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COMPARATIVE STUDY OF SEVEN GLASSES FOR SOLIDIFICATION OF NUCLEAR WASTES

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INTRODUCTION

The relative leaching behavior of seven alkali borosilicate glasses considered for immobilization of high level radioactive wastes was compared using a static 90°C leach test similar to MCC-1.[1] All compositions (Table I) were compatible with the low melting temperature, 1150°C, viscosity and other process variables required for the French AVM process. The quantity of simulated waste products was from 10.9-15.9 weight %.

EXPERIMENTAL PROCEDURE

Leaching times studied were 1, 3, 7, 14 and 28 days with ratios of glass surface area (SA) to solution volume (V) being SA/V = 1.0 cm^{-1} and 0.1 cm^{-1}. The pH of the D.I. water prior to leaching was 5.5. After leaching the solution pH was measured with a pH microelectrode and concentrations of Si^{4+}, B^{3+}, Al^{3+}, Mo^{6+} determined by ICP spectroscopy, Na^{+} by atomic absorption, and Fe^{3+} by atomic emission spectroscopy. Normalized, average leach rates were calculated as in the Marcoule Research Program. All sample surfaces were polished to a 600 grit surface with dry SiC paper and analyzed before and after leaching with infrared reflection spectroscopy (IRRS).[2,3] The IRRS spectra were normalized to a reflection intensity of 80 for the 1120 cm^{-1} Si-O-Si molecular stretching vibration of vitreous silica by using a shutter in the reference beam of a Perkin-Elmer 467 IR spectrometer

RESULTS

Figure 1 compares the IRRS spectra of the seven glass compositions after 7 days leaching at 90°C, SA/V = 0.1 cm^{-1}. Glasses M1 and M2 show extensive reduction of intensity over the entire spectrum, with M1 being affected the most. This behavior is characterisitic of network dissolution following selective ion leaching.[3,4] This causes roughening of the surface, scattering of the incident IR beam, and a decrease in reflected intensity. Glass M3 is not altered by 7 days leaching, M4 and M6 show evidence of silica-rich film formation, and M5 and M7 show the beginnings of network damage of the surface.

After 14 days, the extent of surface attack progresses for all seven glass

TABLE 1

NUCLEAR WASTE COMPOSITIONS (WEIGHT %)

Oxide (%) \ Glass	M 1	M 2	M 3	M 4	M 5	M 6	M 7
SiO_2	47.6	42.7	51.13	45.6	50.0	48.4	46.1
Al_2O_3	-	8.6	4.05	4.9	3	2.0	5.0
Na_2O	12.4	14.2	13.19	8.8	12.5	11.26	12.5
B_2O_3	18.6	17.8	13.56	22.0	14.41	18.47	14.2
Fe_2O_3	6.4	4.0	1.601	2.8	2.96	2.96	2.96
CaO	-	-	4.10	-	2	3.7[illegible]	4.1
MgO	-	-	0.348	-	-	-	-
MoO_3	2.47	2.09	1.592	2.62	1.7	1.7	1.7
Li_2O	-	-	-	-	2.0	-	2.0
S.W.P.*	15	12.7	10.9	15.9	12.22	12.22	12.22

* Simulated Waste Products

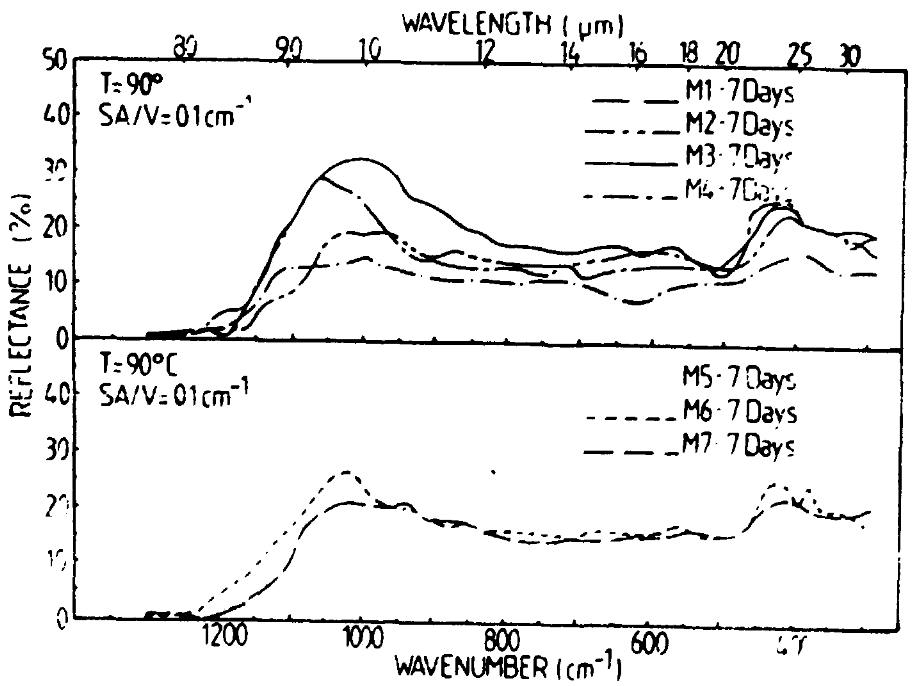

Fig. 1. IRRS after 7 days of corrosion (SA/V = 0.1 cm^{-1}).

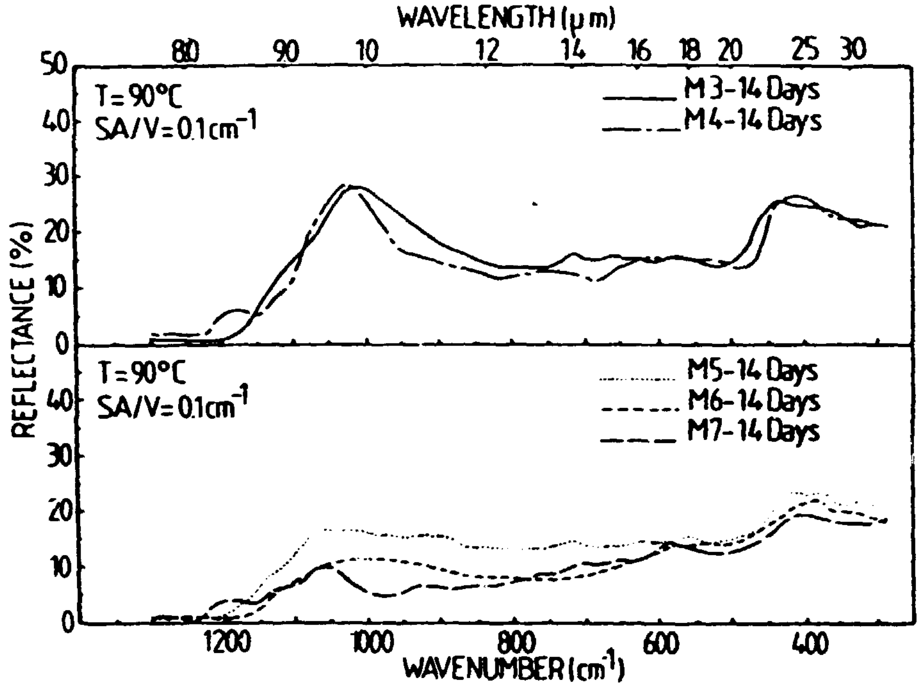

Fig. 2. IRRS after 14 days of corrosion (SA/V = 0.1 cm^{-1}).

(Fig. 2). Glasses M1 and M2 are not included in Fig. 2 because the IRRS reflection intensity is too low to be measured for those glasses due to rapid surface attack. Glass M3 shows the least attack with the spectrum still nearly the same as before leaching. M4 shows dealkalization since the intensity from 950 cm^{-1} to 800 cm^{-1} is reduced. Sharpening of the Si-O-Si stretching vibration at 1030 cm^{-1} indicates that a silica-rich layer has formed. Glass M5, M6 and M7 show more surface attack. Twenty eight days is sufficient time for all seven glasses to show surface deterioration by IRRS, Fig. 3. Glass M3 is considerably more leach resistant than the other formulas, with its original IRRS spectra only slightly affected by leaching. Results for leaching at SA/V = 1.0 cm^{-1} are approximately the same as shown above except glass M7 shows considerably more resistance to leaching.

The rate of glass surface attack is strongly dependent on the concentration of network formers in the glass, Fig. 4. On the ordinate of Fig. 4 is plotted the number of days required for a glass surface to be attacked sufficiently for its IRRS spectrum at 950 cm^{-1} (Si-O-alkali region) to be decreased by 15%. The abscissa is the sum of various combinations of glass network formers. The graph shows that a critical concentration of $SiO_2 + Al_2O_3 + Fe_2O_3 >$ approximately 55% (by weight) or $SiO_2 + Al_2O_3 > 53\%$ must be present in the glass for the surface to be resistant to leaching.

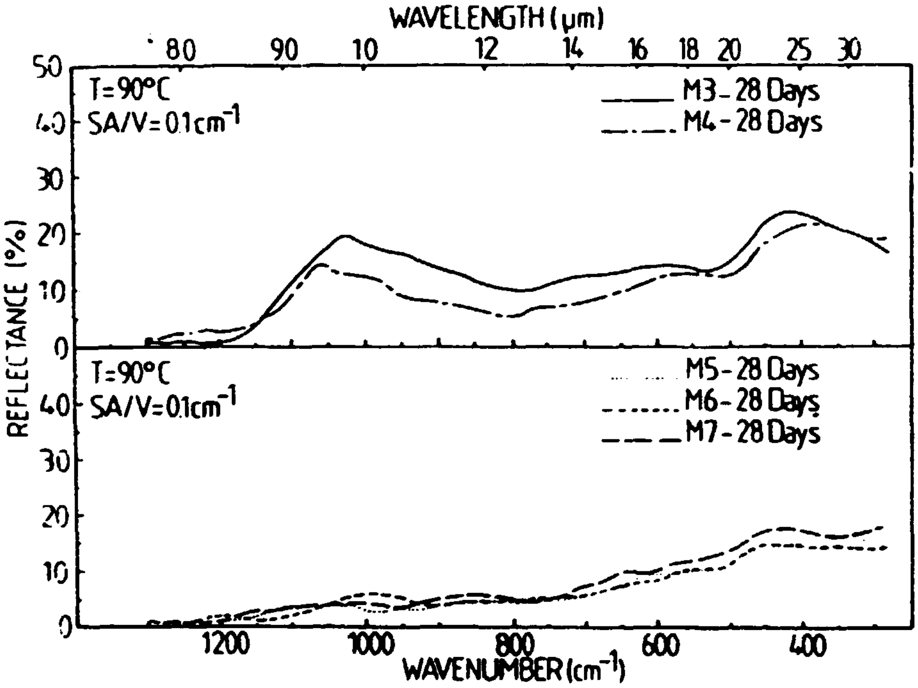

Fig. 3. IRRS after 28 days of corrosion (SA/V = 0.1 cm^{-1})

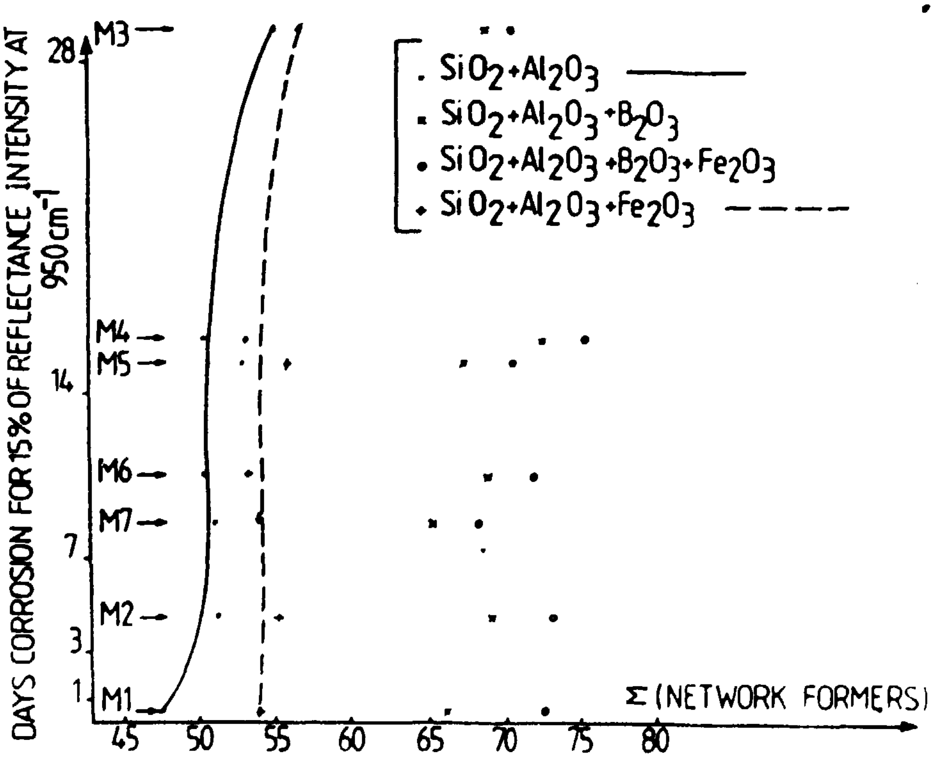

Fig. 4. Influence of network formers.

The time dependence of pH and leachant concentration of Si, B, and Na are shown in Figs. 5, 6, 7, and 8, respectively. All leachant solutions increased in pH with time, with M3 being the slowest and reaching the lowest pH value by 28 days. Leach rates for Si, B, and Na also showed considerable composition dependence with M3 being consistently lower. The cyclic behavior of the leach rates at short times is not fully understood at this time but is probably related to changes in dissolution and precipitation rates of cations that are very sensitive to pH fluctuations.

DISCUSSION

The relative resistance to 90°C static leaching at SA/V = 0.1 cm^{-1} for the seven compositions based upon three analytical criteria is:

(1) IRRS M3 > M4 > M5 ≡ M6 ≅ M7 > M2 > M1

(2) pH M3 > M4 > M6 ≡ M5 ≡ M7 > M1

(3) Solution Analysis M3 > M7 > M5 > M4 ≡ M6 > M2 > M1

Therefore, the final ranking of the seven glasses is:

(4) Overall Resistance M3 > M7 > M4 > M5 ≡ M6 > M2 > M1 .

Results obtained at SA/V = 1.0 cm^{-1} are generally the same but less conclusive due to the small solution volume which makes chemical analyses less accurate.

The above ranking showed that glass M3 performed well in all analyses. At the beginning of the leaching glass M7 had high average leach rates concurrent with a rapid decrease in IRRS intensity and increase in the solution pH. But after 14 days of leaching, the surface layer developed is thick enough and sufficiently impermeable to give very low average leach rates. The most important condition for the nuclear waste glass chemical durability is to have low leach rates ; glass M7 behaves in this manner. Glass M4 yields good results for IRRS analysis but the relatively high average leach rates show that the diffusion through the surface layer is rather easy. The other compositions (M5, M6, M2 and M1) give relatively poor IRRS and leaching rates corresponding to a lower chemical resistance. The worse glass composition of the series studied is glass M1. Average leach rates for the two best glasses, M3 and M7 after 28 days corrosion in 90° C water at SA/V = 0.1 cm^{-1} are :

$$L_{Si}\ (0,28) \cong 2.10^{-5}\ g.cm^{-2}.d^{-1}$$

$$L_{B}\ (0,28) \cong 2.10^{-5}\ g.cm^{-2}.d^{-1}$$

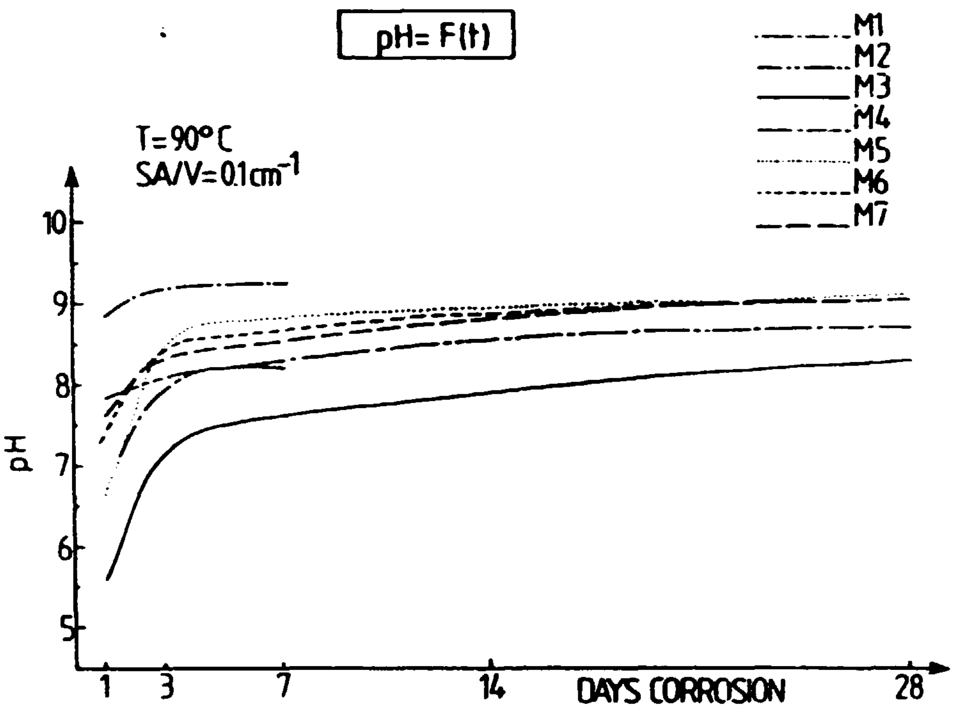

Fig. 5. pH = F(t).

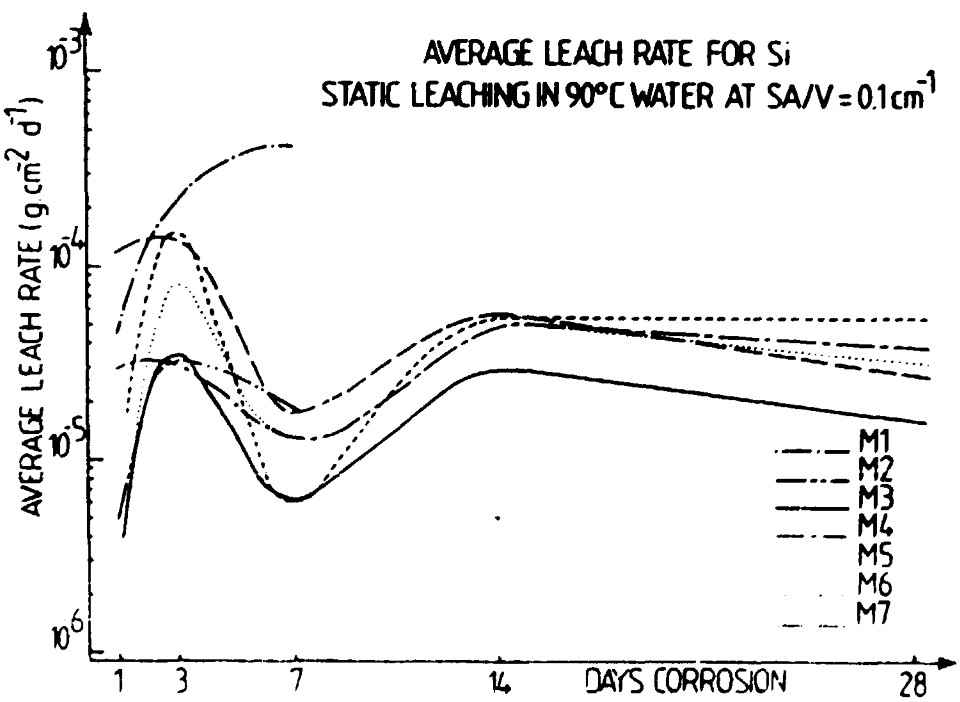

Fig. 6. Average leach rates for Si.

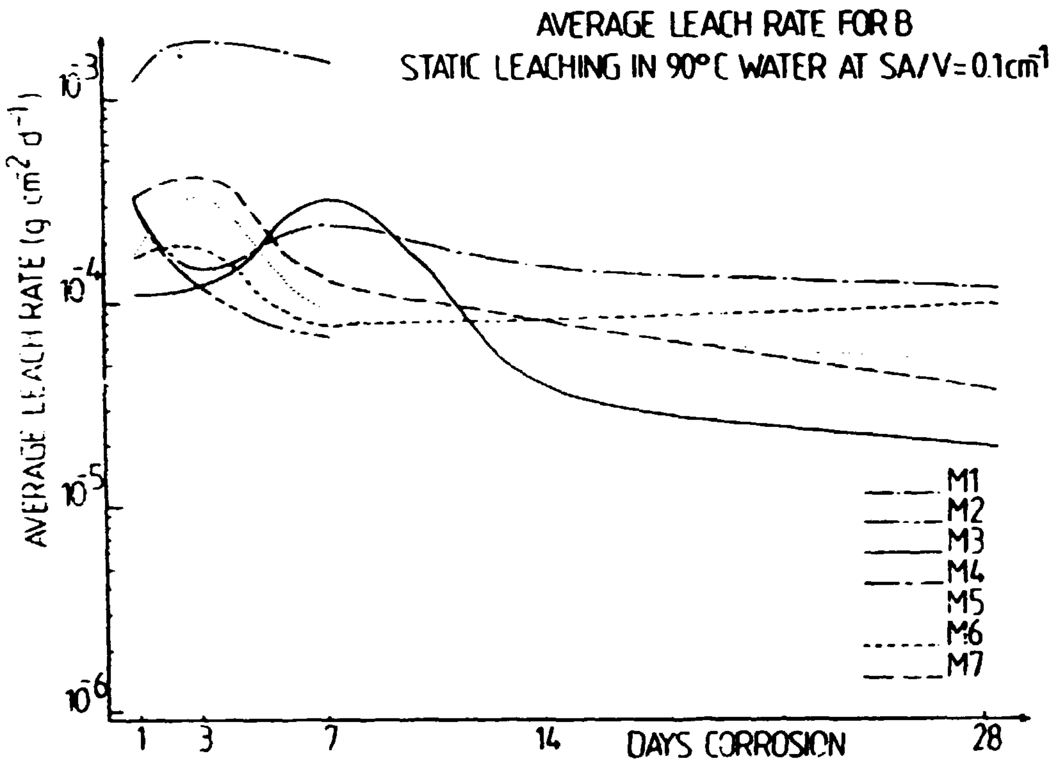

Fig. 7. Average leach rates for B.

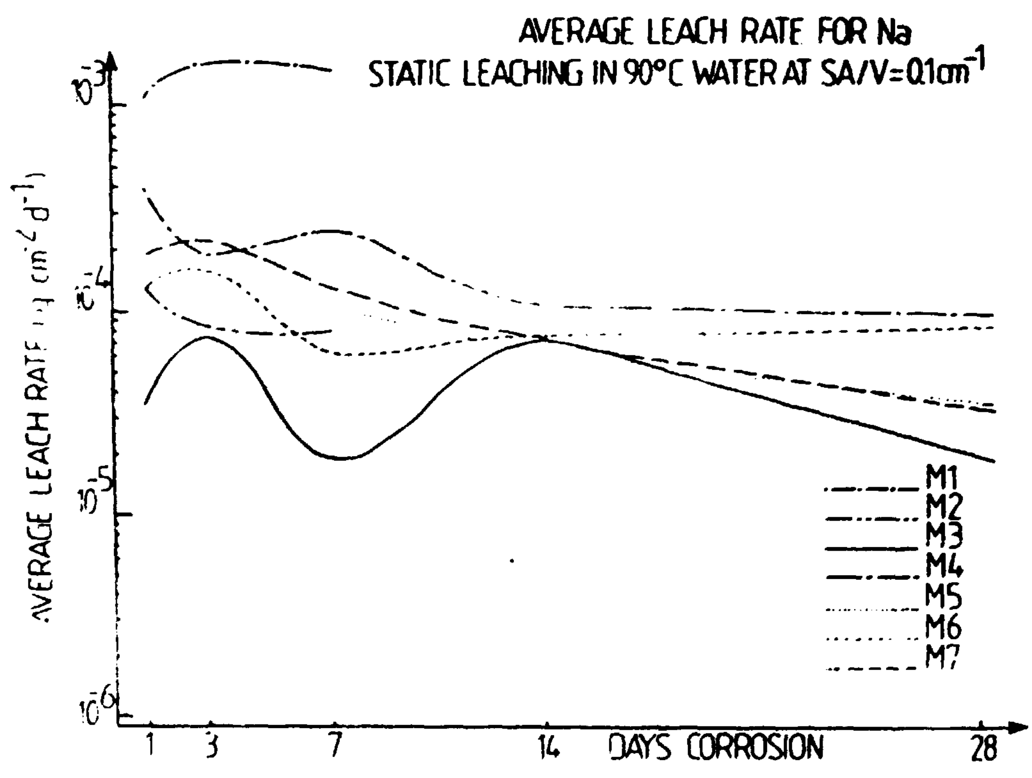

Fig. 8. Average leach rates for Na.

L_{Na} (0,28) $\cong 2.10^{-5}$g.cm^{-2}.d^{-1}

L_{Fe} (0,28) $\cong 3.10^{-7}$g.cm^{-2}.d^{-1}

CONCLUSIONS

With the range of glass compositions studied, it was not possible to determine the effect of each element on leaching behavior, however some conclusions regarding the general influence of the glass network formers can be made:

(1) The addition of Al_2O_3, between 2 and 5% (weight) results in a large increase in the chemical durability of the glass.

(2) The presence of Fe_2O_3, between 1.5 and 3% (weight) is necessary to develop with Al_2O_3 a second protective layer on top of the silica-rich film that results from rapid dealkalization.

(3) To obtain good durability the glass composition must contain more than 51% (weight) of (SiO_2 + Al_2O_3) and more than 54% (weight) of (SiO_2 + Al_2O_3 + Fe_2O_3).

(4) The best result was obtained with glass M3 which contains 55.18% (weight) of (SiO_2 + Al_2O_3) and 56.78% (weight) of (SiO_2 + Al_2O_3 + Fe_2O_3). High leach resistance and good surface stability was present even though this glass contained the largest quantity of Na_2O (13.19%) in the series.

(5) The difference between the results obtained at SA/V = 1.0 cm^{-1} and SA/V = 0.1 cm^{-1} shows the importance of understanding both the effects of glass composition and solution concentrations on the behavior of nuclear waste glasses.

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REFERENCES

1. MCC-1 Static Leach Test (1980) Materials Characterization Center, Battelle Pacific Northwest Laboratory, Richland, Washington.
2. Sanders, D. M., Person, W. B. and Hench, L. L. (1972) Appl. Spectroscopy, 26, 530-536.
3. Clark, D. E., Pantano, C. G. and Hench, L. L. (1972) in Glass Corrosion, Books for Industry, New York, New York.
4. Sanders, D. M. and [illegible]