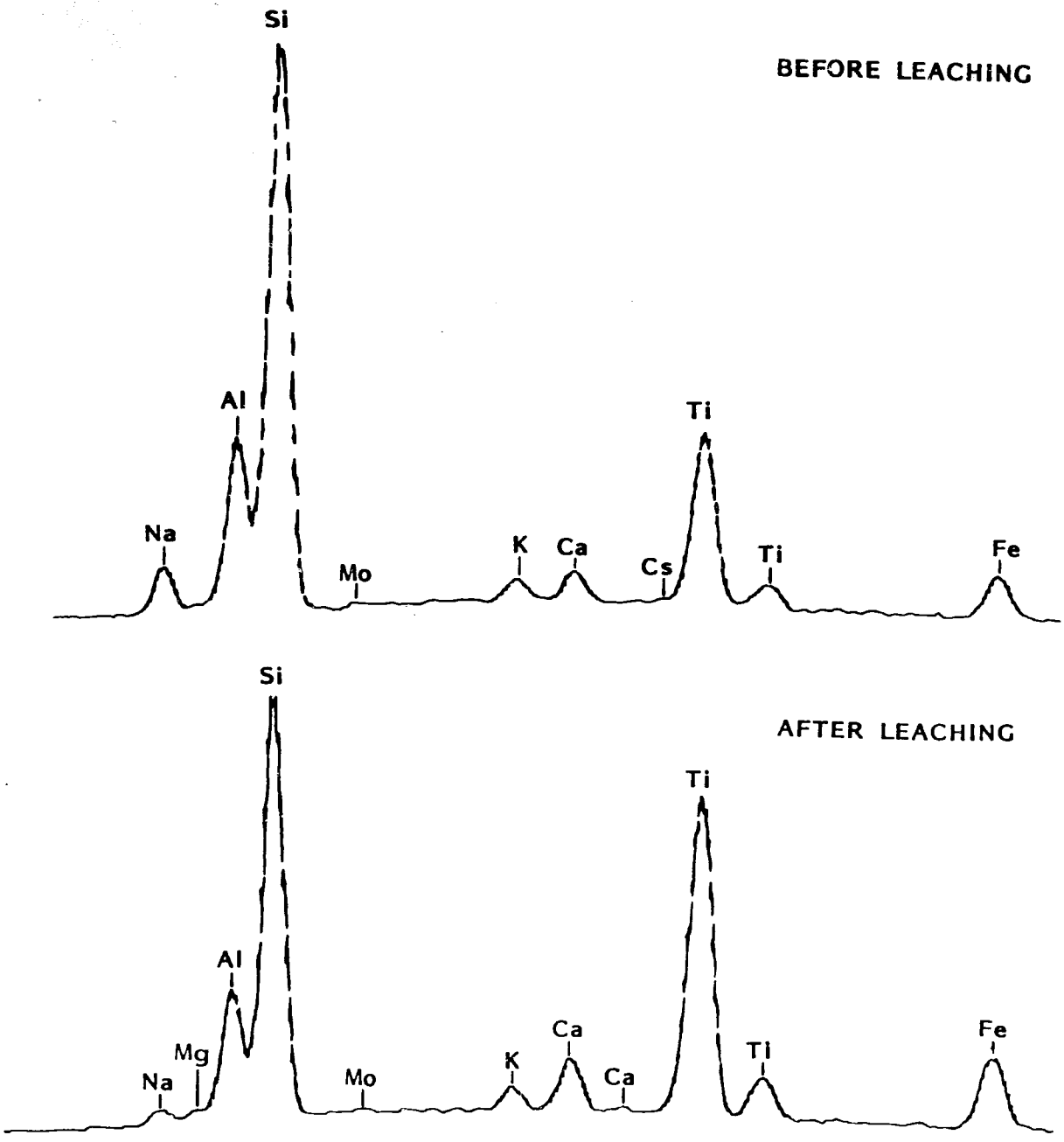
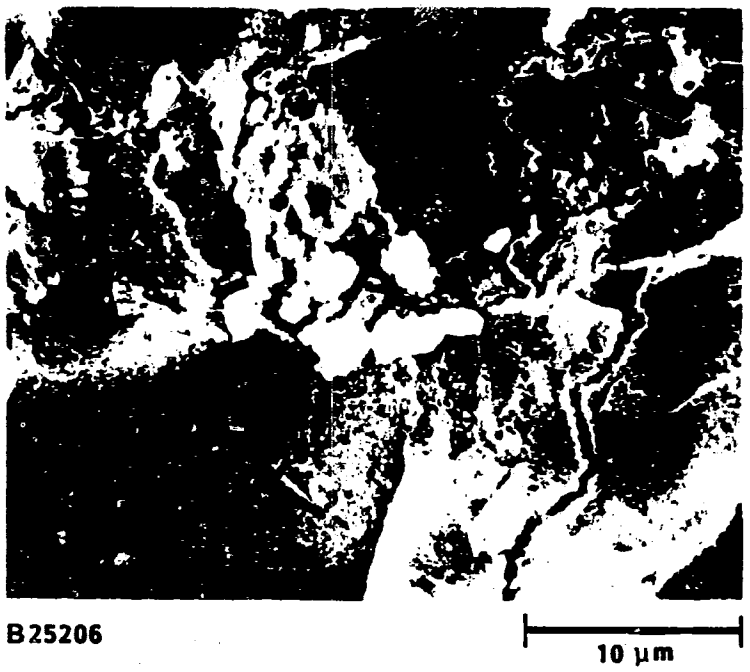


FIGURE 9. EDX Traces of Surfaces of ZVDP-4 Glass (Middle); Specimens Before and After Leaching (See Figures 7 and 8)



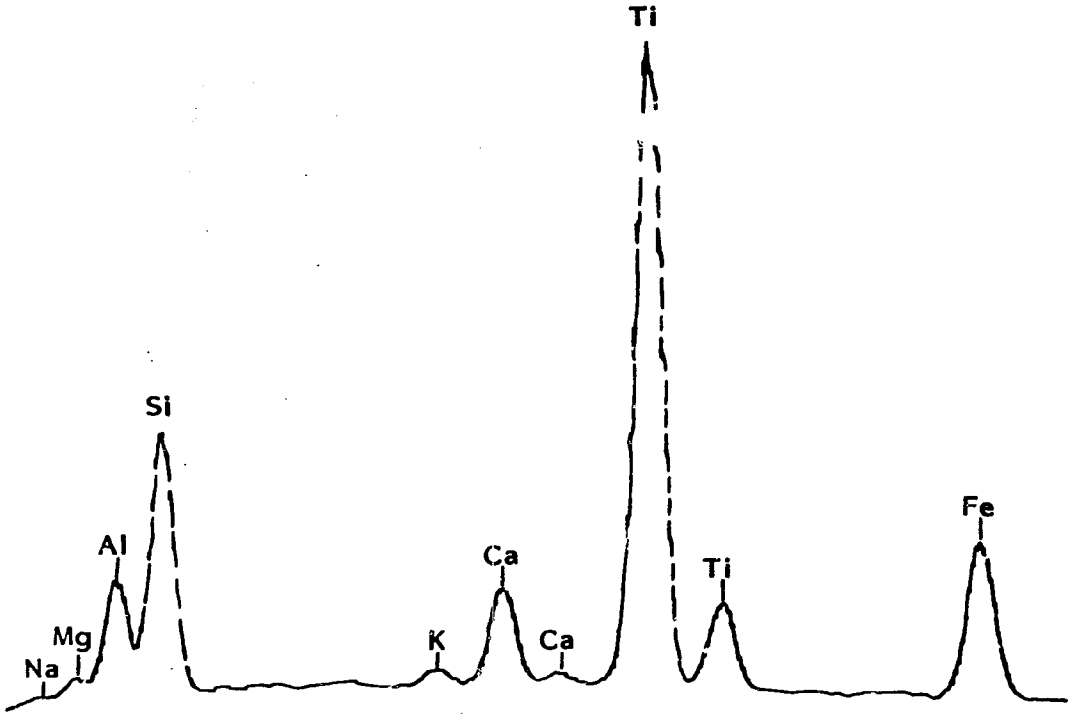


FIGURE 10. SEM Micrograph and EDX Trace Identifying a Small Titanium-Rich Phase on the Leached Surface of a ZVDP-4 Glass (Middle) Specimen

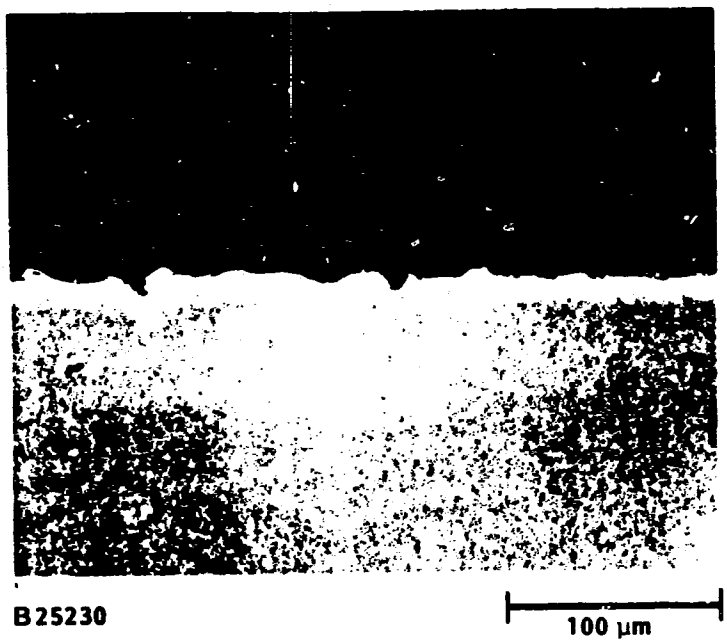


FIGURE 11. SEM Micrographs of Polished Sections of ZVDP-4 Glass (Middle) Before and After Leaching

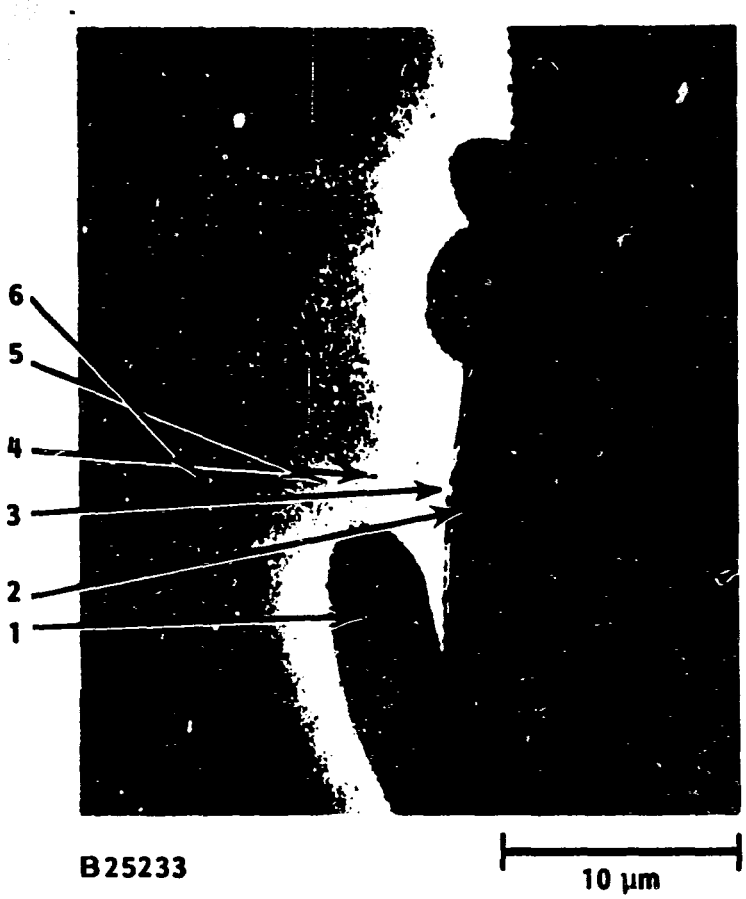


FIGURE 12. SEM Micrograph of Polished Section of ZVDP-4 Glass (Middle) After Leaching. Numbers refer to areas analyzed by EDX (see Figure 13).

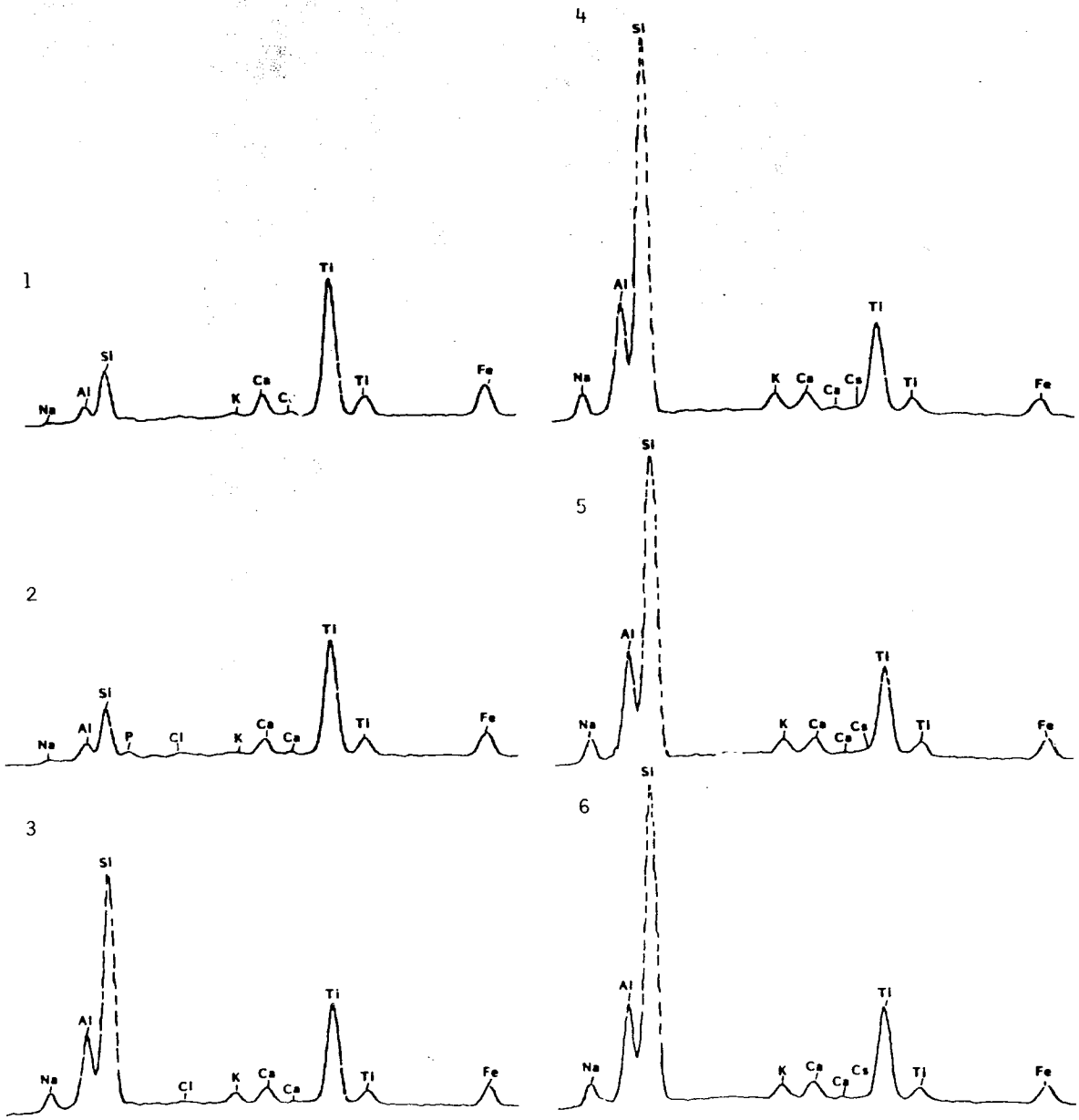


FIGURE 13. EDX Traces of Areas Identified in Figure 12

SPLITTING TENSILE STRENGTH

Two kinds of mechanical tests were conducted on glass specimens from the middle of ZVDP-4 to assess the mechanical integrity of the vitrified zeolite. The first was the splitting tensile strength test, performed according to the procedure outlined in MCC-11P.[3] This test provides data on the short-term static fracture strength of the material. A satisfactory waste form must be able to sustain compressive and bending loads without excessive fracture from the tensile stresses resulting from the loading. In the MCC-11P test method, a specimen disk 12.5 mm diameter x 6.3 mm thick is compressed diametrally under controlled conditions. The disk fractures when the tensile stress perpendicular to the applied load axis exceeds the tensile strength of the material.

Test results on ZVDP-4 are summarized in Table 6 for the seven replicate specimens tested. The fracture strength was calculated from the equation

$$F = \frac{2P}{\pi DL},$$

where F = fracture strength, MPa
P = fracture load, newtons
D = specimen diameter, mm
L = specimen length, mm.

The average tensile strength was 30.9 MPa, with a relative standard deviation of 24.3 percent. For comparison, the average strength of the MCC 76-68 reference glass is 30.3 MPa, with relative standard deviation of 13.1 percent. Thus the average strength of the vitrified zeolite in ZVDP-4 is the same as in MCC 76-68 glass. The larger relative standard deviation may have resulted from the relatively large casting of glass contained in the ZVDP canisters, which might result in significant residual stresses. The MCC 76-68 reference glass was cast in short bars (25 x 25 x 304 mm) and annealed in order to minimize cooling stress.

TABLE 6. Splitting Tensile Strength of ZVDP-4 Glass (Middle)

Specimen Number	Diameter mm	Length mm	Fracture Load, N	Fracture Strength, MPa
1	12.81	6.35	2870	22.5
2	12.83	6.40	5090	39.5
3	12.95	6.32	3600	28.0
4	12.87	6.43	3047	23.4
5	12.95	6.43	3470	26.5
6	12.95	6.43	5070	38.8
7	12.83	6.35	4780	37.4
ZVDP-4 Average Strength				30.9 (4480 psi)
		Standard dev.		7.5
		Relative std. dev.		24.3%
Reference glass MCC 76-68 (Average Strength)				30.3
		Relative std. dev.		13.1%

BRITTLE MATERIALS IMPACT TEST

The second mechanical property test conducted on ZVDP-4 glass was the high-energy impact test, following the MCC-10S procedure.[4] The resistance of a waste form to fracture under impact loading is relevant to safety in handling and disposal. The potentially airborne fraction [<200 μm aerodynamic equivalent diameter (AED)], the inhalable fraction (<15 μm AED), the respirable fraction (<3.5 μm AED) and the total surface area of the particulates produced are the properties of interest. The surface area of the waste form has a possible direct effect on radionuclide release rate, especially under inadvertent conditions of relatively high flow rate of a liquid in contact with the waste form. The amounts of inhalable and respirable fines provide a basis for assessing the hazard of vitrified zeolite to other waste forms with respect to potential airborne release subsequent to impact.

The cylindrical specimens, nominally 12.6 mm diameter by 31.8 mm long were subjected to the impact of a free-falling weight. The weight was 221 kg

dropped from a height of 30.5 cm onto a stiff rod in contact with the flat end of each specimen. In the test, the falling weight is arrested after specimen impact to avoid crushing the fractured material. The resulting particles are totally contained during impact. Particle size distribution is determined by sieving with 425 μm, 212 μm, and 45 μm sieves followed by aerosolization of the <45 μm size fraction to obtain <15 μm and <3.5 μm size fractions. The aerodynamic size classifier consists of a vertical tube for elutriation of <15 μm AED particles and a cyclone for separation of <3.5 μm AED particles.

Size distributions reported are fractions by weight in each size range. The results of the sieving and airborne particle collection are given in Table 7 for both the ZVDP-4 vitrified zeolite and the reference MCC 76-68 glass specimens. The specimen recovery after impact, based on summation of the weights of the various fractions, generally ranged from about 99.2 to 99.8 percent of the original specimen weight. The unrecovered material cannot be reasonably attributed to any particular size range and does not introduce significant error unless it was concentrated entirely in the size range <15 μm. In the present case, because of the known accidental loss of material from specimen 1 during sieving, the data for specimen 2 are considered more representative of the particulate characteristics.

Table 7 shows that about 0.17 percent of the solid specimen was fractured to an inhalable particle size (<15 μm) upon impact, including about 0.01 percent in the respirable range (<3.5 μm). Both these values are about 50 percent greater than the amount of corresponding particle sizes observed in tests on MCC 76-68.

The surface area of the impact test particles can be derived from the data in Table 7 by first calculating the cumulative weight percent of particles smaller than each of the three sieve sizes (Table 8). The values of D_g (geometric mean diameter, the diameter at which 50 wt% of the particles are larger) and σ_g (geometric standard deviation of the log normal size distribution) can

TABLE 7. Sieving and Airborne Particle Analyses of Brittle Impact Tests

Specimen	Specimen Weight	Percent Recovered	Size Distribution[a] Percent <3.5 μm[b]	Percent 3.5-15 μm[b]	Percent <45 μm[c]	Percent 45-212 μm[c]	Percent 212-425 μmb[c]	Percent <425 μm[c]
ZVDP-4 Glass (Middle)								
Specimen 1[d]	10.3566	99.47	0.006	0.078	3.34	11.09	11.82	73.22
2	10.8023	99.78	0.011	0.156	3.07	8.54	8.03	80.14
MCC 76-68 (Avg of 5 specimens)	11.8816	99.46	0.006	0.092	3.29	8.09	6.97	81.12
Std. Dev	0.0239	0.019	0.004	0.055	0.31	0.55	0.54	0.93
Rel. S.D.,	0.2	0.2	67	60	9.4	6.8	7.7	1.2

(a) Percent of initial specimen weight.
(b) Aerodynamic equivalent diameter as measured with an aerodynamic size classifier.
(c) Sieve size diameter.
(d) Some fine particles (<45 μm) were lost from this sample during sieving.

TABLE 8. Particle Size Distribution
(Based on data in Table 7)

Specimen	Wt. Percent <425 μm	Wt. Percent <212 μm	Wt. Percent <45 μm	D_g (μm)	σ_g
ZVDP-4 Glass (Middle)					
Specimen 1	26.25	14.43	3.34	1480	6.68
2	19.63	11.61	3.07	2970	9.36
Average	22.94	13.02	3.20	2225	8.02
MCC 76-68 (Average of 5 specimens)	18.35	11.38	3.29	3732	10.8
Std. Dev.	1.07	0.77	0.31	635	1.6
Rel. SD,	5.8	6.7	9.4	17.0	14.8

be determined by a least squares fit to the size data (Figure 14). The surface area per unit volume ($S_F/\alpha V_o$) term for these materials then is calculated by

$$S_F/\alpha Vo = e^{1/2 \ln^2 \sigma_g} / D_g,$$

where S_F = surface area, cm^2
V_o = initial volume of specimen, cm^3
α = shape factor $\cong 21$[4,5].

Table 9 shows that the increase in surface area upon impact for the ZVDP-4 vitrified zeolite is about 12% less than that for the MCC 76-68 reference glass. Because of density differences, the surface area per unit of mass is about equal for ZVDP-4 and MCC 76-68 glasses.

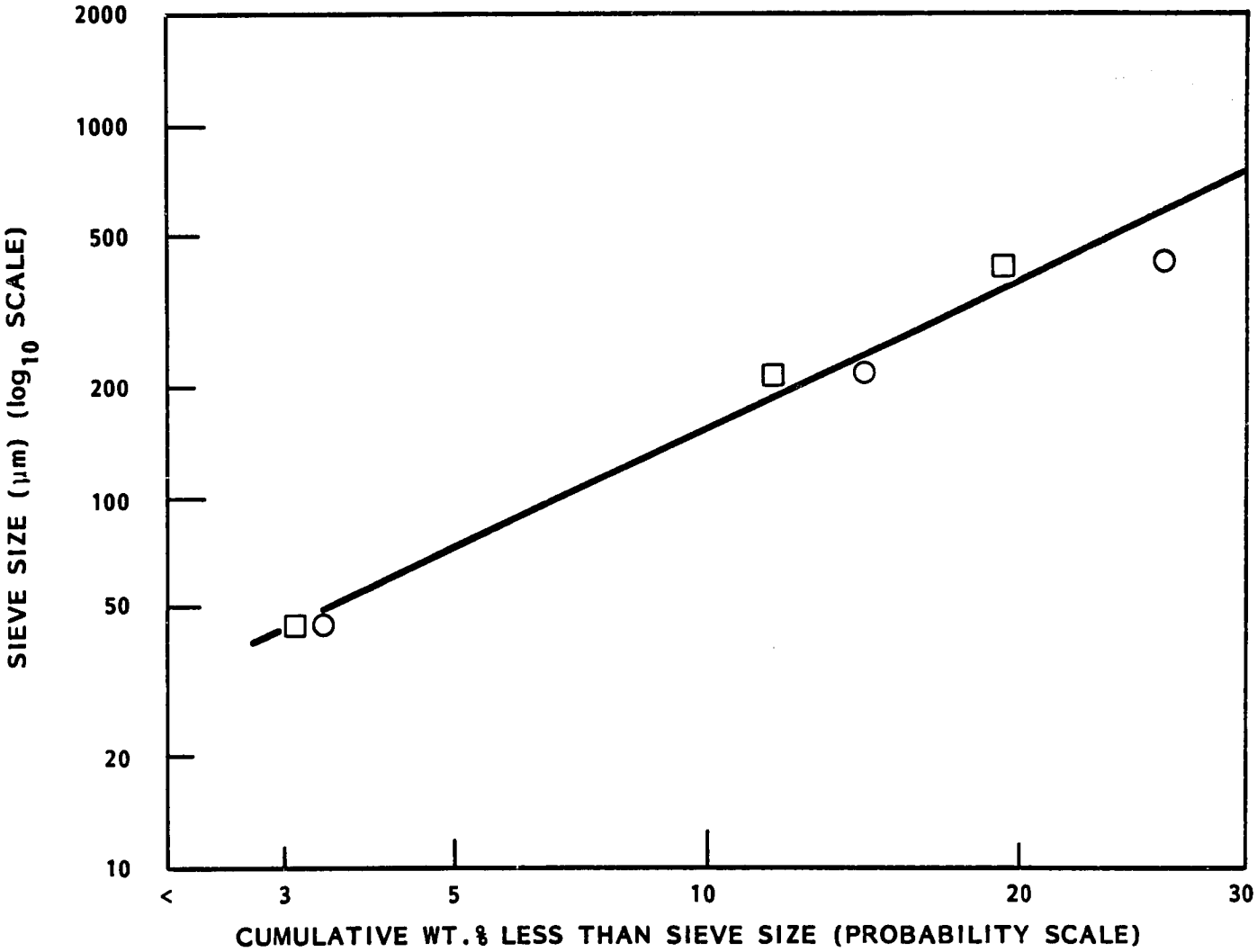


FIGURE 14. Brittle Impact Test on ZVDP-4 Glass; Sieve Size (Log_{10} Scale) Versus Particle Cumulative Weight Percent Less than Sieve Size (Probability Scale)

TABLE 9. Surface Area for Brittle Impact Test Specimens

Specimen	$S_{F/\alpha V_o}$ (a) (cm^2/cm^3)	Surface Area Per Unit Volume S_F/V_o (cm^2/cm^3)	Surface Area Per Unit Mass, S_F/M (cm^2/g)
ZVDP-4 Glass (Middle)			
Specimen 1	41.0		
2	41.1		
Average	41.05	863	337
MCC 76-68 (average of 5 specimens)	46.5	977	326
Std. Dev.	10.2		
Rel. Std. Dev.	21.9		

(a) S_F = surface area; V_o = initial specimen volume; α = shape factor. Assume shape factor α = 21 (see Ref. 4,5).

HIGH-TEMPERATURE VAPORIZATION

Potential vaporization of glass constituents at elevated temperatures (e.g., possible heating during transport or storage) is an important aspect of vitrified material characterization. Vaporization tests were performed on ZVDP-4 (middle) glass samples using a procedure that is being developed as MCC-8S High-Temperature Vaporization Test Method.[4] Since the test method is still under development, its reproducibilty on complex waste forms has not yet been completely determined. Change in equipment design and/or experimental procedures may still be made to eliminate any problems that are identified with additional experience.

Briefly, the equipment and procedure were as follows (Figure 15). Specimens were heated inductively in an 18-mm-diameter platinum crucible. Sufficient specimen was used to fill the crucible to a depth of 10 mm calculated on the basis of room temperature density. ZVDP-4 glass specimens weighed about 6.53 g; specimens were weighed before and after heating. The exposed surface

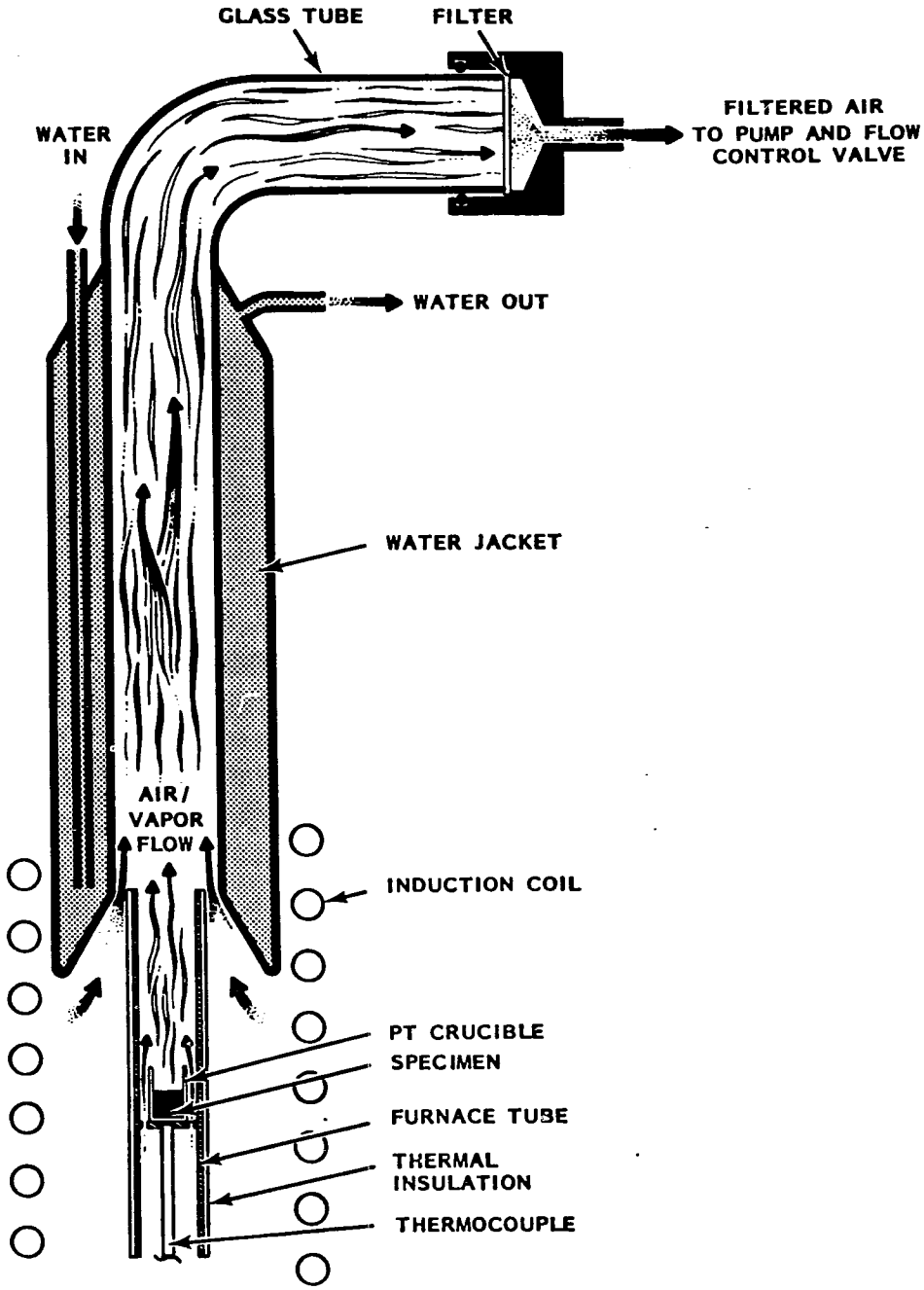


FIGURE 15. High-Temperature Vaporization Apparatus

area of the molten specimens was about 2.5 cm^2. The specimens were heated for 4 hours in room air, and the resulting vapors were passed into a glass chimney capped with a Teflon® filter. Condensed vapors were removed from the filter and chimney and chemically analyzed using ICP and AA.

Four-hour weight loss data normalized to the exposed surface area of the molten specimen in the crucible are shown in Figure 16. The scatter at 1200°C for the ZVDP-4 samples is much larger than experienced with the MCC glass; the cause has not yet been determined. Therefore, the data were simply averaged for the purpose of drawing the line shown. Uncertainties at 1000°C are probably ±0.2 to 0.3 mg, primarily because of the very small weight losses occurring at that temperature.

Figure 16 also shows data for MCC 76-68 glass for comparison. The two glasses exhibit almost identical weight losses at 1100°C, but their temperature dependencies are slightly different. When the data are extrapolated to 800°C (a more realistic accident situation), weight losses of 1.1×10^{-2} and 2.9×10^{-3} mg/cm^2 in 4 hours are obtained for ZVDP-4 and MCC 76-68 glasses, respectively.

Weight-loss data for individual elements are shown in Figure 17. Each point represents the average of up to four samples. Only those elements common to both glasses are plotted. ZVDP-4 glass also loses lithium, but in amounts smaller than those plotted for sodium. Appreciable fractions of molybdenum, ruthenium and tellurium are vaporized from MCC 76-68 glass, although in amounts smaller than plotted for cesium.

The 1000°C point obtained for cesium from MCC 76-68 glass appears to be in error; cesium is the major vapor component and its weight-loss slope should be nearly the same as for the total weight-loss data. Therefore, the cesium line drawn through the two higher temperature points was used, since it has the same slope as that for the total weight-loss data. In all other cases, the lines were simply averaged through all the points.

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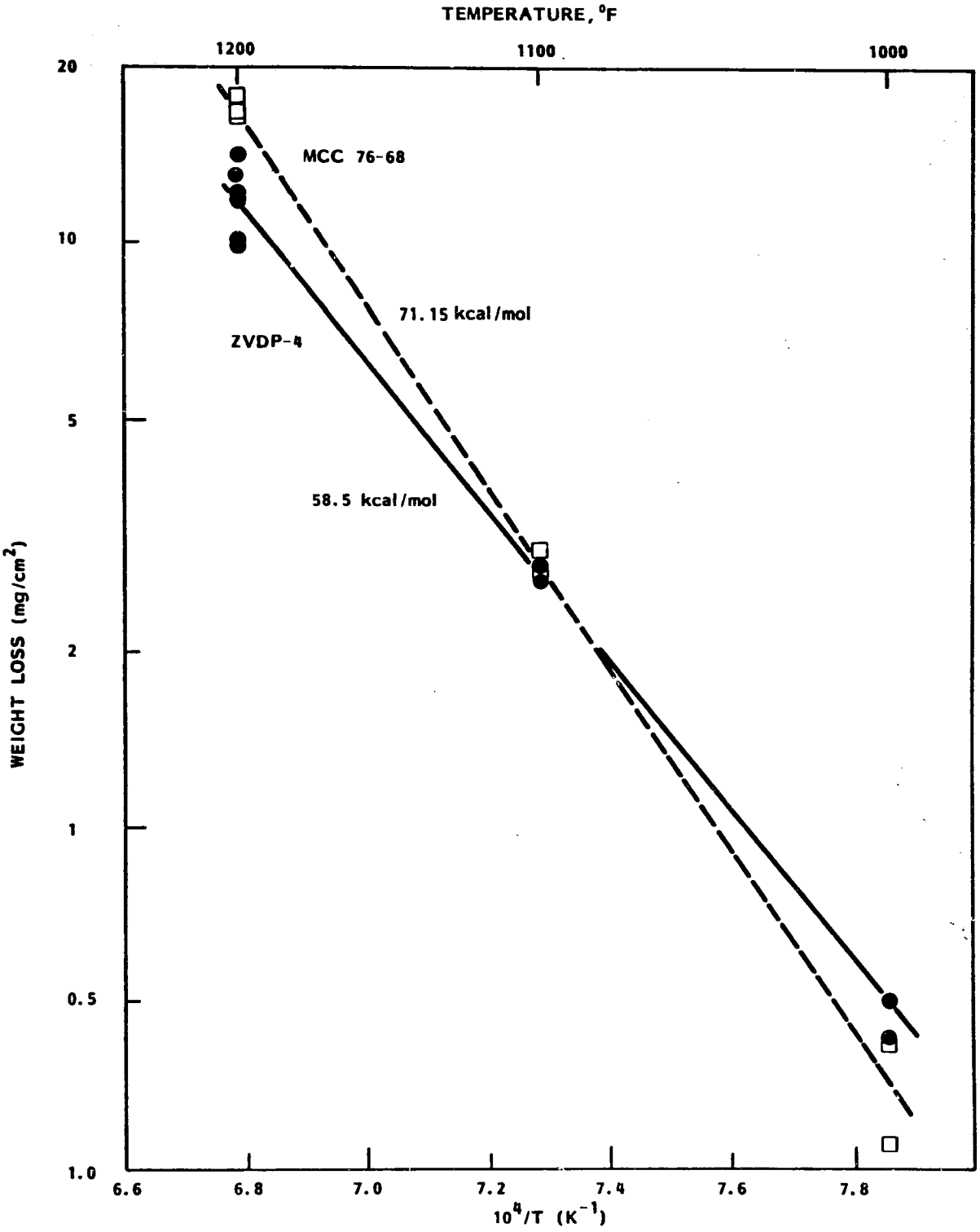

FIGURE 16. Total Specimen Weight Lost by Vaporization in 4 Hours

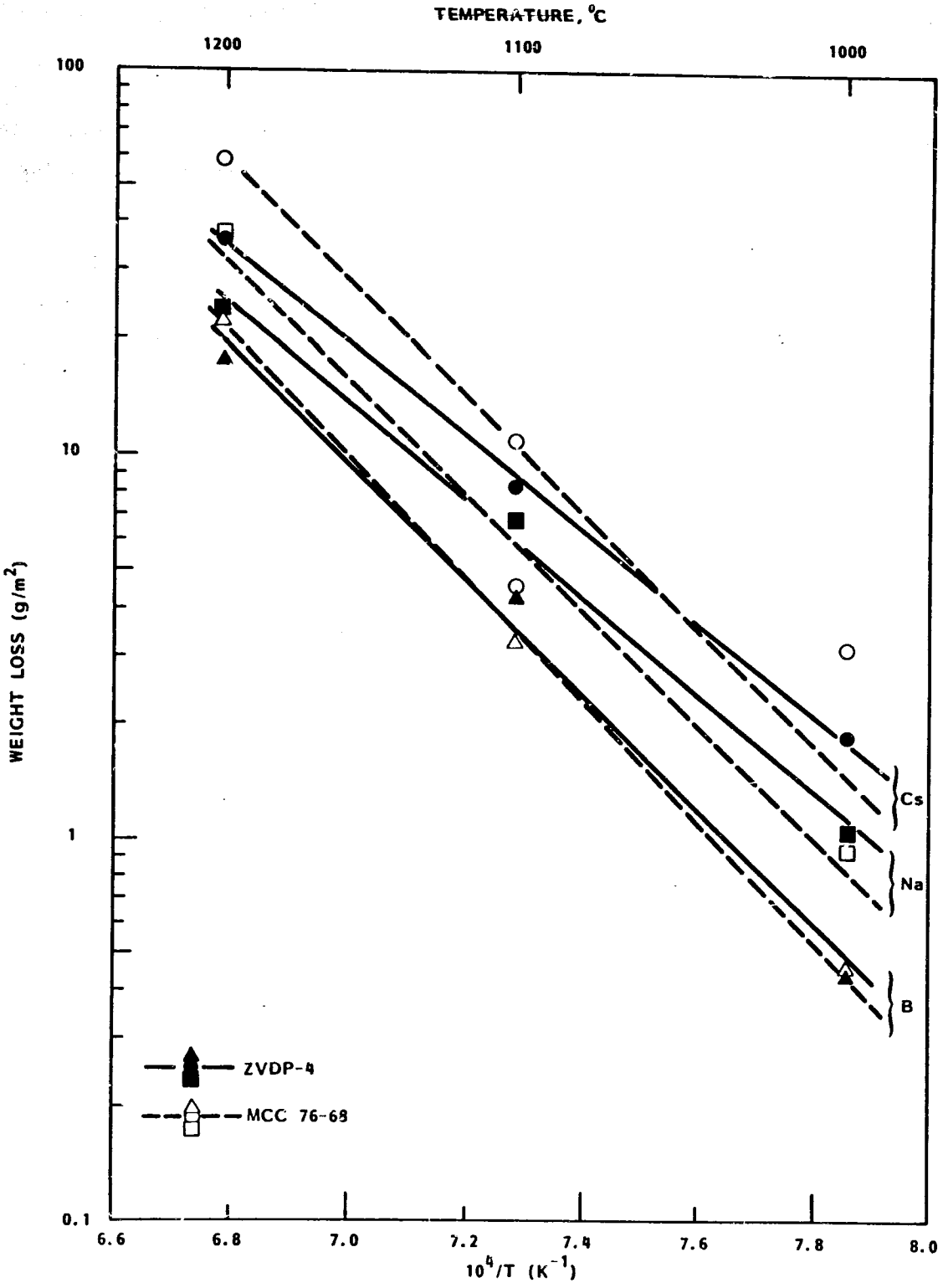

FIGURE 17. Weight Loss of Individual Elements by Vaporization in 4 Hours

An appreciable fraction of the cesium vaporizes from both glasses at high temperatures. However, if the vapor composition is independent of temperature (which is approximately true in the range 1000° to 1200°C), then based on the extrapolation of elemental weight loss data to 800°C, cesium losses would be about 2.2×10^{-3} and 6.3×10^{-4} mg/cm^2 in 4 hours for ZVDP-4 and MCC 76-68 glasses respectively.

As mentioned above, some uncertainties remain in the vaporization test procedure, and therefore in the data presented here. However, it is clear that the vaporization rates of ZVDP-4 and MCC 76-68 glasses at 800°C are very low; the rate for ZVDP-4 glass appears to be about three times that of MCC 76-68.

CANISTER CORROSION

Corrosion of the canisters was evaluated by TMI ZVDP personnel. Each of the four canisters used during the nonradioactive demonstration was fabricated from 304L, 8-in., Schedule 40 stainless steel pipe. Canister corrosion caused by heating to 1050°C during the in-can-melting process was found to be low on both the exterior and interior surfaces of the canisters. Ultrasonic measurements indicated canister wall thickness reductions in the range of 0.004 to 0.020 in. from an average wall thickness of 0.328 in. before heating. This degree of corrosion is about as expected from previous waste canister experience.

CONCLUSIONS

The characteristics of the ZVDP-4 glass generally are similar to those of the borosilicate reference glass MCC 76-68, but with some important differences. The MCC-1P 28-day leach test data show that the leach rate in deionized water is much lower beyond 14 days than for the MCC 76-68 reference glass; behavior is similar to that observed for some other aluminosilicate glasses. Tensile strength of the ZVDP-4 glass is similar to that of MCC 76-68 glass. The impact test on ZVDP-4 glass produced a smaller average particle size and a larger fraction of inhalable particles (<15 μm diameter) than for MCC 76-68 reference glass. Weight loss by high-temperature vaporization at 800°C is estimated to be less than 10^{-4} mg/cm^2 per hour, about 3 times greater than for MCC 76-68.

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