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MIIT; International In-Situ Testing of Simulated HLW Forms- Preliminary Analyses of SRL 165/TDS Waste Glass and Metal Systems

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G.G. Wicks
Westinghouse Savannah River Company
Savannah River Laboratory
P.O. Box 616
Aiken, SC 29802

A.R. Lodding
Chalmers University of Technology
S-41296 Gothenburg, Sweden

P.B. Macedo
Vitreous State Laboratory
The Catholic University of America
Washington D.C. 20064

D.E. Clark
University of Florida
Gainesville, FL 32611

M.A. Molecke
Sandia National Laboratories
Division 6332 [WIPP]
Albuquerque, NM 87185

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INTRODUCTION

The first in-situ tests involving burial of simulated high-level waste [HLW] forms conducted in the United States were started on July 22, 1986. This effort, called the Materials Interface Interactions Tests (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 countries. Also included are almost 300 potential canister or overpack metal samples of 11 different metals along with more than 500 geologic and backfill specimens. There are a total of 1926 relevant interactions that characterize this effort which is being 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 Sandia National Laboratories in Albuquerque, New Mexico, and Savannah River Laboratory at Aiken, South Carolina and sponsored by the U.S. Department of Energy.[1]

MIIT OBJECTIVES

The primary objectives of the MIIT program include the following:

- Assess the performance of Savannah River [SR] Defense Waste Processing Facility [DWPF] waste glass compositions under anticipated and accelerated testing conditions relevant to a salt environment.
- Compare the relative performance and behavior of SR waste glass with the performance of other U.S. and foreign waste glasses, under similar, repository-relevant test conditions.
- Determine any effects of waste package component materials on waste glass durability and provide potential input to waste package designers.
- Provide a standardized, *in situ* data base on waste glass leaching including relevant interactions with metal canister or overpack components, salt and brine. This *in situ* data can then be correlated with other *in situ* data and the large body of existing laboratory data.
- Contribute to mechanistic studies aimed at understanding the behavior of waste glasses by coupling solution analyses with surface studies. This information can help in development of source terms that can be used to describe long-term waste form and package materials' behavior in salt.
- Provide data that can ultimately be useful in a technical data base to help demonstrate compliance with emerging specifications.
- Provide a large body of *in situ* test information, data, results and experience to be freely shared by all test participants and interested parties.

MIIT PROGRAM

The MIIT program supplements other programs currently in progress aimed at understanding and predicting the performance of Savannah River [SR] waste glass under a wide range of conditions and in a variety of geologic media. MIIT experiments involve the burial of 'pineapple-shaped' samples of simulated waste glass, potential canister and overpack materials, and backfill and geologic specimens placed in the salt geology at WIPP. The samples were stacked in seven different sequences producing interfaces and interactions of interest. These configurations result in a seven part program, each part with its own set of specific objectives. MIIT assemblies were inserted into brine-filled boreholes approximately 655 meters below the surface at WIPP in thick bedded salt deposits of the Salado Formation at a temperature of 90°C. MIIT sample units are shown being installed in WIPP in **Figure 1.** Samples and aliquots of solution were removed and studied after 0.5, 1, and 2 years, as part of the 5-year program.

There are many participants and observers involved in the MIIT program, representing national and federal laboratories, universities, and international facilities. In addition to the program co-sponsors from Sandia National Laboratories and Savannah River Laboratory, other U.S. participants include representatives from the Hanford Waste Vitrification Project, Battelle Pacific Northwest Laboratory, Idaho National Engineering Laboratory, the West Valley Nuclear Services Co., the University of Florida, Catholic University of America, University of New Mexico, the Pennsylvania State University, Argonne National Laboratory, Rockwell International Science Center and the Materials Characterization Center. International representatives include Hahn-Meitner Institute (West Germany), Centre D'Etudes Nucleaires (France), the Atomic Energy of Canada, Ltd. (Canada), British Nuclear Fuels, Ltd. (United Kingdom), Studiecentrum Voor Kernenergie/Centre D'Etude de L'Energie Nucleaire (Belgium), Japan Atomic Energy Research Institute (Japan), and the Chalmers Institute of Technology (Sweden). In October of 1988, the first workshop on testing of HLW forms under repository conditions featuring MIIT was held in Cadarache, France and organized by the Commission of the European Communities (CEC), and co-sponsored by CEC, CEA, and US DOE.[2]

There are many unique features associated with the MIIT program. The effort was conceived, organized and managed by members of the technical community most closely associated with data needs. Each participating country was asked to volunteer not only their best analytical tools to study and assess samples, but also their best technical people with those tools and to study not only their samples, but some of other peoples samples as well. The cooperation thus far has been outstanding. Techniques either being used or to be implemented include Scanning Electron Microscopy (SEM), Electron Microprobe Analysis (EMP), Secondary Ion-Mass Spectroscopy (SIMS), Auger Electron Spectroscopy (AES), Transmission Electron Microscopy (TEM), Electron Spectroscopy for Chemical Analysis (ESCA), energy dispersion x-rays (EDX), Rutherford Back Scattering (RBS), and wide angle x-ray diffraction (WAXD). In addition, pre-characterization of all waste form samples was performed by Fourier Transform Infrared Reflection Spectroscopy (FTIRRS).

In addition to the variety of bulk and surface analyses being performed, solution analyses are also being conducted using techniques such as Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Atomic Absorption (AA). These data are being correlated with the bulk and surface studies.

DISCUSSION AND RESULTS

MIIT WASTE FORM COMPOSITIONAL CORRELATIONS

Compositional correlations have been defined that tie together waste form samples supplied by the seven countries involved in the MIIT program. These correlations were made based on structural considerations, bonding energies and surface layer characteristics. The relationships emphasize the similarities between the many different waste glass systems studied world-wide and suggests that behavior of at least many of these systems, such as the borosilicate waste forms, may be very similar, including the mechanisms of leaching. A compositional ternary is shown in **Figure 2** relating all MIIT systems based on structural role of components as network formers, modifiers or intermediates.[3]

PRE-TEST WASTE GLASS/WASTE FORM CHARACTERIZATION AND QA

Waste forms in the MIIT program were characterized by various techniques before being buried in WIPP. One tool that was used to examine the quality of samples prior to burial was Fourier Transform Infrared Reflection Spectroscopy [FTIRRS]. These measurements, which were performed at the University of Florida, provided a non-destructive means to assure that each group of glasses used in MIIT had a similar and reproducible surface finish and was fabricated within a relatively narrow compositional range. Uniform starting samples are necessary to be able to assess changes and leaching behavior in these samples that may occur in the field, due to burial conditions. In **Figure 3**, FTIRRS spectra for all systems used in the MIIT tests, including SRL 165/TDS waste glass, are shown. Low variability in peak position and intensity indicates uniform composition and surface finish. Samples within the narrow distribution were used in these tests. All MIIT waste forms were characterized prior to burial using this technique.

POST-TEST ANALYSES OF WASTE FORMS AND PACKAGE COMPONENTS

The behavior and performance of MIIT waste forms and package components are being assessed in a variety of laboratories and universities in France, Germany, Japan, Canada, the United Kingdom, Belgium, Sweden, and the United States. Although post-test analyses are still in progress, much important information has already arisen and is being documented in workshops, international waste management symposia, and proceedings. Following is a summary of some of the more interesting and recent findings obtained on SRL 165/TDS waste glass after being buried at WIPP for up to 2 years. Also described is a summary of analyses performed on metal samples contained in the MIIT program.

Analyses of SRL 165/TDS Waste Glass

Based on surface analyses using SEM, EDX, WAXD, EMP, FTIRRS and SIMS, along with solution analyses using ICP-MS, SRL 165/TDS waste glass performed exceptional well after being leached in brine in the salt site at WIPP for up to two years. The glass not only performed well in these field tests but its performance improved with time and became even better than would be anticipated from many so-called standardized laboratory leaching studies.

- Surface Studies [SEM/EDX]

Surface analyses using SEM and complementary EDX were performed at SRL on leached 165/TDS waste glasses buried for 6 mo., 1 yr., and 2 yrs in WIPP.[4] From analyses performed on cross-sections of the buried glasses, two distinct zones were identified and characterized; an outermost region which had the morphology of a deposited/ precipitated layer [α] and an glass interaction zone which had the morphology of a glass-like material [β].

The precipitated zone was very heterogeneous and discontinuous over the glass surface [**Figure 4**]. The outermost portion of this layer contained a variety of salt phases and closer to the glass surface, various precipitates and glass components were noted. The chemistry of the precipitated zone was dominated by Mg and Cl from the outside brine. The precipitated zone varied considerably in thickness from less than one micron to many microns, depending on the salt deposit present.

Under the precipitated layer was a microstructure representative of the glass. The chemistry of this area contained the normal glass profile but included significant amounts of Mg and also Cl. A step analysis was conducted moving into the glass to determine when the Mg and Cl completely disappeared. That distance ranged from less than one micron to approximately 3 microns. After that distance, only pristine or unreacted glass could be identified. In **Figure 5**, a cross section of SRL 165/TDS waste glass after burial of 2 years in contact with salt and surrounded by brine is shown with a precipitated zone of 2-3 microns and an interaction zone of 1-2 microns.

- Surface Studies [SIMS]

A more detailed look at the leached surfaces of the MIIT glasses was performed at Chalmers University in Sweden using SIMS.[5] Using this tool, precipitated and interaction zones could be resolved in more layers and additional, more detailed chemical information could be obtained. The precipitated region α consisted of two distinct layers; deposited salt precipitates comprising the outermost layer [α_0] and an adjacent inner layer containing re-precipitated leached components of the glass along with salt constituents [α_1]. The reacted zone β consisted of three distinct layers; a main depletion zone [β_0], a gradient zone containing the main reaction front [β_1], and an innermost diffusion region representing the first interactions of the liquid leachant with the glass matrix [β_2]. The profiles of 17 important elements were obtained throughout glass relevant layers. [The relatively thick outermost deposited layer containing predominately salt precipitates was removed prior to analysis of the glass reaction layers underneath.] The entire interaction zone was well defined and approximately one micron in extent. The rate of growth of this zone decreased with time. A complete SIMS profile for 165/TDS waste glass after 2 years in burial at WIPP is shown in **Figure 6**. A schematic representation summarizing all precipitated and leached layers is given in **Figure 7** and discussed below:

Outermost Precipitated Salt Layer α_0- The outermost layer observed on leached glass surfaces was heterogeneously distributed on the glass surface and consisted of various phases precipitated from brine and surrounding salt geology. This zone was generally enriched in elements such as Mg, Cl, Ca, Na, S and Si, main elements contained in the brine. From analyses performed by Prof. Ewing [Univ. of New Mexico], Dr. Harker [Rockwell International], Dr. Vernez [CEA-France] and SRL, this layer was seen to be made up of amorphous as well as highly crystalline salt precipitates, which included phases such as $MgCl_2$, KCl, $CaSO_4$, NaCl, a variety of mixed silicates, as well as other minor phases.[2] This salt layer, which is a result of the geologic environment and conditions and not glass leaching, is believed to have an affect on subsequent layers formed underneath.

Precipitated Glass Layer α_1- This layer is more uniform and is believed to have been produced when elements of the glass underneath were leached and re-precipitated in this region. The layer is characterized by a significant enrichment of Mg as well as some Cl from the outside brine along with Si which can be from the glass as well as the brine. The layer is further characterized by a depletion in elements such as Al, Zr, and Fe, which are generally leach-resistant components of the glass. Their presence and the ratios of other components suggests that this region is not a selectively leached part of the original glass but instead, a re-precipitated zone. This is also supported by the morphology noted earlier and brine analysis which will be later described.

Major Depletion Zone β_0- This region represents the original glass located directly under the precipitated glass and salt layers. The region is characterized by a depletion of major components of the glass, including network formers and modifiers, and further characterized by the intrusion of major components of the brine such as Mg. The α/β_0 interface marks the beginning of the original glass surface, which is currently being characterized in more detail using marker studies.

Gradient Zone β_1- This area is believed to mark the main interaction front of the brine reacting with the glass. This is noted as a distinct peak on the SIMS profile of potassium, which comes from the outside brine and from the inside glass. The layer is further characterized by a depletion in alkali and alkali earth components of the glass and an enrichment in Mg from the brine. The distance from the beginning of the β_0 zone to the potassium peak in the β_1 zone represents the major region of reaction of glass with the surrounding environment.

Diffusion Zone β_2- This innermost region is characterized by a significant depletion of Li from the glass and an accompanying enrichment of H from the brine. As earlier noted, the thickness of this zone is consistent with diffusion calculations of these components in bulk glass. This region is analogous to the gel-layer which characterizes the beginning of the glass corrosion process.

- Brine Leachate Analyses

Solution analyses were performed at Catholic University of America using ICP-MS.[6,7] Brine leachates from selected MIIT boreholes were analyzed, including boreholes containing 165/TDS waste glass, both undoped as well as doped with chemical tracers. Elements emphasized in this study included Zr, Li, La, and Eu. In addition to measuring elements released to solution and calculating corresponding glass leach rates, the solution analysis also helped to further define the position of the original glass surface and the importance of the outermost α layer formed on leached waste glass systems. From these data, the location of the original glass surface was calculated to be between 0.35 and 0.40 μm deep into the sample, remarkably similar to the position of 0.31 μm as determined from the SIMS profile. In front of this layer is the precipitated α_1 layer.

Selected SRL 165/TDS waste glass samples were doped with chemical tracers La and Eu and irradiated in a Co-60 source prior to burial at WIPP. This was done to simulate features of actual waste glass systems and aging effects. The doped elements represent substitutes for +3 and perhaps +4 actinides that are present in actual radioactive waste. The tracers are especially useful in the current MIIT program because they exist in relatively high concentrations in the glass but are found in relatively low concentrations in the brine. Therefore, when these elements are leached from the glass into solution they can be more easily measured. The concentrations of La and Eu measured in leachates were found to be very low, less than 5 parts per billion [ppb], which is equivalent to approaching the detection limit of the equipment. Consequently, determining a quantitative value for leaching was not possible due to the very low leaching of the glass. However, a worst-case or upper limit of the leach rates can be calculated based on standard deviations of concentration data. These upper limits result in leach rates for La of 3.5 x10^{-4} g/m^{2}d or 0.042 μm/yr and for Eu of 3.0 x10^{-4} g/m^{2}d or 0.036 μm/yr. These are extremely low values which reflect the low leachability of the waste glass system and are consistent with the relatively small interaction depths observed from SEM and SIMS studies.[5,6]

Leach rates were also determined for undoped SRL waste glass based on extraction of Zr and also relatively mobile Li. The leach rate of Zr was also found to be very low, less than 1.6 x 10^{-4} g/m^{2}d, which corresponds to about 0.02 μm/yr of glass leaching. This leach rate is comparable, even slightly lower, than observed for the actinide stand-ins. The leach rate for relatively mobile Li was estimated from SIMS profiles and found to be 0.36 μm/yr. It is important to note that this value represents a maximum in the annual leaching rate for any species present in the glass and even so, still represents a very low leach rate of the product.[5,7]

Analyses of SRL 165/TDS Waste Glass Leached in the Presence of Metals

The leaching behavior of SRL 165/TDS waste glass was studied in the presence and absence of proposed canister and overpack metals. Based on surface studies and solution analysis, there was no significant effect on glass leaching due to the presence of the metal systems studied. The average thicknesses of interaction and precipitated zones as a function of time, analytical technique and for leaching in the presence of metals is summarized in **Table 1.**

Analyses of Metal Canister/Overpack Samples

Analyses of metal samples were performed at Sandia National Laboratories. The metal specimens were initially cleaned of deposited salt precipitates, then rinsed in deionized water, blown dry, and photographed. Any significant corrosion products were sampled and analyzed separately. All retrieved samples were then chemically cleaned using ASTM procedures which removes oxidized surface layers. Samples were weighed to the nearest 0.1 mg and visually evaluated for both uniform and localized attack. Selected samples of special interest were also evaluated in more detail. Control samples exposed only to laboratory air at room temperature were analyzed for comparison.

Titanium grade-2, titanium grade-12, and Inconel 625 samples experienced very little degradation. Copper samples exhibited minor general attack only; discoloration of the surfaces was observed, but there was not evidence of localized attack or stress corrosion cracking. Both mild steel A216/WCA and lead samples corroded severely, adding many ions and particulates to the brine leachate solution.

Titanium grade 12 [TiCode 12] and 304L stainless steel samples, unwelded base alloy as well as those with circumferential welds, were sectioned and metallurgically studied in more detail. None of the TiCode 12 samples showed any evidence of corrosion, cracking, crevice corrosion, pitting, or changes in microstructure. Most of the welded and unwelded 304L specimens exhibited good uniform corrosion resistance. In general, the 304L welded samples appeared to corrode faster than the unwelded samples. These stainless steel samples did show significant susceptibility to choride-induced, transgranualar stress corrosion cracking in both the welded and base metal disks. Shallow pitting 100-150 micrometers deep was also visible in some samples. For the welded disks, the degree of attack appears to be a function of exposure time.

CONCLUSIONS

Based on combining solution analysis with detailed surface studies of leached glasses, the SRL 165/TDS waste glass system appears to perform exceptionally well in the salt environment at WIPP and is not significantly affected by proposed canister or overpack metals. Data and leaching mechanisms indicate that not only does the system perform well, but the rate of dissolution decreases with increasing time. In addition, selective leaching appears to be a main leaching mechanism for the waste glass systems and the leaching process is characterized by the formation of two precipitated layers over three glass interaction zones. Additional studies in progress will further correlate the results of the SRL system with other waste glass systems of other countries, including glasses in actual production overseas and provide more details on the leaching processes and mechanisms involved.

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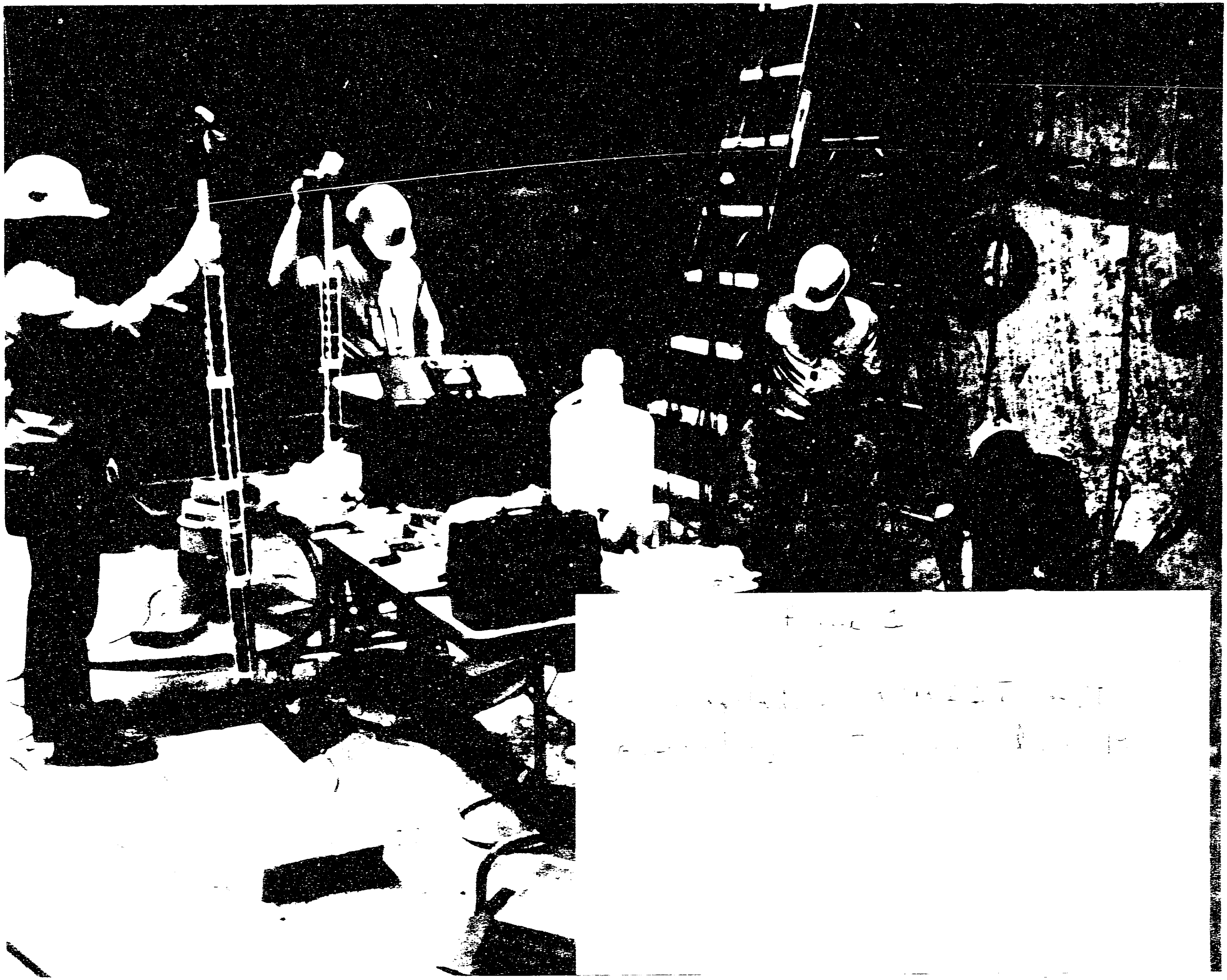


[illegible]

[illegible]

Figure 2

Compositional Correlations of MIIT Systems

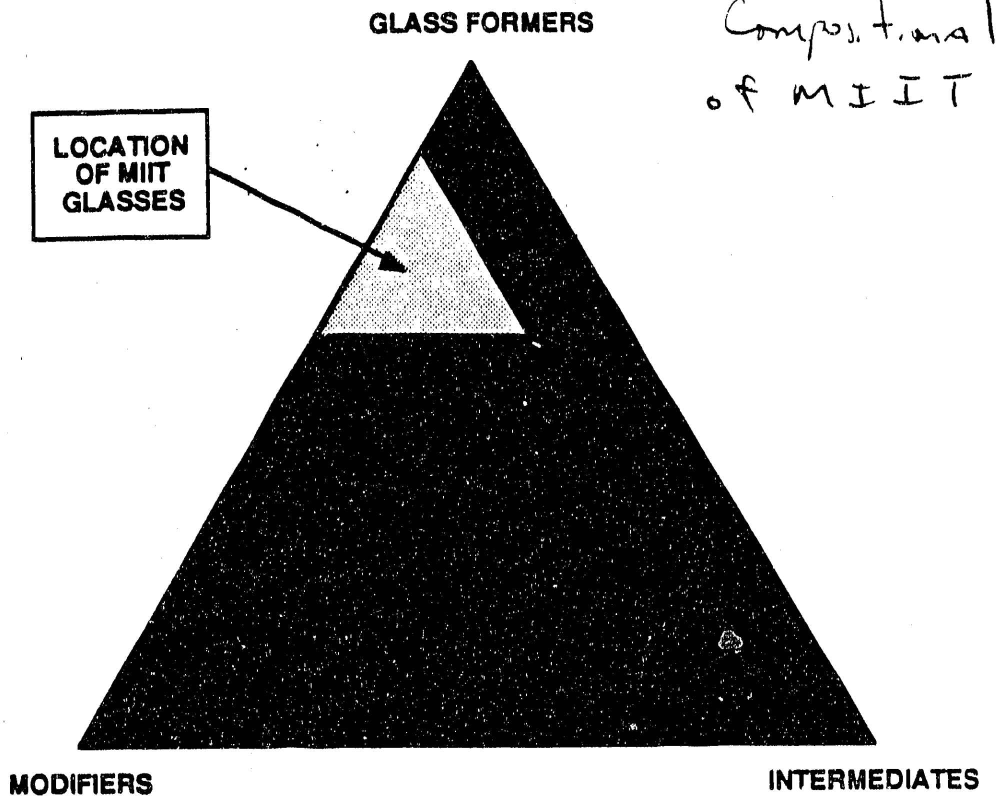
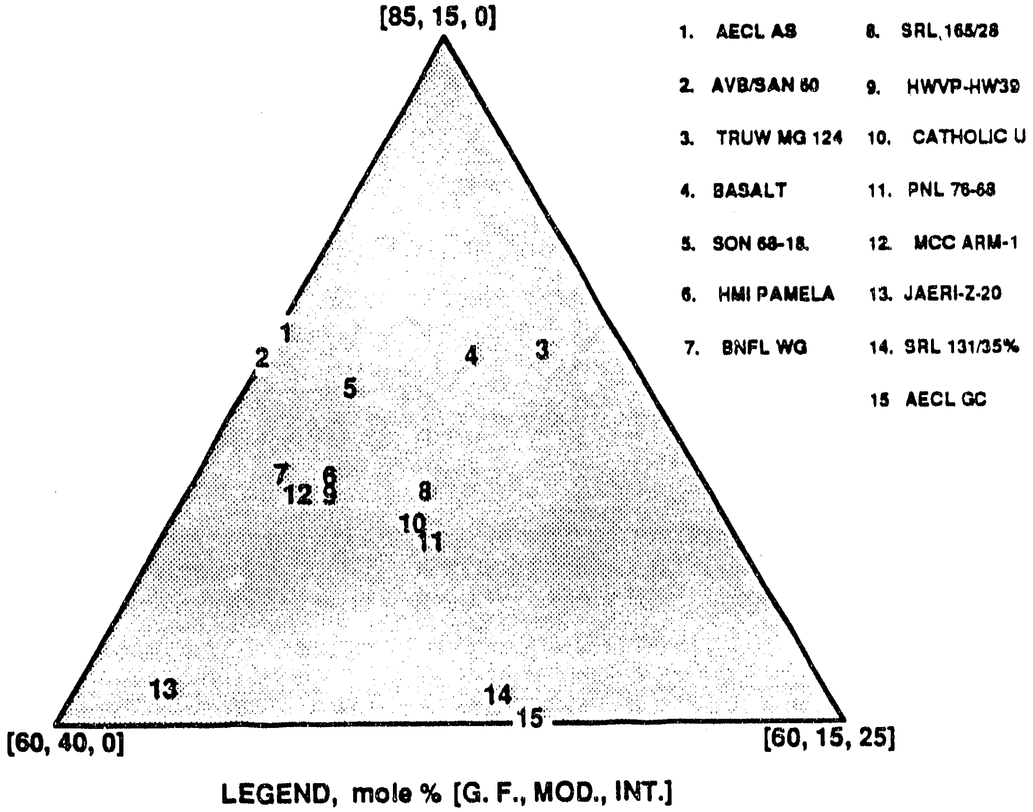


Figure 1. Ternary diagram depicting the compositional region of the MIIT glasses with respect to structural role.



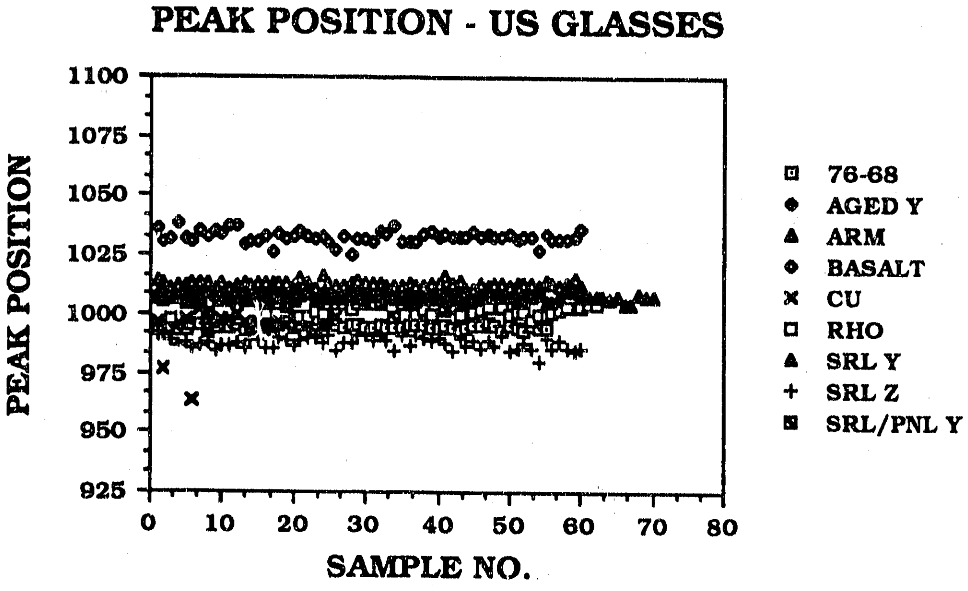
1. AECL AS
2. AVB/SAN 60
3. TRUW MG 124
4. BASALT
5. SON 68-18.
6. HMI PAMELA
7. BNFL WG
8. SRL 165/28
9. HWVP-HW39
10. CATHOLIC U
11. PNL 76-68
12. MCC ARM-1
13. JAERI-Z-20
14. SRL 131/35%
15 AECL GC

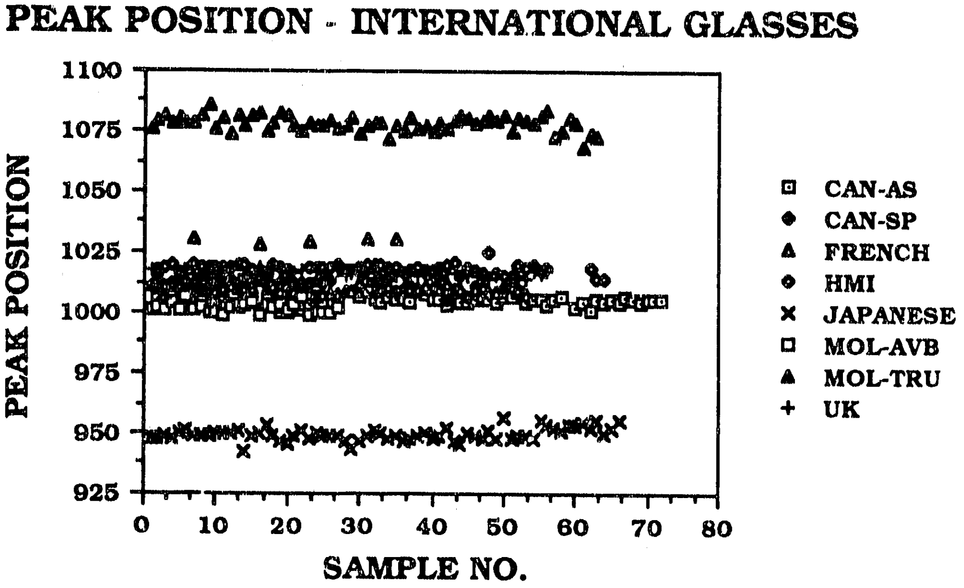
Figure 2. Expanded ternary diagram detailing the MIIT waste glass compositions with respect to stuctural role.

[illegible]

Figure 3

Pre-test
FTIRRS Analyses of MIIT Samples


PEAK POSITION - US GLASSES


PEAK POSITION - INTERNATIONAL GLASSES

Note: SRL Y denotes SRL 165/TDS Waste Glass

Surface Deposits on SRL 165/TDS Waste Glass After 2 YRS Burial At WIPP
(SEM/EDX, Top View)

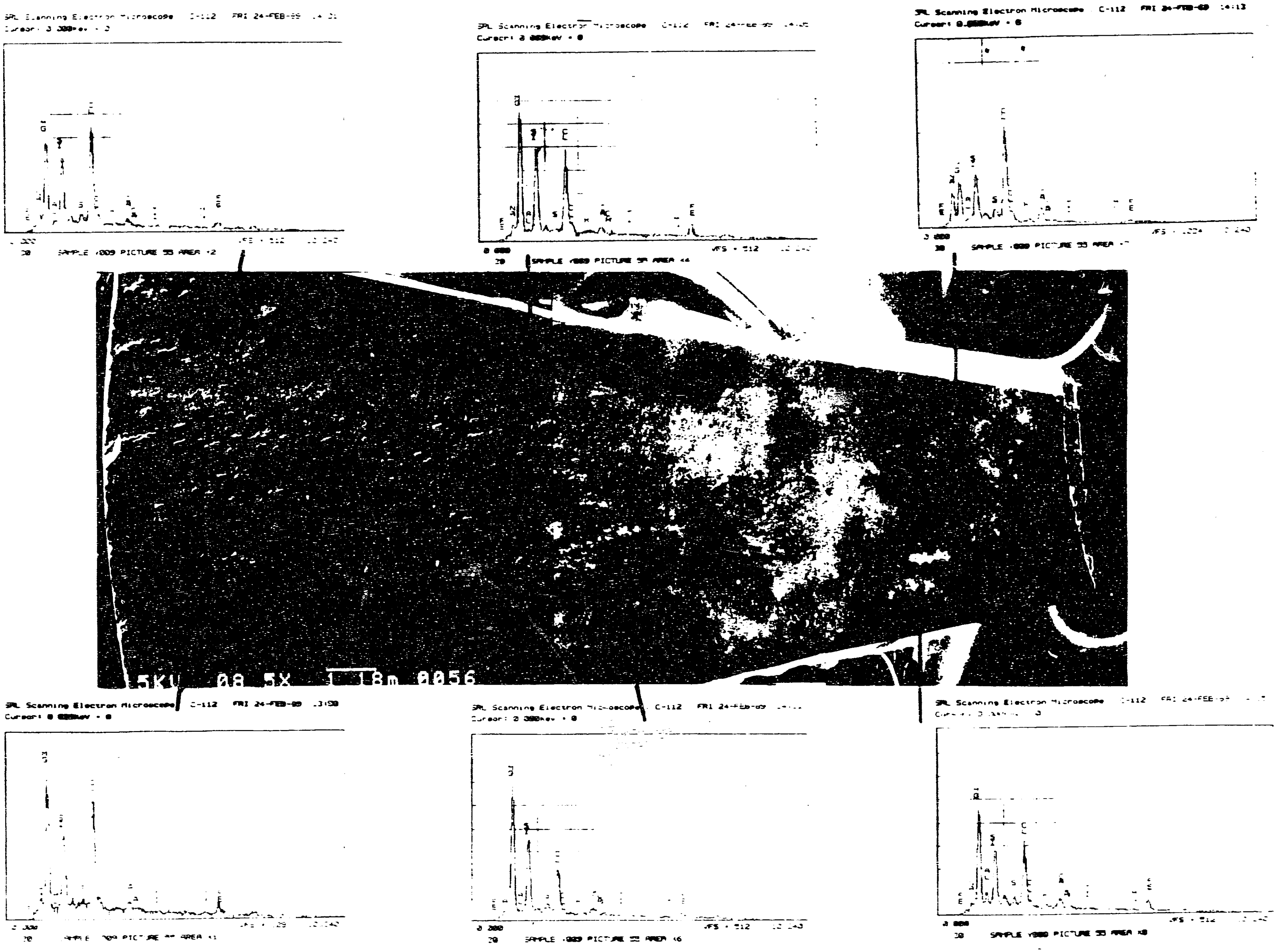
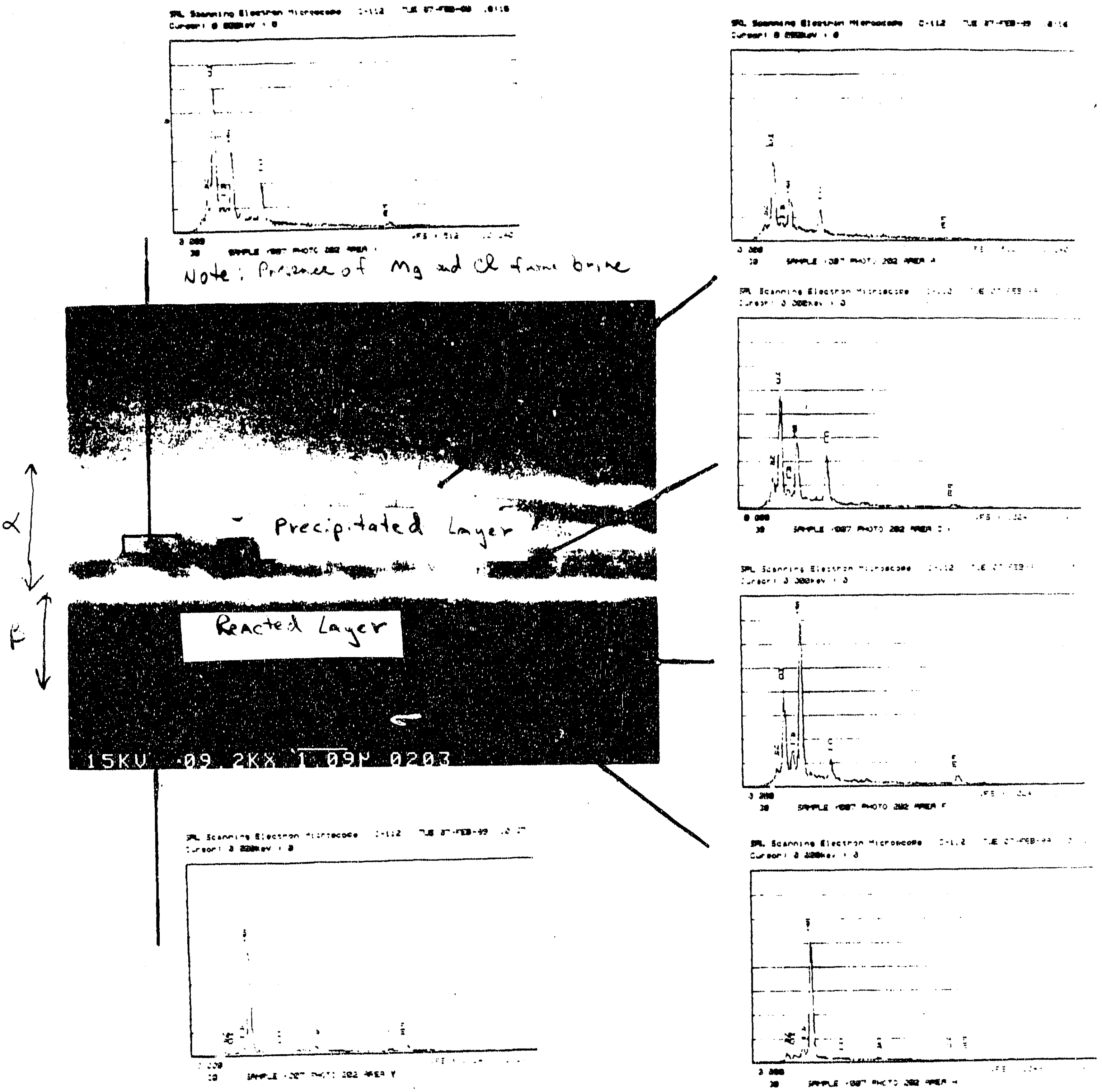


Figure 5

SEM/EDX Cross-section of SRL 165/TDS Waste Glass
After 2 YRS. Burial at WIPP

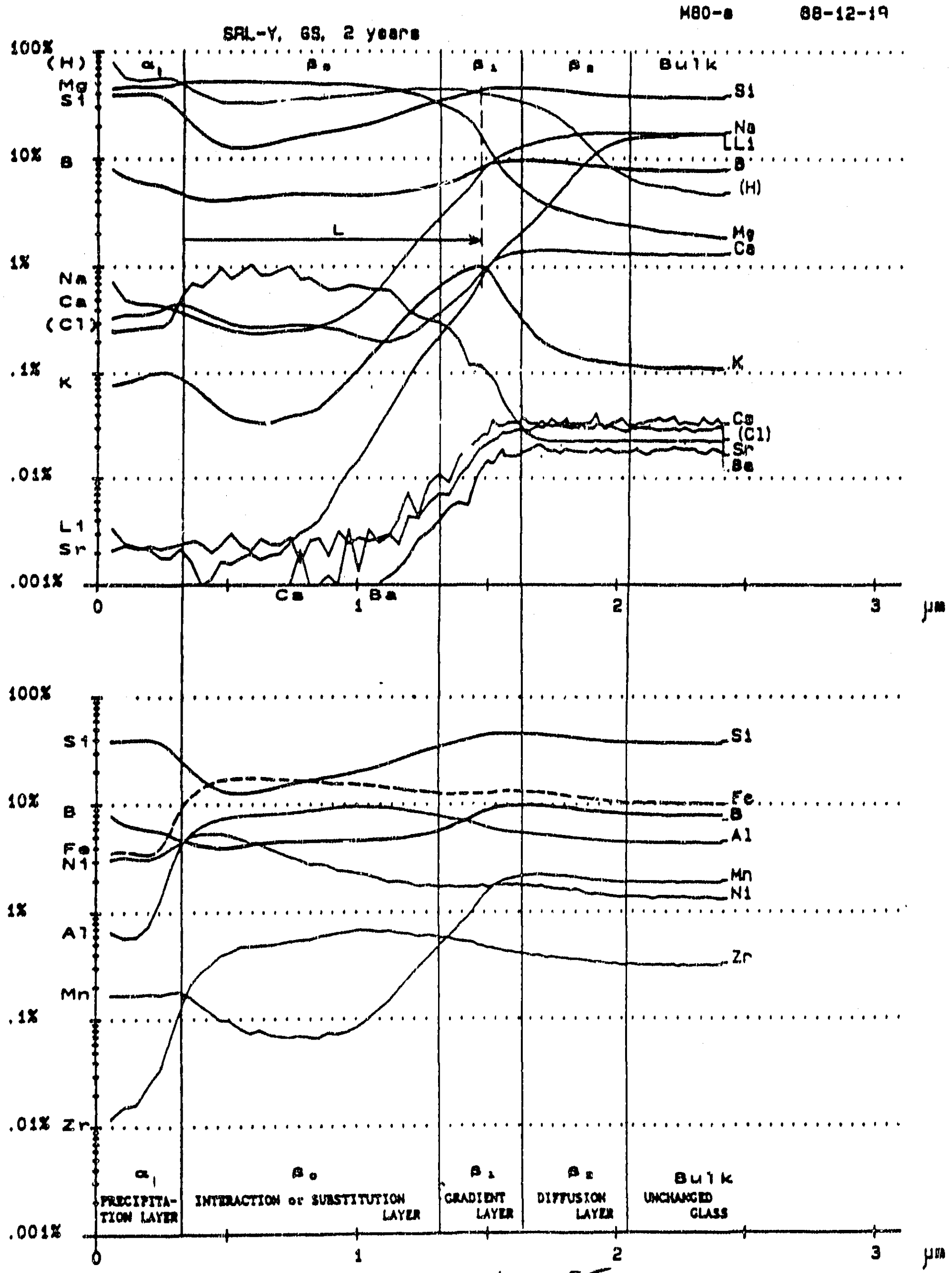


Note: Presence of Mg and Cl from brine

Note: Typical profile of unreacted glass
(No Mg or Cl)

Figure 6

SIMS Concentration Profiles of Elements in Leached Layers on SRL 165/TDS Waste Glass



.31 .36 .21 .55

$\leftarrow$ β = 1.12μm $\rightarrow$

$\leftarrow$ L = 0.47μm $\rightarrow$

Figure 7

Precipitated and Leached Layers;
IIIT Waste Glasses [SRL 165/TDS, 2 Yrs. in WIPP]

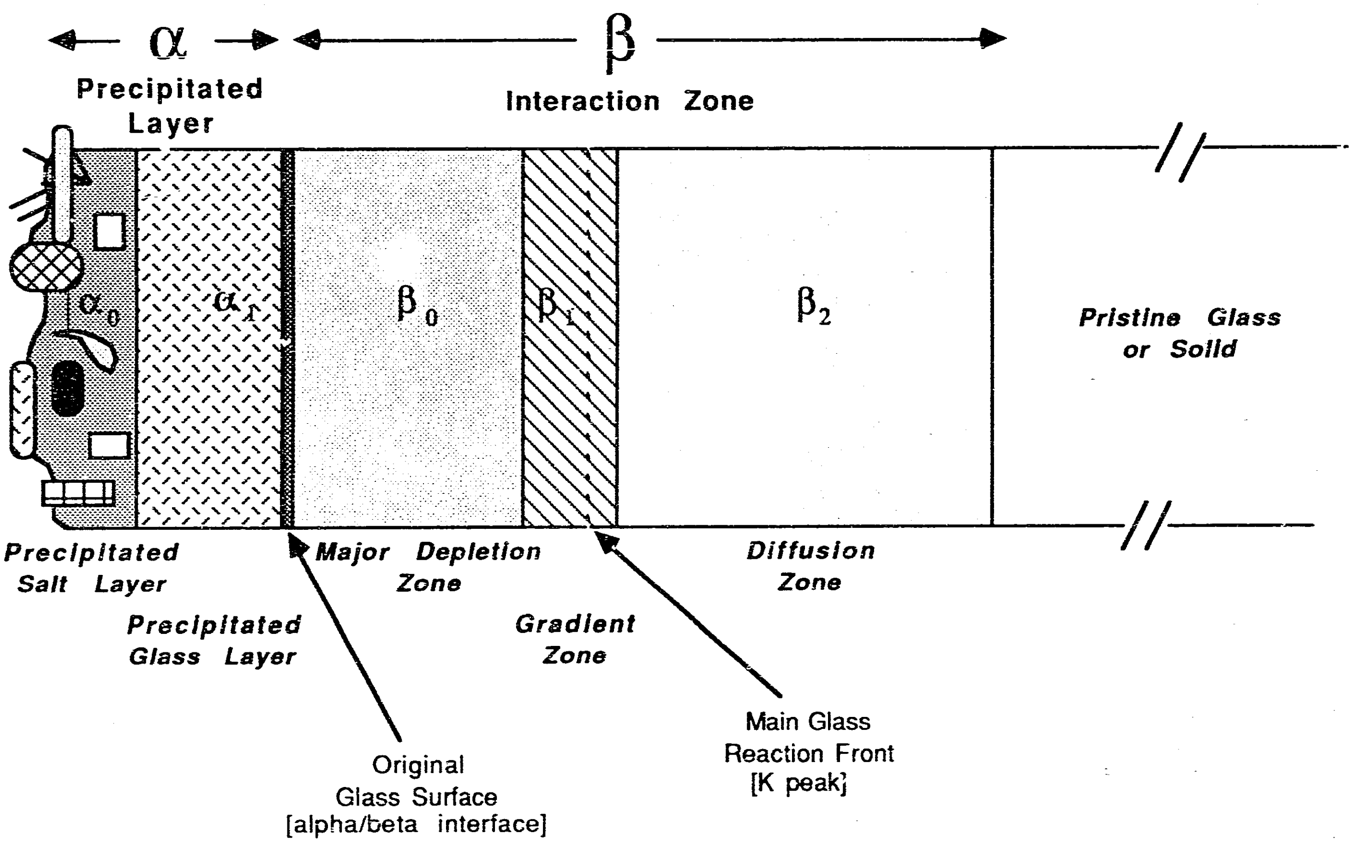


Table 1

AVERAGE THICKNESSES OF INTERACTION [β] & PRECIPITATED ZONES [α]

[AS A FUNCTION OF TIME, ANALYTICAL TECHNIQUE, AND FOR LEACHING IN THE PRESENCE OF METALS FOR GLASS/GLASS INTERFACES]

			INTERACTION ZONE*			***PRECIPITATED ZONE*****		
			$[\beta=\beta_0+\beta_1+\beta_2]$			$\alpha_0 + \alpha_1$	α_1	α_1 [Calc.]
			SEM-EDX		***SIMS***	***SEM-EDX***	***SIMS***	***BRINE ANAL.***
WASTE GLASS	***METAL***	***6 Mo.***	***1 Yr.***	***2 Yr.***	***2 Yr.***	***2 Yr.***	***2 Yr.***	***2 Yr.***
165/TDS	None	<1μ	1-2μ	1-2μ	1.12μ [.36+.21+.55]	1-6μ	0.31μ	0.35-0.40μ
165/TDS	304L	<1μ	1-2μ	1-2μ				
165/TDS	TiCode 12			~1μ				
165/TDS	Lead			1-2μ				
165/TDS	A216			<1μ				

* Total depth of 'interaction zone' is relatively small [~1-2 μ] depending on test condtions

* The presence of metals during glass leaching appears to have no significant effect on the thicknesses of the 'interaction zone' produced

* Growth of 'interaction zone' increases initially [between time = 0, 6 mo. and 1 yr.] but then slows down after longer time periods [1 to 2 years]

** The outermost α_0 'precipitated zone' consists mainly of deposited salt phases

** The α_1 'precipitated zone' represents a layer composed of elements leached from the glass along with major elements entering the glass from the brine

END

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