

AECL 90 4 4

Field Burial Results and SIMS Analysis of the Chalk River Glass Blocks

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In 1959, 25 2-kg hemispherical blocks of aluminosilicate glass, each containing ≈ 90 MBq/g of mixed fission products, were buried in a sandy soil aquifer in the waste management area at the Chalk River Nuclear Laboratories. A second set of blocks, containing ≈ 260 MBq/g mixed fission products, was buried in 1960. One block from each test was retrieved in 1978 to undergo chemical and surface analysis. This report reviews the migration of the ^{90}Sr and ^{137}Cs plume in the soil and presents the results of SIMS depth profiling of the surface of a glass block.

After several years, investigation into glass compositions suitable for the immobilization of nuclear fuel recycle waste,¹⁻³ Atomic Energy of Canada Limited (AECL) initiated an in-ground burial test in 1958, in a sandy soil aquifer at the Chalk River Nuclear Laboratories, to study the leaching of UO_2 fuel recycle waste immobilized in an aluminosilicate glass matrix. Twenty-five 2-kg hemispheres (blocks) of nepheline syenite-based glass were fabricated, each containing ≈ 90 MBq/g of mixed fission products⁴ (whose activity derived predominantly from ^{137}Cs and ^{90}Sr).

The blocks were removed from the melting crucible and buried 1.2 m below the surface of the aquifer, in a 5 by 5 vertical grid pattern oriented normal to the direction of the aquifer flow.⁵ The radioactivity released from the blocks was monitored by a series of downstream ground-water samplers. After one year, no radioactivity had been detected at the samplers,^{6,7} and in 1976 there was still no radioactivity in the surrounding soil that could be directly attributed to release from the blocks.⁸

The lack of results from the burial test prompted a second burial experiment in a separate location in 1960 using a higher fission product loading of ≈ 260 MBq/g and a closer grid spacing. Laboratory tests on these blocks indicated they would leach about 10 times faster than the first set. Both ^{90}Sr and ^{137}Cs were detected in soil samples taken at downstream locations but only ^{90}Sr was detected by the ground-water monitors.⁹

The ground water and soil were periodically sampled and monitored until 1974 when sampling was discontinued. In 1978, a block from each burial test was retrieved to undergo chemical and surface analyses. The results of the field tests on the second set of blocks will be briefly reviewed and recent surface analysis results using secondary ion mass spectrometry (SIMS) to perform an elemental depth profile through the leached surface of a block from the first burial test will be discussed.

Experimental Procedure

Details for the preparation of the 2-kg glass hemispheres can be found in earlier publications.^{3,5,6} The base-glass composition was a mixture of 85 wt% nepheline syenite rock and 15 wt% CaO; the analyzed composition is given in Table I. The fission product mixtures were nitric acid solutions of UO₂ fuel recycle waste whose compositions are given in Table II. The solutions were added to the base-glass composition (1 L/kg) before melting.

The blocks were retrieved from the burial site in 1978 and several surface and interior chips were fractured from each for radiochemical and surface analysis.¹⁰ Fresh surface and interior chips were recently taken from the first block for SIMS depth profiling and analyzed at the Swiss Federal Institute for Reactor Research

Table I. Base Glass Composition (wt%) for the Chalk River Glass Blocks

SiO ₂	51.20	CaO	15.0
Al ₂ O ₃	20.44	Na ₂ O	8.53
K ₂ O	4.26	Fe ₂ O ₃	0.06
MgO	0.02	TiO ₂	<0.01

Table II. Analysis of Waste Solution used for Burial Tests 1 and 2

	Burial Test 1	Burial Test 2
Acidity	6.8 mol/L HNO ₃	8. mol/L HNO ₃
Density	1.24 kg/L	1.39 kg/L
Total solids	44.5 g/L	227. g/L
Nonvolatile solids	22.5 g/L	100. g/L
U	1.9 g/L	9.2 g/L
Pu	0.35 g/L	1.2 g/L
Fe	3.4 g/L	17.1 g/L
Na	4.68 g/L	28.5 g/L
Al	0.75 g/L	3.2 g/L
Ni	0.52 g/L	1.7 g/L
Cr		2.9 g/L
Mg		1.3 g/L
¹³⁷ Cs	6.1 × 10 ⁷ Bq/mL	3.3 × 10 ⁸ Bq/mL
⁹⁰ Sr	3.2 × 10 ⁷ Bq/mL	2.8 × 10 ⁸ Bq/mL
¹⁴⁴ Ce	2.8 × 10 ⁷ Bq/mL	7.0 × 10 ⁷ Bq/mL
¹⁰⁶ Ru	9.2 × 10 ⁶ Bq/mL	7.0 × 10 ⁶ Bq/mL
Total β	2.1 × 10 ⁸ Bq/mL	7.0 × 10 ⁸ Bq/mL

(EIR) using an A-DIDA-SIMS,* which had been modified to accommodate radioactive samples.¹¹ A 12-keV O_2^+ ion beam was used for ion sputtering and an electron beam was used for charge neutralization. Samples were also analyzed at the Whiteshell Nuclear Research Establishment (WNRE) using a commercial instrument[†] and a 4-keV Ar^+ ion beam for profiling.

Field Results

Preburial leach tests on the 1958 and 1960 glass block compositions showed leach rates, at 25°C, in replenished ground water similar to that in the aquifer, of 1.2×10^{-12} and $6.2 \times 10^{-12} \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ respectively, based on ^{137}Cs or ^{90}Sr release.¹² The fractional release rates for these ions were much greater than those for ^{106}Ru or ^{144}Ce .

In 1971, field measurements showed that the ^{90}Sr release front had migrated $\approx 33 \text{ m}$ (108 ft) from the blocks. The leach rate of the blocks in 1974 (at $\approx 6^\circ\text{C}$ ambient), calculated from total ^{90}Sr released,⁸ was $\approx 5.8 \times 10^{-15} \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Soil-sample results indicated that most of the Cs and Ce was irreversibly bound to the soil, while a fraction of the Sr ions reversibly exchanged with the soil¹² and moved at a rate of $\approx 0.75 \text{ cm} \cdot \text{day}^{-1}$ as compared with the ground water velocity of 15 to 20 $\text{cm} \cdot \text{day}^{-1}$ (seasonally dependent). The Cs and Sr plume positions in 1963 are shown for comparison in Fig. 1. No actinides have been detected on any soil samples at 0.3 m from the blocks.

Field measurements of ^{137}Cs released to the downstream soil from the second set of blocks showed that, in 1979, $>90\%$ of the Cs was still within 30 cm (1.2 ft) of the blocks while the remaining Cs was within 7.5 m (25 ft).¹³

The Sr plume data have been interpreted¹⁴ using a computer program to model the sorption of Sr onto the various mineral fractions present in the soil. The migration behavior of the Sr in the aquifer suggests that it is controlled by both fast ion exchange with the soil and by sorption on an iron-oxhydroxide grain coating and a ferromagnesian fraction on the sand. Studies on ^{137}Cs migration at the Chalk River Nuclear Laboratories (CRNL) have not progressed sufficiently to allow assessment of the ^{137}Cs field data. Neither laboratory nor field leach rate measurements indicate a congruent (t^0), or diffusion-controlled ($t^{-0.5}$) dissolution mechanism for the glass. The leach rate time dependence, inferred from the ^{90}Sr ground-water concentrations, is in the range $t^{-0.8}$ to $t^{-1.3}$, and it has been suggested that dissolution is being inhibited by a surface layer.¹⁴

Surface Analysis

Earlier optical and scanning electron microscopy (SEM) studies of samples taken from the outer surface of both test blocks showed no evidence of a surface layer.¹⁰ Electron spectroscopy (ESCA) studies indicated that the outermost few atomic layers were depleted in Ca, Na, and K relative to their values in the unleached bulk glass.¹⁵ There were minor enhanced concentrations of Sr, Cs, Cr, Zn, Fe, and Pb on the surface. These analyses, however, gave no measure of the depth of water penetration into the glass nor any information on elemental concentrations beyond the first few atomic layers.

The SIMS depth profile of a sample from the uncorroded bulk of the first Chalk River glass block is shown in Fig. 2(a). The major glass constituents (Ca, Na, Al, Si, and K) appear to reach a steady state ion intensity within about 20 nm

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[†]SIMS II, Physical Electronics Industries, Inc., Eden Prairie, MN.

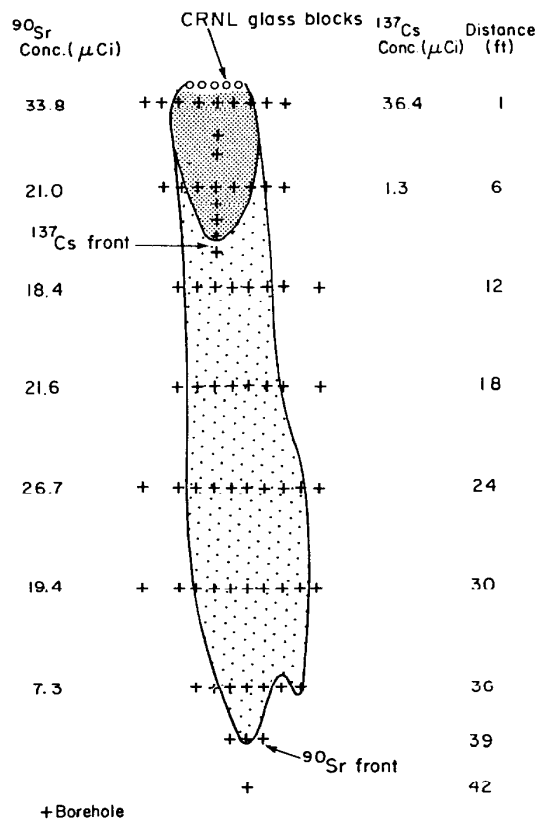


Fig. 1. Position of the ^{90}Sr and ^{137}Cs downstream plume from the second burial test of the CRNL glass blocks in 1963.

of the surface, indicating that beam damage or charge neutralization effects are limited to the near-surface region. The depth profile of the corroded surface is shown in Fig. 2(b). The surface is significantly enriched in Mg, which could be due to the formation of an Mg-silicate mineral from the Mg-rich ground water. The Ca, Cr, Fe, and Na are slightly depleted down to a depth of about 70 to 80 nm, while Si, K, and Al remain virtually unaffected beyond 20 nm. The radionuclides U and La appear to be marginally depleted at the surface relative to Ba and Cs.

In an attempt to improve resolution using a lower sputtering rate, a second corroded sample was profiled at WNRE. The concentration-depth profiles obtained were calculated in terms of cation atomic percent as a function of depth (Fig. 3(a),(b)) using the computer program MASS.¹⁶ The major glass constituents Al, Ca, and Na are all depleted to depths of approximately 20, 35, and 90 to 100 nm, respectively, while Si is enriched to a depth of ≈ 60 nm (Fig. 3(a)). The ion concentrations for K and Cr (and La, Cs, and Ba; not shown) remain almost at their bulk value throughout the profile. The surface also appears to be slightly enriched in Fe and Mg to a depth of ≈ 45 nm and U to ≈ 100 nm, and highly enriched in Th to a depth of ≈ 100 nm.

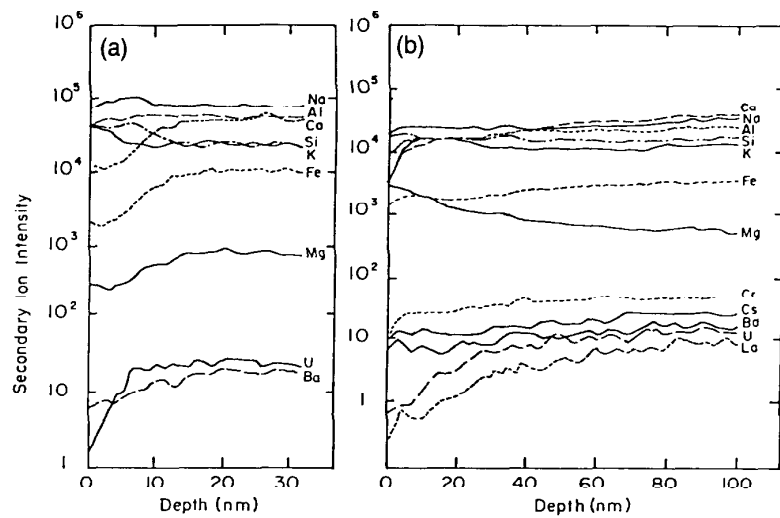


Fig. 2. (a) SIMS depth profile of the interior bulk of a CNRL glass block from the first burial test; (b) SIMS depth profile of the corroded surface of a CRNL glass block from the first burial test.

Profiling of a freshly cleaved interior bulk surface showed that the bulk concentration value (0.05 at.%) for Th was reached after about 10 nm and corresponded closely to the value reached after 100 nm in the leached glass. (Thorium does not appear in Table I, as no chemical analysis was performed for this element.) It is likely that the surface enhancement of Th in the leached glass is due to its retention in the layer formed as the glass dissolves. If it is assumed that, due to its low solubility, no Th is lost to the ground water and that it remains in the leached layer, it can be estimated that from 340 to 400 nm of glass has been dissolved. Based on the total ⁹⁰Sr release from the second set of blocks and their calculated field leach rate of $5 \times 10^{-15} \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, the thickness of the leached

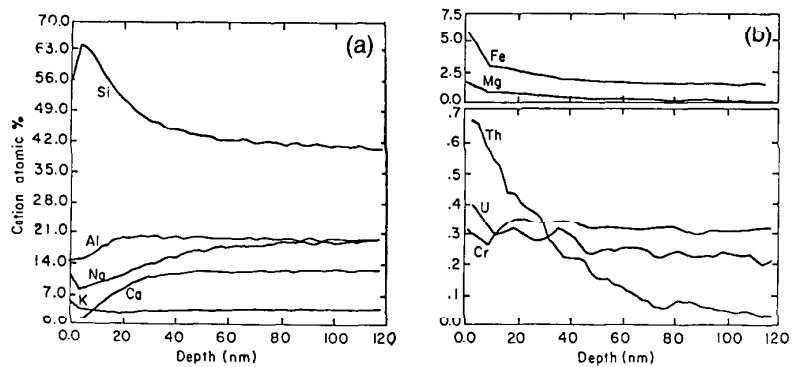


Fig. 3. SIMS depth profiles (at.%) of the corroded surface of a CRNL glass block from the first burial test.

layer was estimated¹⁵ to be ≈ 35 nm. The 400-nm thickness calculated here implies that the leach rate is at least an order of magnitude higher, which suggests that some Sr may be retained near or at the surface of the blocks. There is experimental evidence for the presence of a fragile surface layer, which was destroyed during the recovery of the block since, during probing for the block position, one block from the second burial test was disturbed and several days later a ⁹⁰Sr spike corresponding to release from a fresh surface for the whole block appeared at the closest ground-water monitor. This suggests that a surface layer had been disturbed, allowing fresh access of ground water to the block.¹³

Summary and Conclusions

The field leaching results from 1960 to 1974 for the second set of Chalk River glass hemispheres buried in a sandy soil aquifer have been reviewed. The ⁹⁰Sr and ¹³⁷Cs leach rates measured from the total release to the downstream soil were much lower than the leach rates measured in the laboratory. This can be attributed in part to the lower temperature of the burial site than that of the laboratory test. It has also been suggested that a mineralized layer may have formed at the surface of the blocks, which can inhibit radionuclide release. The ⁹⁰Sr migration in the aquifer appears to be controlled by both ion-exchange processes and by sorption on iron oxyhydroxide in the soil.

The SIMS depth profiling studies of the surface of a retrieved block show that Ca, Na, Cr, and Fe are depleted within 100 nm of the surface while Si, Mg, and Th are surface-enriched. The enrichment of Mg is consistent with the formation of an Mg-silicate mineral from Mg in the ground water. The thickness of material removed during the 20-year burial test was estimated from the Th enrichment and corresponded to a 400-nm loss from the original surface, suggesting a leach rate about an order of magnitude higher than that predicted from the ⁹⁰Sr release data. The SIMS results alone do not necessarily confirm the existence of a layer providing a barrier to radionuclide release but, in conjunction with the ⁹⁰Sr release behavior, do suggest its presence.

Acknowledgments

The authors wish to thank P. J. Hayward and T. T. Vandergraaf for their helpful comments on the manuscript.

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