Conf-9206194--3

WSRC-MS--91-562

DE92 015928

MIIT: INTERNATIONAL IN-SITU TESTING OF NUCLEAR-WASTE GLASSES - PERFORMANCE OF SRS SIMULATED WASTE GLASS AFTER 5 YEARS OF BURIAL AT THE WASTE ISOLATION PILOT PLANT (WIIP) (U)

by

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A paper proposed for presentation at the
3rd International Conference on Advances in Fusion and Processing of Glass
New Orleans, Louisiana
June 10 - 12, 1992

This report was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

MIIT; INTERNATIONAL IN-SITU TESTING OF NUCLEAR WASTE GLASSES-PERFORMANCE OF SRS SIMULATED WASTE GLASS AFTER 5 YEARS OF BURIAL AT THE WASTE ISOLATION PILOT PLANT (WIPP)

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ABSTRACT

In July of 1986, the first in-situ test involving burial of simulated high-level waste [HLW] forms conducted in the United States was started. This program, called the Materials Interface Interactions Test or MIIT, comprises the largest, most cooperative field-testing venture in the international waste management community. Included in the study are over 900 waste form samples comprising 15 different systems supplied by seven nations. Also included are about 300 potential canister or overpack metal samples along with more than 500 geologic and backfill specimens. There are almost 2000 relevant interactions that characterize this effort which has been conducted in the bedded salt site at the Waste Isolation Pilot Plant (WIPP), near Carlsbad, New Mexico. The MIIT program represents a joint effort managed by the Savannah River Technology Center (SRTC) in Aiken, S.C., and Sandia National Laboratories (SNL) in Albuquerque, N.M., and sponsored by the U.S. Department of Energy. Involved in MIIT are participants from national and federal laboratories, universities, and representatives from laboratories in France, Germany, Canada, Belgium, Japan, Sweden, the United Kingdom, and the United States.

In July of 1991, the experimental portion of the 5-year MIIT study was completed on schedule. During this time interval, many in-situ measurements were performed, thousands of brine analyses conducted, and hundreds of waste glass and package components exhumed and evaluated after 6 mo., 1 yr., 2 yr. and 5 yr. burial periods. Although analyses are still in progress, the performance of SRS waste glass based on all data currently available has been seen to be excellent thus far. Initial analyses and assessment of Savannah River (SR) waste glass after burial in WIPP at 90°C for 5 years will be presented.

INTRODUCTION

In order to assess, understand and to be able to predict the long term behavior of SR waste glass forms under a wide range of conditions, a multiphase experimental program has been in progress at the Savannah River Site for more than ten years (Figure 1). One of the most important components of this program involves repository interactions testing which includes (a) laboratory scale waste glass leaching studies (b) repository simulation experiments (rock-cup tests) and (c) in-situ or field testing of waste glass and package components.

There have been four joint international field testing programs involving burial of SRS waste glass forms. These include burial of Savannah River (SR) glasses in (a) the granite geology of the Stripa mine in Sweden, (b) boom clay in Mol, Belgium, (c) limestone in the United Kingdom, and (d) the salt geology of the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, U.S.A.

By putting together these various components of the repository interactions testing efforts, one can obtain as thorough an understanding as practically possible of the performance of SR waste glass forms under realistic repository conditions.

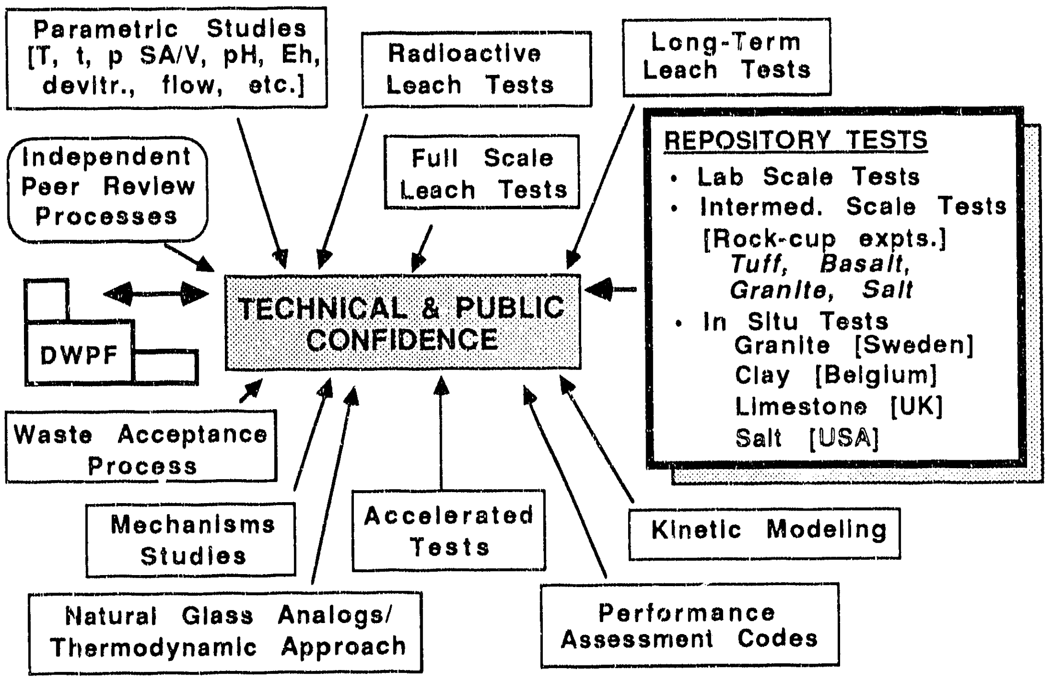

Figure 1. Overview of the Savannah River Waste Glass Program

MIIT PROGRAM

A primary objective of the MIIT program is to assess the behavior of simulated Savannah River Defense Waste Processing Facility [DWPF] waste glass, along with proposed package components, under anticipated and accelerated testing conditions, in a realistic salt environment. It is also desirable to relate this behavior to that of other national and international systems as well as other potential geologic repository environments [1]. In MIIT, simulated waste glass, potential canister and overpack materials, and backfill and geologic specimens were fabricated in the shape of pineapple-slices'. Sample surfaces were then ground and polished to a high quality and reproducible, mirror-like finish. The samples were then stacked on heater rods in various stacking sequences in order to produce interfaces of interest. There were seven different stacking sequences used in MIIT in a total of fifty assemblies. The completed units were then inserted into boreholes located in a test room at WIPP approximately 650 meters below the surface, in the bedded salt Salado Formation. Brine was added to most of these boreholes and the samples and surrounding geology heated to 90°C over the entire 5-year testing period. Various in-situ measurements and brine analyses were conducted at the boreholes at pre-determined time intervals and at 6 mo., 1 yr., 2 yr. and 5 yrs., samples were exhumed for detailed analyses and performance assessment. Due to the unique design of these assemblies, there were several important capabilities in MIIT not found in most other field tests. First, as a result of the modular assembly design, time dependent data could be obtained from a single borehole. And second, because of the simple interactions existing in many of the boreholes, solution data could also be obtained and ultimately, correlated with detailed surface analyses. In Figure 2, the fifty MIIT sample assemblies are shown prior to burial .

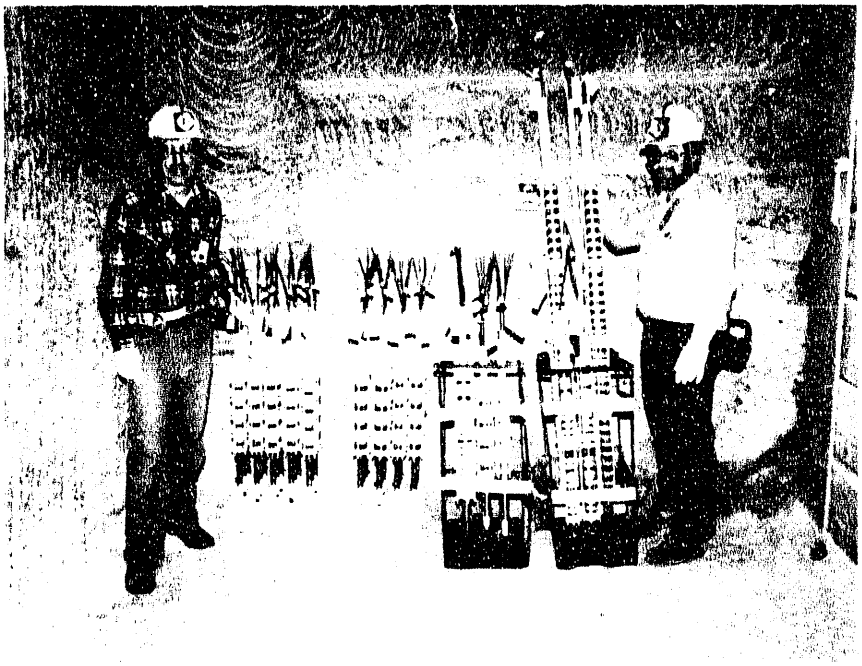

Figure 2. MIIT Sample Assemblies

The logistics associated with the MIIT program, including selection and procurement of samples, fabrication and installation of assemblies, and tracking of the hundreds of pre- and post- test samples and analyses performed, which involved many participants from universities, national, federal, and international laboratories, were computer assisted. In Figure 3, an overview of the past, present and future logistics associated with the entire MIIT program is summarized.

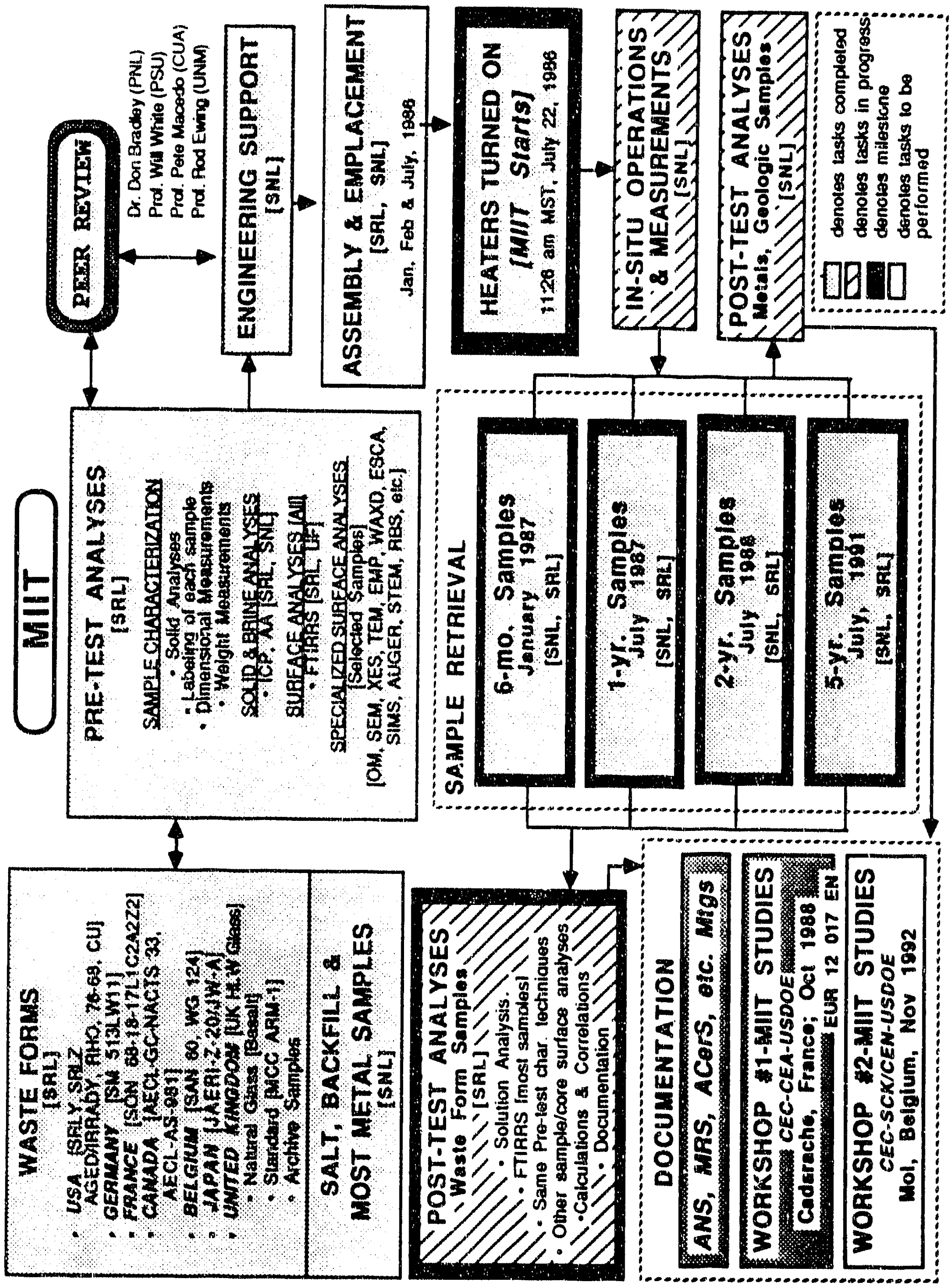

Figure 3. Overview of MIIT Program

MIIT ANALYSES

MIIT samples were exhumed from WIPP at 6 mo., 1 yr., 2 yrs, and 5 yrs. These samples were examined using a variety of analytical tools in laboratories around the world, and later correlated with solution analyses. This paper will focus on the performance of SR waste glass and will emphasize contributions from Chalmers University in Sweden, Catholic University of America, University of Florida, Clemson University, Georgia Institute of Technology, and SRTC. Analyses discussed will involve results from Optical and Scanning Electron Microscopy (OM/SEM), Energy Dispersive X-rays (EDX), Secondary Ion-Mass Spectroscopy (SIMS), Fourier Transform Infrared Reflection Spectroscopy (FTIRRS), and Wide Angle X-ray Diffraction (WAXD). In addition to the variety of surface studies performed, brine analyses using Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS), will also be presented. These data will then be correlated and compared to existing regulations.

RESULTS

At first look, the waste compositions from different countries and the glass formulations designed to immobilize those wastes appear to vary considerably. However, from glass science, we know that all of the different waste and glass components can play only one of three major roles in the glass structure; network formers, intermediates or modifiers. By grouping constituents for each waste form into these three categories, a ternary was constructed (**Figure 4**). Note how this representation emphasizes the compositional similarities between the many different waste forms studied world-wide, which further suggests, that the behavior of defense waste glass forms such as the SR composition, might be expected to be similar to commercial waste glass formulations, such as those in actual production overseas **[2]**.

Salt and Glass Interaction Layers

Cross-sections of reacted glasses interfaces were examined by SEM/EDX for SR 165/TDS waste glass buried for five years at 90°C. Two general interaction layers were identified; an outermost *precipitated zone* (α), consisting mainly of deposited salt phases and underneath, a *glass reaction zone* (β).

Precipitated Zone (α)

The precipitated zone was characterized by enrichment of elements such as Mg and Cl, which are found in the salt and surrounding brine, along with additional minor constituents. The precipitated region can vary in thickness and is generally heterogeneous. Based on analyses conducted at the University of New Mexico, Rockwell International, the CEA-France, and SRTC, both crystalline and amorphous phases were observed. Crystalline phases included NaCl, KCl, $MgCl_2$, $CaSO_4$, silicates, as well as a variety of other minor constituents **[3]**.

The α zone was further resolved into two distinct layers at Chalmers University-Sweden using SIMS. These layers were defined as α_0 and α_1- a precipitated salt layer and precipitated glass layer, respectively. The outermost precipitated layer α_0 consisted primarily of the various amorphous and crystalline salt

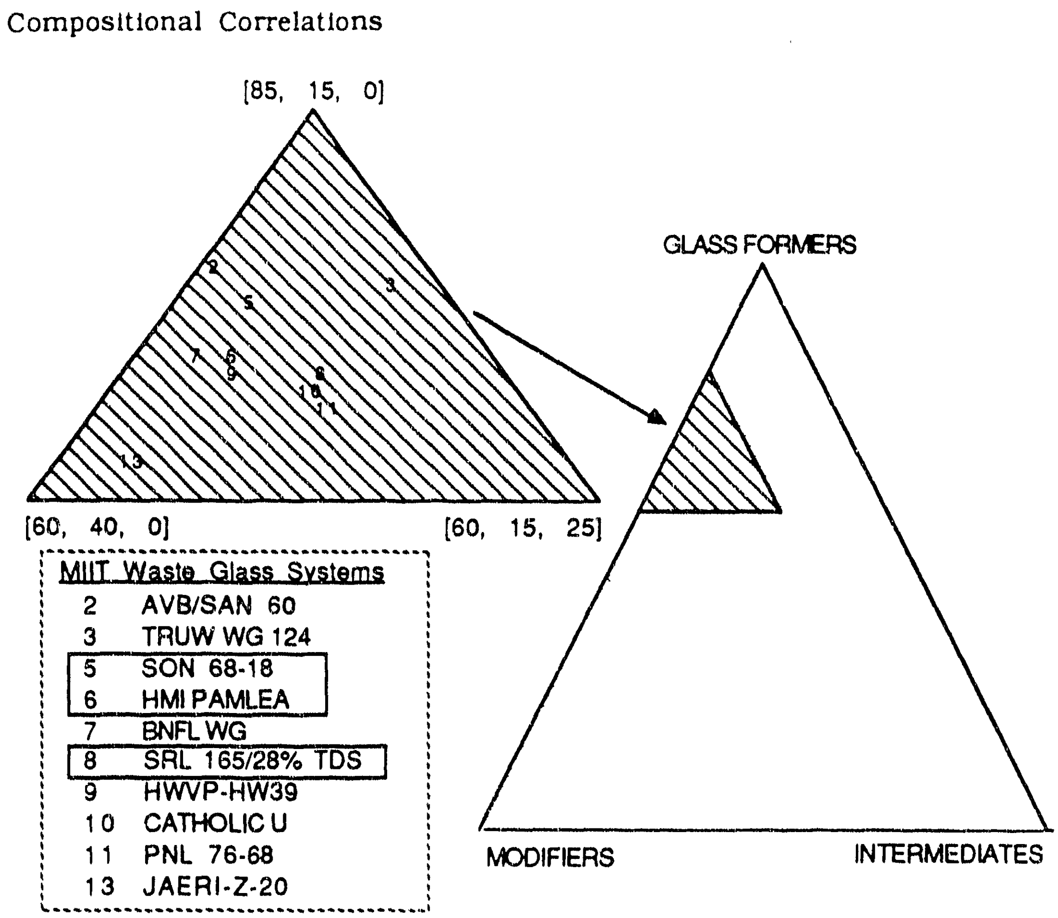

Figure 4. MIIT Waste Form Compositional Correlations

deposits defined above and immediately under this layer, adjacent to the glass surface, was a thin precipitated glass layer α_1. This region was observed to be more uniform than the outermost layer and contained elements from the glass that were leached and precipitated within this region. The chemistry of this layer was characterized by a relative enrichment of Mg and Cl, along with Si, and relative depletion of Al, Zr, and Fe (elements which are generally among the least leachable components in the glass).

Glass Reaction Zone (β)

Directly under the precipitated zone is the glass reaction zone (β), and in between these two regions is the α/β salt/glass interface. The amount of glass leached during these tests is best reflected by changes in the glass reaction zone.

Examinations of the glass reaction zone were performed on pre- and post- test samples, by the University of Florida using Fourier Transform Infrared Reflection Spectroscopy (FTIRRS). These data showed that changes in Si-O and Si-O-alkali peak intensities and positions were small, indicating that disruption to the network structure and leaching of the glass, were also small. The total amount of interaction occurring in this region was then placed on a semi-quantitative scale by measuring, via SEM/EDX at SRTC, the depth of penetration of major components of the surrounding geology and brine (Mg and Cl) into the glass surface. These measurements were performed as a function of different testing conditions and time, and include not only the interactions of SR 165/TDS waste glass alone, but also leaching of this composition in the presence of proposed package components **[3,4,5]**. These data, which are summarized in **Table 1**, show that (a) only a very small amount of interaction occurs between the SR 165/TDS waste glass and salt environment, (b) the rate of glass interaction slows down with increasing time, and (c) that there is no significant effect of the metals tested on leaching of this waste glass system.

Table I. Measured Thicknesses of the Glass Reaction Zone (β) for SR Waste Glass (165/TDS) as a Function of Time and Canister Materials

	Burial Times			
	6 Mo.	**1 Yr.**	**2 Yrs.**	**5 Yrs.**
SR 165/TDS Thicknesses (μ)	<1	1-3	2-3	2-6
Average Penetration Rates (μ/yr)		~2.0	~1.25	~0.8
SR 165/TDS + 304L SS				~2-6
SR 165/TDS + TiCode 12				~2-6

The most quantitative analysis of the glass reaction zone was performed by Chalmers University in Sweden using Secondary Ion-Mass Spectroscopy (SIMS), which has a detection sensitivity in the ppm range and a depth resolution of approximately 50 Å **[6,7]**. As many as 35 key elements were profiled in this region, which was resolved into three distinct layers; β_0 [Major Depletion Zone], β_1 [Gradient Zone], and β_2 [Diffusion Zone]. A typical SIMS profile is shown in **Figure 5**.

The β_0 [Major Depletion Zone] layer is located immediately under the α_1 layer and marks the start of the first of three glass reaction regions. This layer is characterized by enrichment of major brine components such as Mg and H, and depletion of major glass components. Under the β_0 layer is the β_1 [Gradient Zone] layer. This region is also characterized by enrichment of major brine components, including Mg and H, but also by depletion of alkali and alkali earth components of the glass. This zone also contains an interesting feature, the presence of a potassium peak. The distance from the α/β interface to the potassium peak in β_1 represents the main reaction front of the glass after interacting with the salt/brine environment. The third and final layer in the glass reaction zone is designated β_2 [Diffusion Zone]. This region represents the innermost glass leached layer. It is similar to the gel layer which forms in many simpler glass systems when leached. This zone is characterized by enrichment of H from the solution and depletion of Li from the glass.

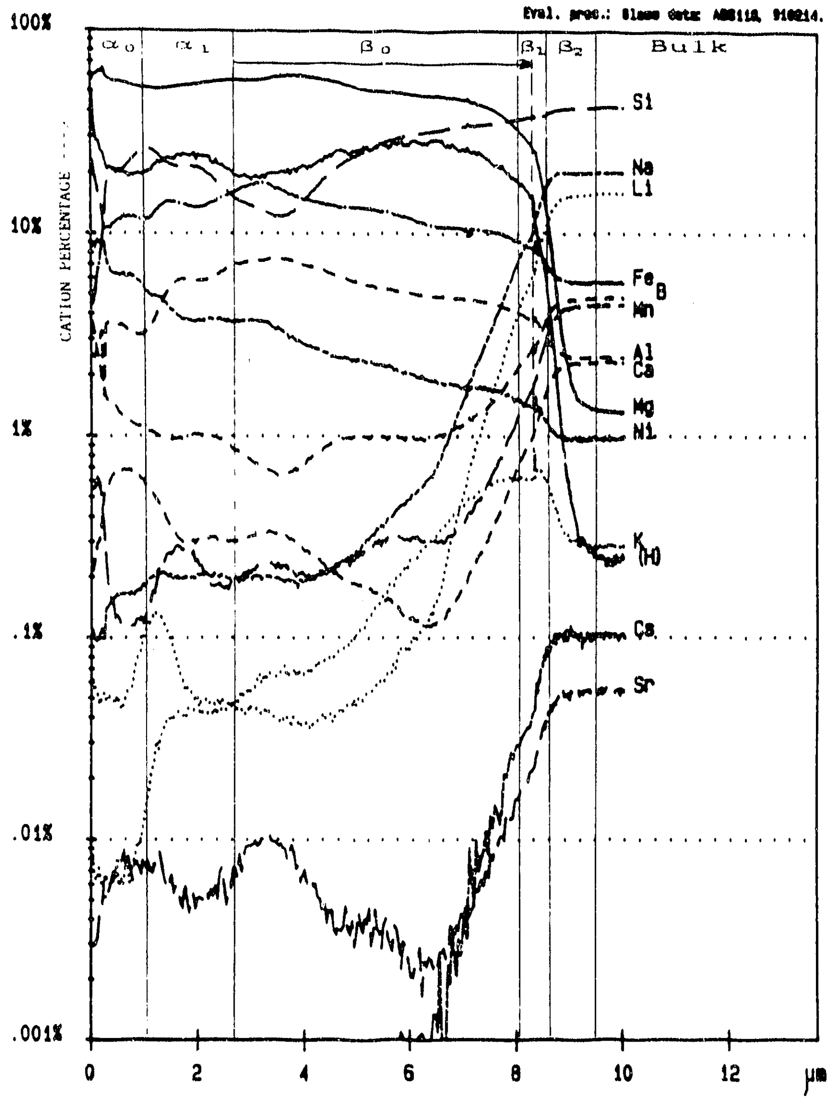

Figure 5. SIMS Profile- SRL 165/TDS , Glass/Salt Interaction, 5Yrs, 90°C

The two layers in the precipitated zone and the three layers comprising the glass reaction zone, as characterized by OM, SEM, EDX, WAXD, FTIRRS, and SIMS, are summarized schematically in **Figure 6.**

Brine Analysis

Brine analyses were performed by Catholic University of America (CUA) using Inductively Coupled Plasma- Mass Spectrometry **[8,9]**. The MIIT program is the only in-situ testing effort which allows solution analysis to be obtained and later correlated with surface studies to assess glass leaching. Solution analysis of boreholes containing leached SR 165/TDS waste glass were emphasized, including a doped SR glass containing simulated actinide components. Leachates were examined to determine the amounts of elements of interest that were extracted from the glass and found in the surrounding solution. The standard addition method was used to assess concentrations of various elements including La, Eu, Zr, Ce, Nd, Y, Pr, Th and U at predetermined time intervals over one year of continuous leaching at 90°C.

The concentrations measured in solution of species of interest by CUA was extremely low, (detection limit of the instrument is about 5 ppb) indicating that no significant amount of leaching occurred for key elements in the MIIT experiment. Because of this very low amount of release, it was not possible to obtain a direct quantitative assessment of the leaching of the glass. However, an upper limit of leach rates was determined by CUA from the standard deviations of concentration values determined by the standard addition method [9]. Calculations show that these upper leach rate limits for La and Eu for SR 165/TDS waste glass were 3.5×10^{-4} and 3.0×10^{-4} g/m^2-d, respectively. From an earlier study, upper leach rates were also obtained for other elements. Based on brine analyses alone, leach rates of species of interest for SR compositions are all less than 5×10^{-4} g/m^2-d and for all other MIIT waste glasses studied thus far, less than 8×10^{-4} g/m^2-d. These low leach rates indicate excellent glass performance in regard to the above mentioned species and have recently been shown to meet important regulatory release rate criteria.

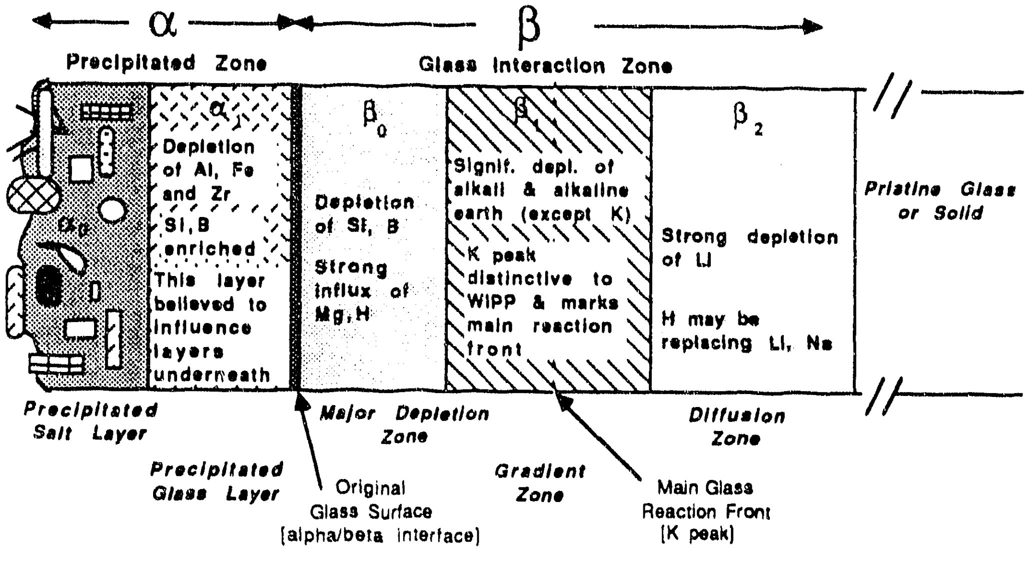

Figure 6. Precipitated and Glass Reaction Zones in MIIT Waste Glasses

CONCLUSIONS

MIIT is the largest and most cooperative in-situ testing program in the world, designed to help assess performance of waste forms and package components in a realistic repository setting. Although analyses are still in progress, already important conclusions can be drawn. Based on both solution analyses and detailed surface studies, and based on all data and analyses currently available [3,10,11], the following can be stated:

- SR waste glass exhibits excellent chemical durability after 6 mo., 1 yr., 2 yrs. and 5 yrs. of burial at the WIPP site
- No significant effect of the presence of 304L or TiCode 12 on glass leaching
- Leaching behavior of SR waste glass also improves with increasing time
- The leaching behavior of SR waste glass systems is similar to other international waste glass systems, including those in production overseas
- An improved understanding of leaching mechanisms has been achieved

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