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ANALYSES OF SRS WASTE GLASS BURIED IN GRANITE IN SWEDEN AND SALT IN THE UNITED STATES (U)

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ABSTRACT

Simulated Savannah River Site (SRS) waste glass forms have been buried in the granite geology of the Stirpa mine in Sweden for two years. Analyses of glass surfaces provided a measure of the performance of the waste glasses as a function of time. Similar SRS waste glass compositions have also been buried in salt at the WIPP facility in Carlsbad, New Mexico for a similar time period. Analyses of the SRS waste glasses buried in-situ in granite will be presented and compared to the performance of these same compositions buried in salt at WIPP.

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INTRODUCTION

Long-term, safe disposal of high-level nuclear waste (HLW) is a significant problem facing many nations today. One method of disposal of HLW is immobilization in a high-integrity waste form and emplacement in a suitable geologic repository [1]. Today, glass is the material of choice for immobilizing hazardous radionuclides in nuclear HLW due to its excellent performance features and processing characteristics [2]. The fabrication of nuclear waste glass is a relatively straight-forward process that has been demonstrated world-wide [3]. Nuclear waste glass has also been shown to be stable and perform well under many different types of anticipated as well as accident conditions [2-4]. However, most of these tests have been conducted in controlled laboratory environments. It is the purpose of the present study to summarize waste glass performance under more realistic repository conditions [5] and more specifically, to assess and compare the behavior of SRS simulated waste glass buried in granite in Sweden and in salt in the United States. The objectives of this effort are as follows:

(1) characterize, assess and summarize, the performance of SRL 131/TDS, SRL 131/35% TDS, and SRL 165/TDS waste glasses after being buried for one and two years, at 90°C in granite at Stripa and

(2) compare the performance of SRS waste glass 165/TDS in granite at Stripa with its performance in salt at WIPP.

SUMMARY

• The chemical durability of SRL waste glass compositions buried for up to two years in granite at Stripa was excellent and also improved with increasing time.

• These glasses were characterized by the formation of two main surface layers. The outermost layer, α, consisted of deposited material due primarily to the surrounding environment, while the layer underneath, β, was the glass interaction zone.

• Quantitative analyses of the glass interaction zone showed that less than 1 μm of the glass had interacted with the environment, after being tested under accelerated conditions of 90°C for two years.

• The glass exhibiting the best chemical durability was SRL 165/29.8% TDS, the reference composition. Next best was the high waste loading glass SRL 131/35% TDS followed by the lower waste loading glass SRL 131/29.8% TDS.
• Comparison of the performance of SRL 165/TDS waste glass after being buried at 90°C in granite and salt for up to two years, shows that the glass performed well in both environments and in a very similar manner.

BACKGROUND

STRIPA: A cooperative project involving the Swedish Nuclear Fuels Safety Division of the Nuclear Fuel Supply Co., the University of Florida (UF), and the Savannah River Laboratory (SRL) was initiated in 1982 [6,7]. Experiments were conducted on Swedish and SRL simulated nuclear waste glasses buried in granite in the Stripa mine in Sweden. In this pioneering effort, three SRL nuclear glass compositions, 165/29.8% TDS, 131/35% TDS, and 131/29.8% TDS, were used. (Table 1). The glass samples were fabricated into two configurations, "pineapple slices" and "mini-cans" and were tested at 90°C and ambient conditions after 1, 3, 6, 12 and 24 months of burial in granite.

Table 1. SRL Waste Glass Compositions Buried in Stripa, Sweden

Component	131/29.8% TDS	165/29.8% TDS	131/35% TDS
Glass Frit			
SiO_2	40.6	47.7	37.6
Na_2O	12.4	9.1	11.5
B_2O_3	10.3	7.0	9.6
TiO_2	0.7	—	0.7
Li_2O	4.0	4.9	3.7
MgO	1.4	0.7	1.3
ZrO_2	0.4	0.7	0.3
La_2O_3	0.4	—	0.3
Simulated Waste			
Fe_2O_3	13.4	13.4	15.8
MnO_2	3.9	3.9	4.5
Zeolite	2.9	2.9	3.4
Al_2O_3	2.7	2.7	3.2
NiO	1.6	1.6	1.9
SiO_2	1.2	1.2	1.4
CaO	1.0	1.0	1.2
Na_2O	0.9	0.9	1.0
Coal	0.7	0.7	0.8
Na_2SO_4	0.2	0.2	0.2
Cs_2CO_3*	0.1	0.1	0.2
$SrCO_3$*	0.1	0.1	0.2
U_3O_8*	1.1	1.1	1.3
Total:	100.0	99.9	100.1

* TDS waste was doped with Cs, Sr, and U

WIPP: The largest international field testing program, involving burial of simulated nuclear waste glasses, is the joint WIPP/SRL Materials Interface Interactions Tests (MIIT) [8,9]. This effort involves the participation of eight nations including France, Germany, Belgium, Japan, Canada, Sweden, the United Kingdom and the United States. The MIIT program includes the burial of almost 2000 samples of simulated waste forms, canister and overpack metals, and geologic specimens, buried in the salt geology of the Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM. SRL compositions studied include 165/29.8% TDS and 131/35% TDS waste glass systems, ARM-1 (an NBS reference glass), and synthetic basalt (a natural glass known to be stable for millions of years). The overall chemical compositions of SRL waste glasses were similar to those used in Stripa, although they did not contain zeolite or uranium. All glass samples were fabricated into the shape of "pineapple slices", similar to those used in the Stripa tests. In this five-year program, samples were tested at 90°C for 6, 12, and 24 months of burial, thus far.

EXPERIMENTAL PROCEDURE

The Stripa tests were the first in-situ experiments involving burial of Savannah River simulated waste glass compositions in a geologic formation. While two different types of sample configurations were used in these tests, only data from the "pineapple slice" configuration will be discussed in this paper. After fabrication and assembly, the samples were buried in 3-meter deep bore holes, 345 meters below the surface in the Stripa mine. At these locations, heater rods were placed through 20-mm holes located in the center of each of the samples, which subsequently were used to heat the samples and surrounding geology to 90°C. The samples were removed at time intervals of one month, three months, six months, one year, and two years [10]. There have been many post-test studies and analyses performed on these systems and reported elsewhere [10-18]. The sample matrix for the present cooperative venture is summarized in Table 2 and represents only a small part of the more extensive Stripa and WIPP programs.

Table 2. Sample Matrix for Current Joint Study

	Stripa: OM	Stripa: SEM	Stripa: XES	Stripa: WAXD	Stripa: FTIRRS	Stripa: SIMS	WIPP: SIMS
1 Mo.						Univ. of Chalmers- SWEDEN	
165/29.8% TDS						X	
131/35% TDS						X	
131/29.8% TDS						X	
3 Mo.							
165/29.8% TDS						X	
131/35% TDS						X	
131/29.8% TDS						X	
6 Mo.							
165/29.8% TDS							
131/35% TDS							
131/29.8% TDS							
12 Mo.	SRL						
165/29.8% TDS	X	X	X	X			X
131/35% TDS		X	X	X			
131/29.8% TDS							
24 Mo.					Univ. of Fla.		
165/29.8% TDS	X	X	X	X	X	X	X
131/35% TDS		X	X	X	X	X	
131/29.8% TDS					X	X	

The current study involves assessing SRL compositions by the use of a joint interlaboratory approach. This includes the use of Optical Microscopy (OM), Scanning Electron Microscopy/ X-ray Energy Spectroscopy (SEM/XES), Wide Angle X-ray Diffraction (WAXD), and Electron Microprobe Analysis (EMP) performed at Savannah River Laboratory, Fourier Transform Infrared Reflection Spectroscopy (FT-IRRS) conducted at the University of Florida, and Secondary Ion Mass Spectroscopy (SIMS) performed at Chalmers University in Sweden.

Optical Microscopy was used to provide a quick, qualitative overview of the reacted glass surface. Data obtained from WAXD helped to characterize the phases formed on the outermost surface of the leached glass, which resulted primarily from the geologic environment. SEM/XES analysis was used to define the morphology and what elements were qualitatively present on and throughout the leached surface of the glass. EMP revealed both qualitative and quantitative concentrations of elements of interest in the the main outermost surface layer. FT-IRRS provided information pertaining to the glass structure and how the Si-O and Si-alkali bonds were disrupted due to interactions with the geology [19,20]. Finally, SIMS profiles examined the leaching depths and provided quantitative concentrations and profiles of chemical species present in each of the leached surface layers [10,21]. These techniques, along with others used in the program, are summarized schematically in Figure 1.

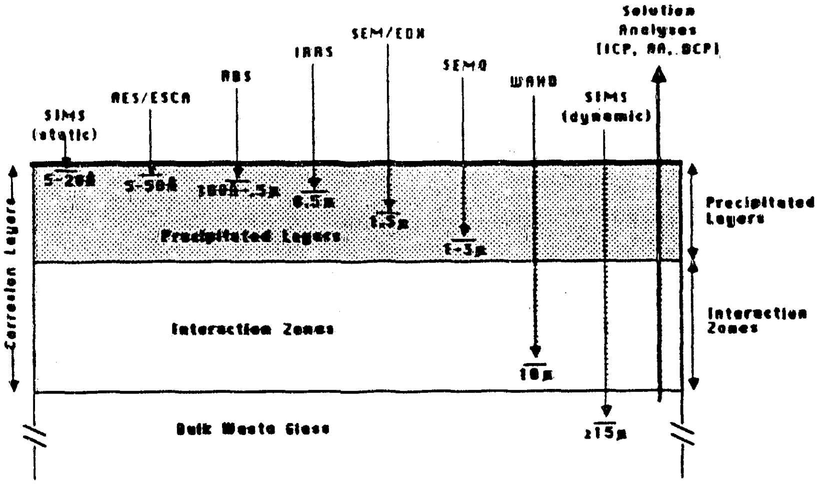


Figure 1. Analytical Tools Used in the Stripa and WIPP Studies

RESULTS AND DISCUSSION

A. Performance of SRL Waste Glass Compositions Buried in Granite at Stripa for up to Two Years

<u>Morphology and General Characterization of Deposited and Leached Glass Surfaces (OM, WAXD, SEM/XES, and EMP)</u>

From optical microscopy, outer deposits were noted on all waste glasses buried in the granite geology at Stripa. The thicknesses of the deposits varied and were inhomogeneous. WAXD showed primarily amorphous patterns on all glass samples, indicating that the deposits examined were either non-crystalline or contained phases of very small crystallites. SEM and XES examined the cross- sections of the simulated nuclear glass systems and showed that the deposited outermost layer varied from 1 to 6 μm. For the glass composition most representative of DWPF production, SRL 165/TDS, this layer was less than 2 μm thick and the glass interaction layer underneath, was less than 1 μm thick. In addition, there was not large differences noted between glass/glass interfaces compared to glass/granite interfaces. The outermost layers were generally characterized by significant amounts of silicon, aluminum, iron, barium and calcium. An enrichment of uranium was also observed in some of the layers studied.

In Figure 2, SEM/XES analyses are shown for SRL 165/TDS waste glass buried in Stripa for one year. Corresponding WAXD profiles show no significant amount of crystallinity present on the surfaces of the samples. From these analyses, it can be noted for the reference glass SRL 165/TDS, that an outermost layer (α), consisting primarily of deposited phases derived from the surrounding environment, forms over most of the glass samples. Under this layer, is a interacted glass zone, which begins the original glass surface and provides a measure of the amount of interaction experienced by the waste glass system (β). This interaction zone was seen to be very small in all cases, thus indicating that the glass performed well and exhibited good chemical durability in these tests.

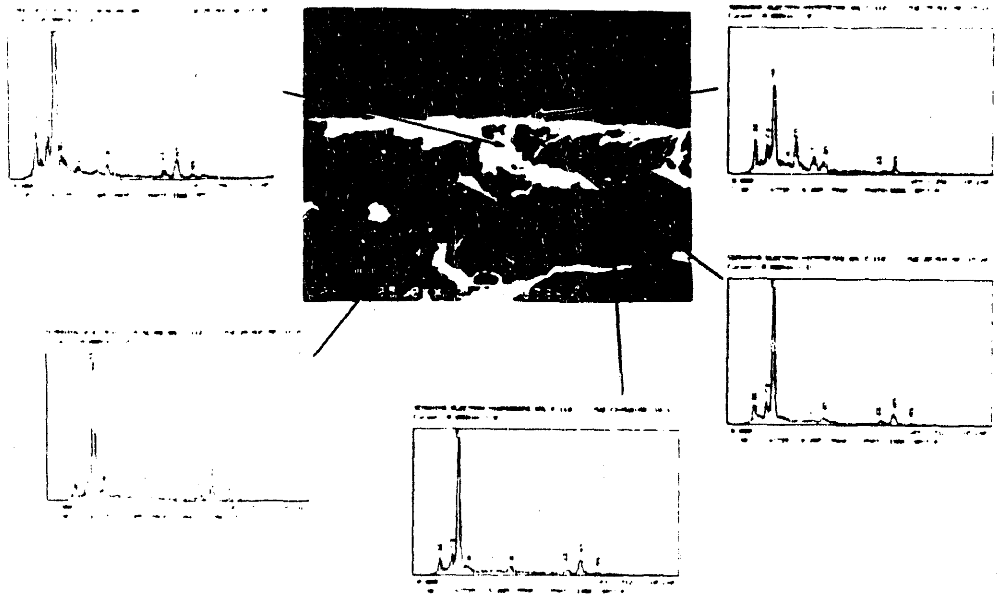
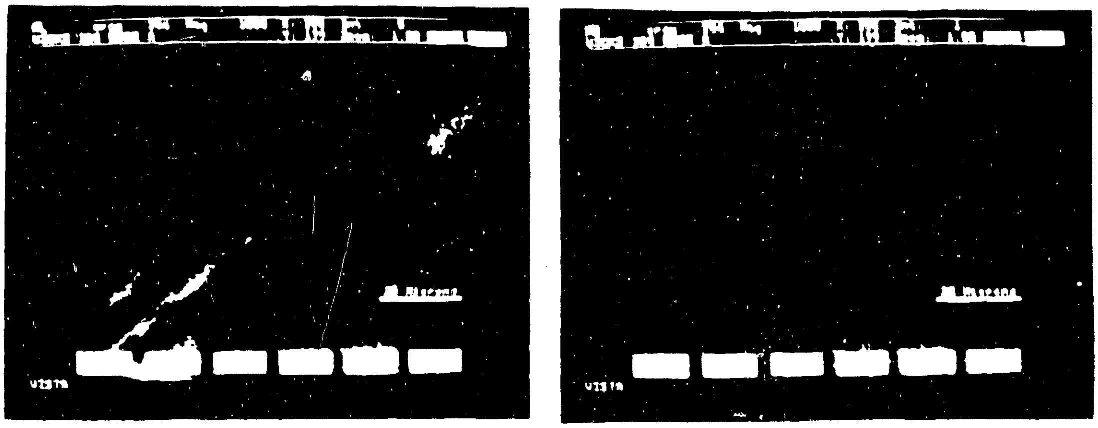


Figure 2. SEM/XES Analyses of SRL 165/TDS Waste Glass in Stripa after One Year

Elemental mapping was performed using electron microprobe analysis. From these analyses of 165/TDS waste glass, buried in Stripa for two years, silicon was a dominant species found throughout the leached layers, in large quantities and mostly uniformily distributed. In Figure 3, elemental maps of aluminium and magnesium show that some outer precipitates contain aluminum-rich phases, which are also depleted in magnesium.



Aluminum *Magnesium*

Figure 3. Elemental Maps of Al and Mg for 165/TDS Waste Glass in Stripa after Two Years

Effects of Glass Composition, Temperature and Degree of Leaching (FT-IRRS)

FT-IRRS was used to provide a semi-quantitative picture of the relative durability of the three SRL waste glass compositions in Stripa. In Figure 4, profiles of all three glasses are summarized after burial for two years in the granite site, both at 90°C and at ambient temperture (8-10°C). For comparison, the profiles of the unreacted or unchanged glasses are superimposed [14].

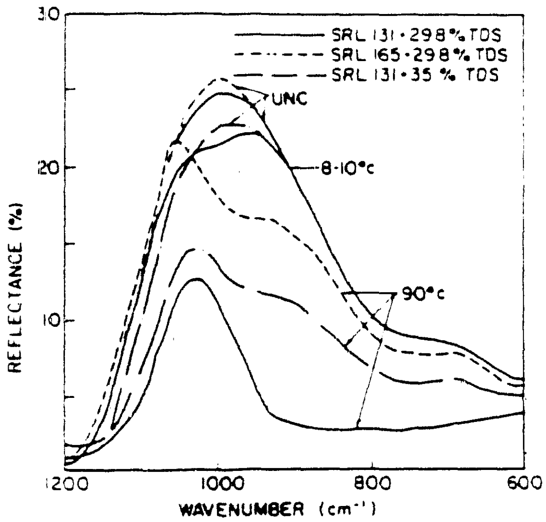
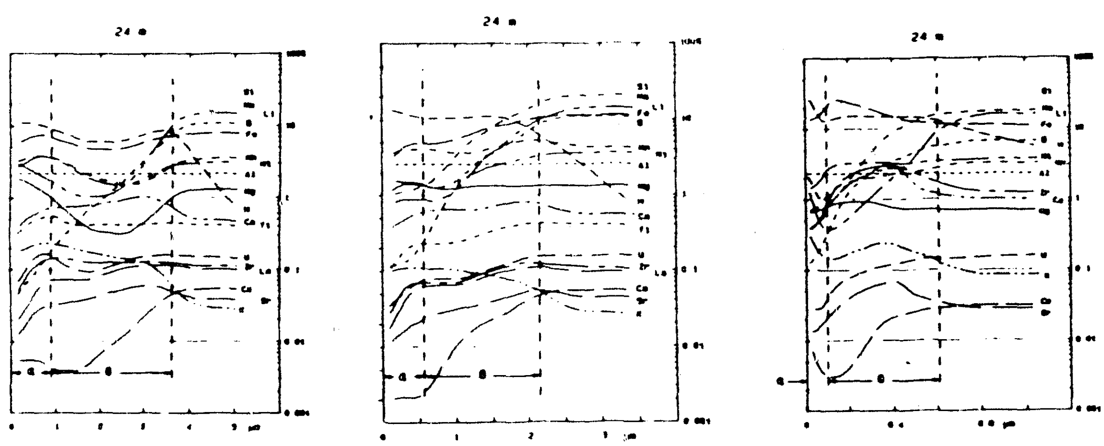


Figure 4. FT-IRRS Analyses of SRL Waste Glasses in Stripa

These profiles represent the Si-O and Si-alkali interactions. The degree of leaching is related to the amount of change in these profiles, before and after testing. As noted in the figure, the higher the temperature, the more change that is observed, indicating that glass leaching increases as temperature increases, which is to be expected. Also, the most durable glass (smallest change) is noted as the reference composition, 165/TDS. The next most durable, is the high waste loading composition 131/35% TDS and the least durable, is an early formulation designated as 131/TDS. For all of these compositions, the intensity changes were determined and found to be relatively small, even for the relatively less durable glasses, thus indicating good leaching behavior. These findings are consistent with the SEM/XES results which indicate good glass behavior and are consistent with other laboratory tests which have shown (a) 165/TDS waste glass has excellent chemical durability and (b) the high waste loading glass of 131/35% TDS performs better than the lower loaded composition 131/29.8% TDS.

Quantitative Depth Profiling of Elements of Interest Throughout Leached Glass Surface Layers (SIMS)

In Figure 5, profiles of key elements and definitions of precipitated and leached layers are summarized by SIMS for all three glass compositions after being buried for 2 years in granite at Stripa [21]. In the outermost region α, elemental distributions are very different than seen within leached layers of the glass underneath. This outermost region is characterized by a significant amount of Si that is present and a near absence of B. A dominant element in the surrounding granite environment is silica. Below α is the β interaction zone, which is characterized by a relative 'enrichment' in Si, Fe, Al, and H, and a relative 'depletion' in B and the alkali elements.



SRL 131/29.8% TDS SRL 131/35% TDS SRL 165/29.8% TDS

Figure 5. SIMS Analyses of SRL Waste Glasses in Stripa as a Function of Waste Glass Composition

In Figure 6, the growth of these layers for reference glass 165/TDS, after 1, 3 and 24 months is also shown [21]. There are many important points contained within these data. Included are the observations that elemental tendencies are very similar for the three leaching time intervals, and the depth of the glass leaching zone is very small, and its rate of growth appears to be decreasing with time.

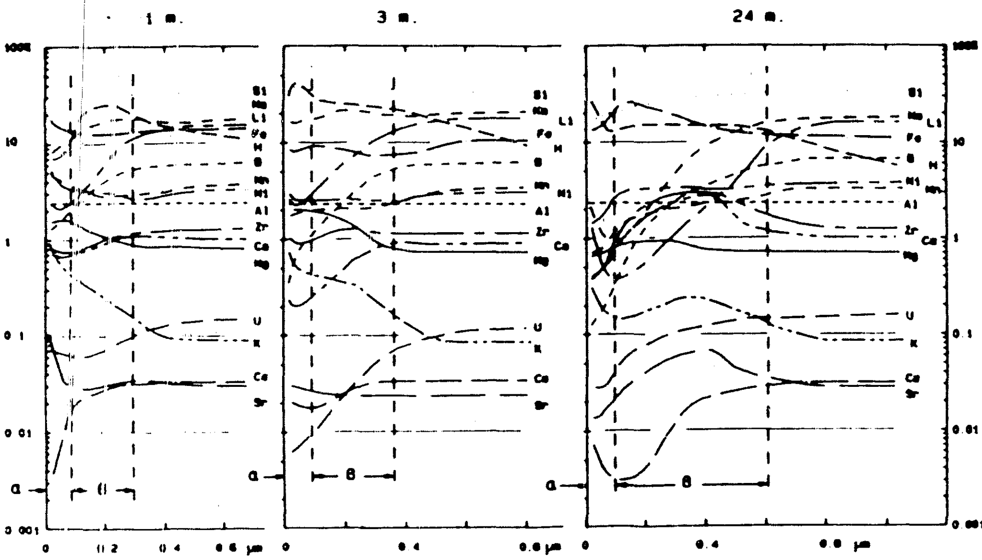


Figure 6. SIMS Analyses of SRL 165/TDS Waste Glass in Stripa as a Function of Time

The SIMS data are consistent with observations made by SEM/XES and FT-IRRS, but provide another level of detail of elements of interest, their profiles through leached layers, and a quantitative determination of depths of precipitated and glass interaction zones. The glass interaction zone, β, can even be broken-up to higher levels of detail, if desired. These analyses clearly show that the waste glass systems buried in granite at Stripa for up to two years, exhibit not only excellent resistance to leaching, but the leaching performance improves with increasing time.

B. Comparison of the Performance of SRL 165/TDS Waste Glass Buried In Granite at Stripa and In Salt at WIPP, at 90°C, for Two Years

Similar SRL 165/TDS waste glass compositions were buried in the Stripa mine in granite in Sweden and in the salt facility at WIPP, located in New Mexico. SIMS analyses were used to compare the performance of SRL waste glasses buried for up to two years in both geologies [21,22]. While the precipitation layer, α, is primarily a function of the geologic conditions, the amount of glass reacted or leached, is most directly related to the glass interaction zone, β [23,24]. These measured depths taken from SIMS profiles are summarized graphically in Figure 7. From these data and for these testing conditions, we see that SRL 165/TDS waste glass performs similarly in granite as in salt.

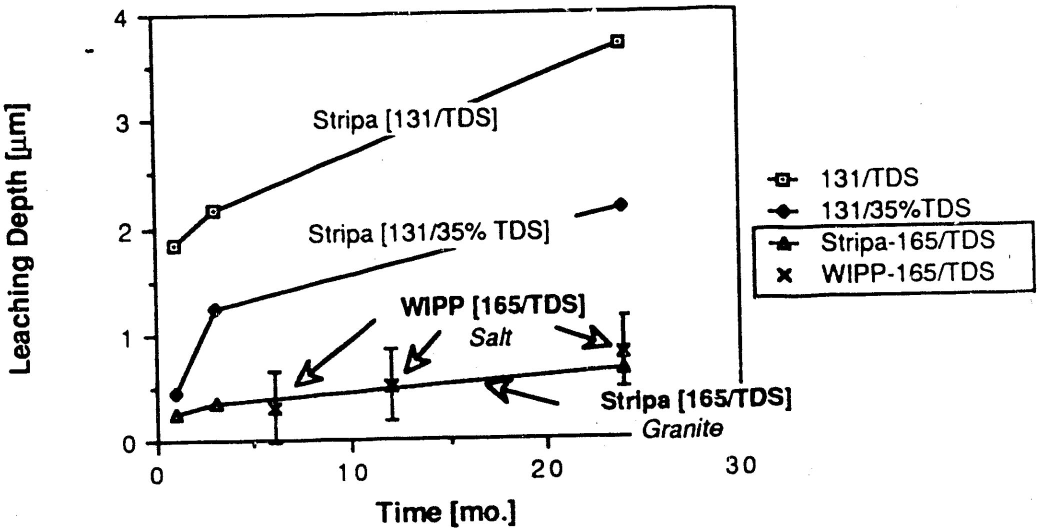


Figure 7. In-Situ Testing of SRS Waste Glass in Granite (STRIPA) and SALT (WIPP)

CONCLUSIONS

Based on all analyses performed to date on glasses tested in both Stripa and WIPP, the performance of SRL waste glasses is excellent, in both the granite and salt environments. In addition, the in-situ testing programs have also shown that the behavior of Savannah River reference waste glass is similar in the two different geologic media. Finally, the field data supports laboratory tests and findings which indicate that the chemical durabilty of SRL waste glass is not only very good, but actually improves further with increasing time.

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