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WIPP/SRL IN-SITU TESTS: MIIT PROGRAM-THE EFFECTS OF METAL PACKAGE COMPONENTS (U)

by

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INTRODUCTION

The Materials Interface Interactions Tests or MIIT is the largest in-situ testing program in progress, involving burial of many simulated nuclear waste systems and accompanying package components. This international cooperative program is discussed elsewhere [1-6] and is the subject of other papers at this Symposium.

In MIIT, waste glass samples were fabricated into the shape of 'pineapple slices', polished on one side. Proposed package components were also made into a similar configuration and the various glasses, metals, and geologic samples were then stacked onto heater elements within Teflon assemblies. This produced interactions of interest by creating glass/glass, glass/salt, and glass/metal interfaces. Since the outer diameter of the metal was smaller than the outer diameter of the glass, a lip was created which also produced a glass/liquid interface, which was also studied.

Overall, a total of 50 stacks or assemblies of pineapple slices were created in seven different stacking arrangements. Each individual assembly was then installed in an instrumented borehole at WIPP. Brine was then added to most of the boreholes and the assemblies heated and maintained at 90°C. This was achieved by energizing the central heating rod that traversed through the middle opening of each of the pineapple slices in each assembly. Due to the design of these units, glass, metal and geologic samples could be removed at time intervals of 6 mos., 1 year, 2 years, and 5 years. Currently, all but the 5 year samples have been removed from test and are being evaluated in laboratories of MIIT participants.

OBJECTIVES

Many studies have been performed and many others are still in progress on the 6 mo., 1 year, and 2 year samples. These investigations are being conducted in eight countries and a variety of federal, national and university laboratories in the U.S. Some results have been presented and documented in a special workshop in Cadarache, France sponsored by the Commission of European Communities [7], a session on MIIT at the Fourth International Symposium on Ceramics in Nuclear Waste Management, sponsored by the American Ceramic Society [8], and in other national and international forums.

The primary objectives of the present study are two-fold:

(1) to examine glass/metal interfaces of SRL Y (165/TDS) waste glass with metal canister and overpack materials, and to determine what effect these metals have on leaching of the SRL waste glass and
(2) to assess the corrosion behavior of the metal systems used in MIIT, which represent potential canister or overpack materials.

Glass analyses were performed using Optical Microscopy (OM), Scanning Electron Microscopy [SEM] with complementary Energy Dispersive X-rays [EDX], Wide-Angle X-ray Diffraction, Fourier Transform Infrared Reflection Spectroscopy (FT-IRRS) and Secondary Ion Mass Spectroscopy. For the present study, SEM/EDX results of glass/metal interfaces will be emphasized and correlated to similar analyses performed on the same waste glass system tested in the absence of metal. [8]

Metal analyses were performed using standard metallurgical techniques. Changes in microstructure will be reported along with weight loss studies and microhardness investigations.

SUMMARY

• There was no significant effect observed on leaching of SRL Y waste glass due to the presence of 304L S.S., the reference Defense Waste Processing Facility (DWPF) waste glass and canister material.
• There were also no large effects observed on the leaching of SRL Y waste glass when leached in the presence of other metal systems.
• Leached glass layers were characterized by two regions; a precipitated layer and an interaction zone. The depths of these regions were seen to increase with increasing time. However, the rate of increase of the thickness of the interaction zone decrease with increasing time.
• Interaction zones, which provide a measure of glass interaction and leaching, indicated that the SRL Y waste glass interacted only a very small amount with surrounding brine and salt geology [<1-2 μ], even after being in test at WIPP for 2 years at 90°C.
• Metal systems such as TiCode-12, Inconel 625, and copper, and 304L stainless steel, exhibited generally good corrosion resistance, while other metals such as A216 and lead, corroded very significantly and 'stuck' or 'fused' to adjacent glass.

EXPERIMENTAL PROCEDURES

SRL Waste Glass

There are fifteen glass or waste glass compositions and over 1000 waste form samples in the MIIT program. One of these compositions is 165/TDS waste glass, designated SRL Y, which is a reference Defense Waste Processing Facility (DWPF) composition for the Savannah River Site **(Table 1)**. In the current effort, six SRL Y waste glass samples in contact with potential canister or overpack metals were studied. The first group of samples represent a time dependent study involving SRL Y/304L S.S. interactions after burial for 6 months, 1 and 2 years. The remaining samples involve other metal/glass interactions evaluated after 2-yrs. of testing and include SRL Y/ TiCode-12, SRL Y/ A216 carbon steel, and SRL Y/ lead.

Table 1. Composition of SRL Y Glass (165/TDS)

COMPONENTS	WT. %	COMPONENTS	WT. %
SiO_2	54.1	MnO_2	2.9
Na_2O	10.3	Al_2O_3	4.1
B_2O_3	6.8	NiO	0.9
Li_2O	4.7	CaO	1.5
MgO	0.8	$CsNO_3$	0.1
ZrO_2	1.2	$Sr(NO_2)_2$	0.1
Fe_2O_3	12.3		

A representative MIIT assembly involving glass/metal interactions is shown schematically in **Figure 1**, along with an enlarged and more detailed view of one of the four sub-assemblies in **Figure 2**. Samples in the current study were obtained from similar units. After the assemblies were removed from test at WIPP, the pineapple slices were cut into 1/8 wedges and studied in the laboratory. Four of the wedges were analyzed using a variety of analytical techniques as described elsewhere **[8]**, while the rest of the pineapple slice was stored as a library sample. A 1/8 wedge or smaller was analyzed in the present study.

In order to assess the behavior of leached MIIT glasses, an integrated study approach is being used. This combines solution analyses with many detailed surface and bulk studies. The various analytical tools being used, provide different information on the composition or structure of elements of interest within the leached glass surface layers. **[9]** In the present study, SEM/EDX analyses were used to examine and characterize deposited salt precipitates, leached glass surfaces, and overall depths of leaching. The samples were prepared for analyses by cutting into segments 1/8 of a slice or smaller, which could then be easily mounted and studied in the SEM. Next, a carbon coating was applied on the sample in order to minimize charging effects and improve electrical conductivity before examining it in the microscope. This method of sample preparation was the least destructive to fragile surface layers that formed during leaching.

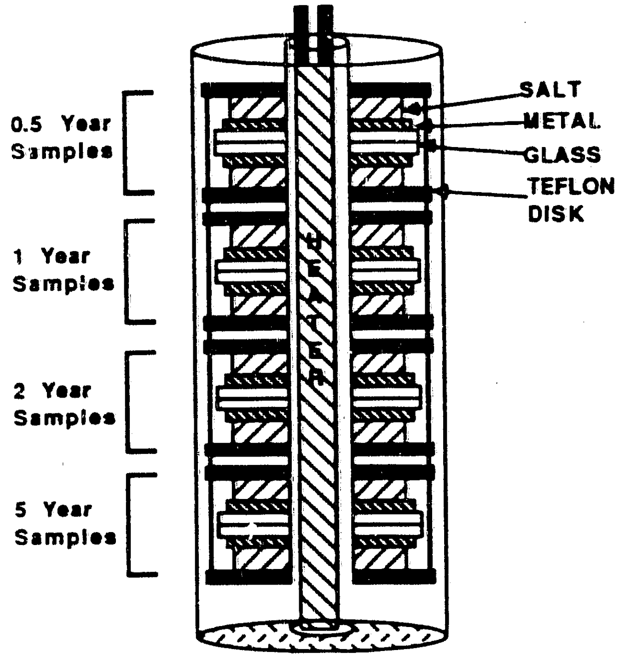

Figure 1. WIPP MIIT Assembly

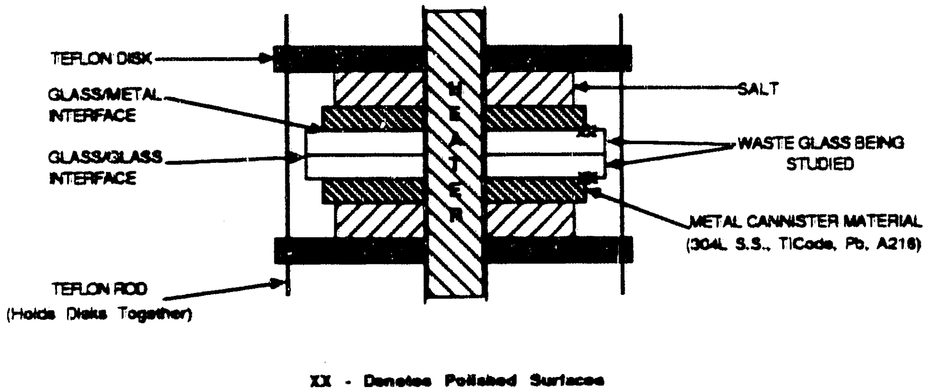

Figure 2. Enlarged View of Section of MIIT Assembly

Once the sample was in the scanning electron microscope, microstructures and leached layers were photographed and morphological features studied. The chemical composition of leached layers and interfaces of interest were then examined by energy dispersive x-rays. This included examination of two sides; one side of the glass in contact with an adjacent glass and the other side of the glass in contact with the adjacent metal. Since the outer diameter of the metal was smaller than the outer diameter of the glass, a lip was created which represented a glass/liquid interface and this region also was studied. EDX was performed over each of these surfaces and the chemistry of the glass/glass, glass/metal, and glass/liquid interfaces defined. Additional spectra were recorded on the cross-section of the glass, traveling from the outermost leached surfaces to the pristine bulk glass. **(Figure 3)**

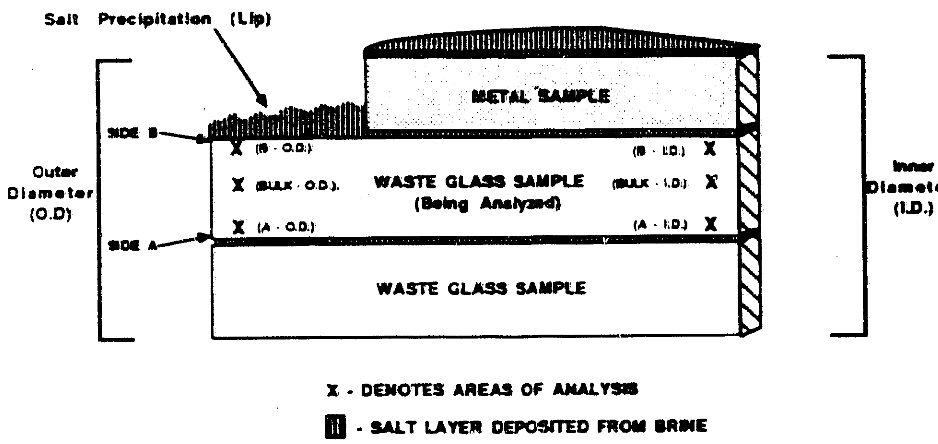

Figure 3. Cross-Sectional View of Glass and Metal Wedges

Metal Samples

Eleven metal samples of potential canister and overpack materials are being evaluated as part of this study. These included (1) ASTM Grade-12 Titanium [TiCode 12], with and without welds, (2) 304L Stainless Steel, with and without welds, (3) Lead, (4) Cast Mild Steel [ASTM A216/ Grade WCA], with and without welds, (5) Inconel 625, with and without welds, (6) Copper (7) ASTM Grade-2 Titanium (chemically pure), (8) NS24/AISI 309 Stainless Steel, (9) 316 Stainless Steel, (10) Hastelloy C4, and (11) Belgian Carbon Steel (Bel-C). In addition to these metals, Inconel 600, Inconel 625, and Incoloy 800 were also part of the test matrix since they are the materials of construction for much of the hardware used in the experiments.

Metallurgical examinations of MIIT metal samples were performed at Sandia National Laboratories. Before the metals were studied, they were rinsed in deionized water to remove outermost salt deposits, dried and then photographed. If significant corrosion products were present, they too were analyzed concurrently. ASTM cleaning procedures were used to remove the oxidized surface layers. The metal samples were then visually evaluated for both uniform and localized attack and weighed, to determine weight loss due to corrosion. Selected samples were also cross-sectioned and examined in more detail and compared to the control specimens. **(10)**

RESULTS

SRL Waste Glass

Microstructural investigations of glass surfaces in contact with a variety of metals show that these metals, in general, have little significant effect on glass performance. In **Figure 4**, a cross-sectional view of a glass/glass interface of SRL Y glass buried in contact with Type 304L stainless steel in WIPP for two years at 90°C is shown, along with accompanying EDX profiles. A magnesium-rich salt precipitate is noted on the glass surface, with magnesium enriched in the outermost surface of the glass but rapidly diminishing as the bulk glass is quickly approached.

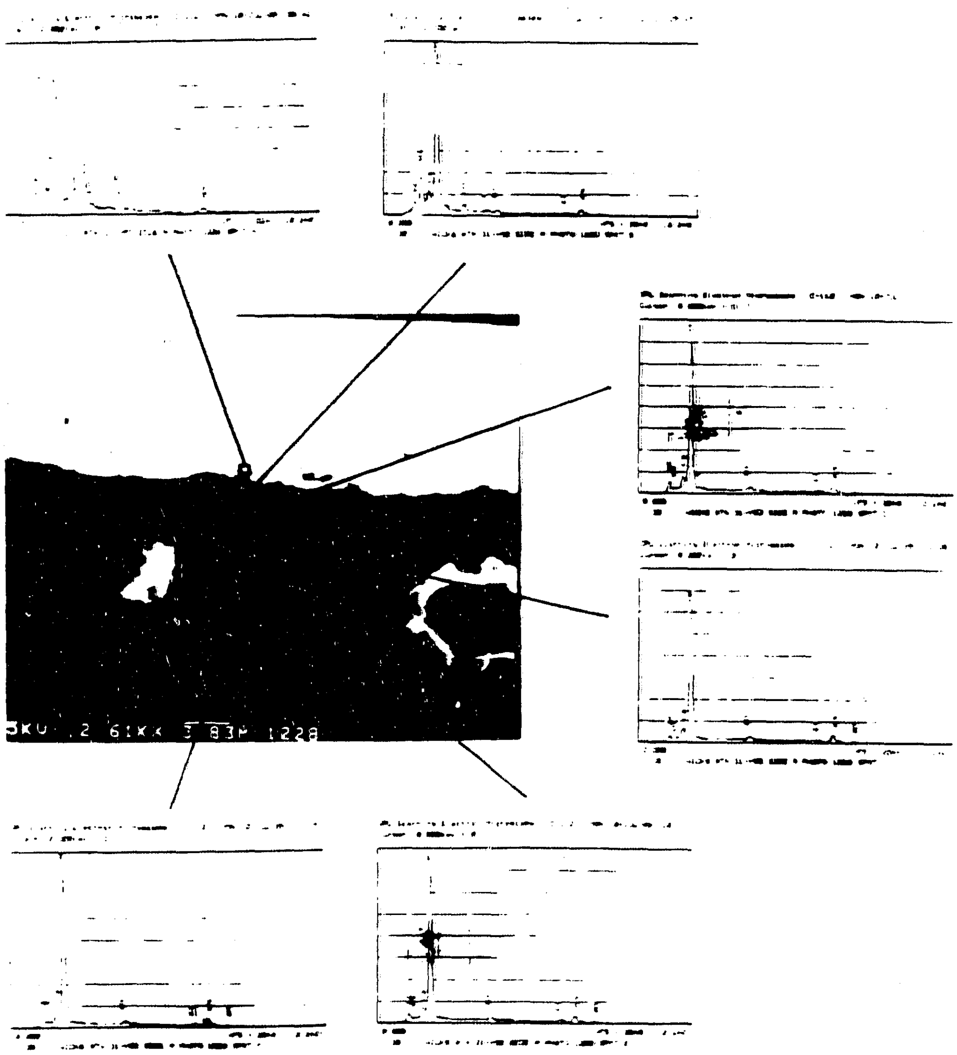

Figure 4. Cross-Section Analysis of SRL Y Glass

Leached glass layers were characterized by two general regions for all glasses analyzed in the MIIT program. This observation was noted for glasses in contact with metal systems as well as glasses buried in the absence of metals. [8] The first or outermost zone is the precipitated or deposited layer, called α, and composed of precipitated salt phases from the surrounding brine and salt geology. The next region is located under the precipitated layer and is referred to as the interaction zone or β . This region represents the actual leaching of the glass and is proportional to the total amount of interaction or corrosion that occurred. These layers are then followed by the pristine or unreacted glass. The depth at which the unchanged glass begins represents the maximum depth or upper limit of leaching. More detailed characterization and quantitative depths of leaching will be obtained by SIMS.

In **Table 2** measured depths of precipitated layers and interaction zones for all six MIIT samples are summarized. It is noted that the metal systems studied have no significant effect on waste glass leaching behavior in these field experiments. In addition, the measured interaction depths are not only very small, but the rate of growth of the interaction zone increases initially, between times of 0, 6 mo. and 1 yr., but then slows down after longer time periods, of 1 to 2 years.

Table 2. Observed 'Maximum' Thickness of Interaction Zone (β)

		INTERACTION ZONE THICKNESS (μm) [Time]		
WASTE GLASS	METAL	6 Mo.	1 Yr.	2 Yr.
165/TDS	None	<1	1-2	1-2
165/TDS	304L S.S.	<1	1-2	1-2
165/TDS	TiCode-12			~1
165/TDS	Lead			1-2
165/TDS	A216			<1

In general, interactions occurring near the outer diameter of the glass pineapple slice were slightly more extensive than those occurring near the inner diameter. The interaction zone near the outer diameter ranged from <1 to 2 microns, while near the inner diameter, this zone ranged from <1 to 1 micron.

Interaction zone measurements were consistent and provided a convenient, semi-quantitative means to assess glass leaching, while more quantitative measurements will be performed later by SIMS. The precipitated layer thicknesses, however, were not constant and varied considerably. This was a result of the different degrees of accessibility of the brine to glass surfaces and the varying amounts of salt phases deposited. It was also noted that this outermost precipitated salt layer was very friable and subject to damage from handling.

Metal Samples

About one-half of the MIIT metal systems have been analyzed to date. Among the most important metals are TiCode-12, considered as an overpack or canister material for a salt environment, and Type 304L stainless steel, the current reference canister material for DWPF waste glass. Analyses of these metal systems, along with studies performed on Inconel 625, copper, A216, and lead, are given below **(10,11)**:

The present study also shows advantages and limitations of metals proposed for canister and overpack applications in potential geologic environments

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