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MIXED WASTES WITH HIGH METAL CONTENTS\***

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## GLASSY SLAGS AS NOVEL WASTE FORMS FOR REMEDIATING MIXED WASTES WITH HIGH METAL CONTENTS

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### ABSTRACT

Argonne National Laboratory (ANL) is developing a glassy slag final waste form for the remediation of low-level radioactive and mixed wastes with high metal contents. This waste form is composed of various crystalline and metal oxide phases embedded in a silicate glass phase. This work indicates that glassy slag shows promise as final waste form because (1) it has similar or better chemical durability than high-level nuclear waste (HLW) glasses, (2) it can incorporate large amounts of metal wastes, (3) it can incorporate waste streams having low contents of flux components (boron and alkalis), (4) it has less stringent processing requirements (e.g., viscosity and electric conductivity) than glass waste forms, (5) its production can require little or no purchased additives, which can result in greater reduction in waste volume and overall treatment costs. By using glassy slag waste forms, minimum additive waste stabilization approach can be applied to a much wider range of waste streams than those amenable only to glass waste forms.

### INTRODUCTION

Vitrification is currently the Best Demonstrated Available Technology (BDAT) for the disposal of high-level nuclear wastes. An innovative vitrification approach, Minimum Additive Waste Stabilization (MAWS), is being developed to treat some of the waste streams present at Fernald, Ohio. MAWS utilizes multiple waste streams as substitutes for additives, otherwise necessary for vitrification, to produce a durable waste form. This approach uses glass as the final waste form [1]. However, two limitations for the production of glass final waste forms restrict the application of MAWS approach to some wastes.

(1) The feed stream requires a minimum amount of fluxing components such as alkalis, boron, or alkaline earth to attain a processable viscosity, and (2) the solubilities of many metal waste components are low so that waste loadings may be unacceptably small.

A homogeneous glass waste form may not be appropriate for all DOE waste streams because of the extreme diversity of wastes and high metal contents. Many DOE sites have large-volume waste streams that contain large amounts of scrap metals (e.g., 22 wt% of the buried wastes at the Idaho National Engineering Laboratory (INEL) Radioactive Waste Management Complex are metals), metal oxides of Cr, Ni, Ti, Fe, Ca, and Mg (e.g., the K-25 pond sludge/soil over 16 million Kg at the DOE Oak Ridge site contains ~25 wt% Fe, 20 wt% Al, and 20 wt% Ca), and only small amounts of flux components. Glass waste forms cannot be produced from these waste streams since even moderate loadings of these waste streams will result in the formation of crystals during vitrification process. The crystals will complicate glass processing and lead to uncertainties in glass durability. Vitrification of such high metal waste streams to produce glass final waste forms will require the addition of large amounts of expensive additives and

significant reduction in waste loadings. Low waste loadings and large amounts of additives can substantially limit the net volume reduction and cost savings during remediation and treatment of these waste streams.

An alternative to homogenous glass waste forms is glassy slag, which permits high waste loading and requires smaller quantities of additives. Argonne National Laboratory is conducting a program to (1) develop and evaluate the use of glassy slag as final waste forms for the remediation of waste streams with high metal contents and (2) demonstrate that utilization of glassy slag waste form will allow MAWS approach to be applied to a much wider range of waste streams than those amenable only to homogenous glass waste forms. Initial work at ANL demonstrated the production of glassy slag waste forms at a laboratory scale. The glassy slag formulations developed through crucible melt tests were also successfully generated in a Retech Plasma Centrifugal Furnace (PCF) [2] at Ukiah, California. The glassy slags produced from crucible at ANL and the glassy slags produced in the Retech PCF were found to be similar in solid characteristics and chemical durability [3].

Initial work focused on determining the distributions of hazardous elements among the glass and crystalline phases. The mixed wastes selected for initial study are large volume mixed wastes, such as scrap metals and contaminated equipment and are those that may have a significant effect on devitrification and chemical durability of the resulting glass. Three major metals, Cr, Ni, and Fe, were selected for this initial scoping study because these represent the major metal wastes which need remediation from DOE sites. About 80% of the metallic wastes at the Radioactive Waste Management Complex (RWMC) of INEL are Fe, Cr, and Ni contained in carbon steel and stainless steel scraps. The carbon steel is 99 wt% Fe and stainless steel contains 1.1 Al, 19.02 Cr, 68.35 Fe, 1.38 Mn, 9.28 Ni, and 0.87 Si in wt%. The scoping tests carried out in 1993 simulated carbon steel and stainless steel wastes by using pure NiO, Cr<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>.

Instead of using purchased additives for the vitrification, contaminated soils were used to form glassy slags from the metal wastes, resulting in a MAWS approach. This approach maximizes waste volume reduction and cost saving of the waste treatment. As a feasibility study, uncontaminated INEL soil was used in this initial study. Plutonium-doped and actual DOE wastes will be used in later research projects. (The term "glassy slag" is used interchangeably with "slag" in this report.)

## EXPERIMENTAL

### INEL Soil Characterization

INEL soil was used in the slag formulation as an additive to achieve high metal oxide loading while maintaining acceptable chemical durability. INEL soil was characterized for the purpose of slag formulations. The soil was first dried at 500°C for about 18 hours with 16.32% of the weight lost during drying. The dried INEL soil was next dried at 1100°C for another 8 hrs with an additional 5.85% of the weight loss. These weight losses were attributed to the loss of water, organics, and other volatile materials. The total weight loss of INEL soil due to drying is 22.17%. The INEL soil composition was analyzed at ANL and the elemental composition after drying is shown in

Table I. The INEL soil also contains small amounts of Ag, As, Cd, Hg, and Se, but the amounts are so small that they are shown as 0.0 in Table I.

### Preparation and Analysis of Glassy Slags

**Slag Preparation.** Glassy slags were produced by melting INEL soil (not dried) with metal oxides (in crucibles) to simulate high-metal content waste streams, such as contaminated carbon steel and stainless steel scraps, tools, and equipment. The formulations in terms of INEL soil and waste metals are shown in Table II. The highest metal loading is 74 wt% (ANL-M2). Since the INEL soil used contains 22.17% volatile materials, the actual metal loading is 78.3% in terms of dried INEL soil. This translates into a 84% metal oxide loading (Table I). Cerium oxide ( $\text{CeO}_2$ ) was added to some glassy slags as a surrogate for actinide wastes. Contaminated sand was used as a source for silica for some of the melts. All these melts represent zero additives, i.e., the waste loading is 100%, because all the feeds were surrogates for actual wastes. A batch of about 300 g of mixture of chemicals and INEL soil was ball milled for more than 4 hours to ensure complete mixing. The mixture was then put into a furnace preheated to about 800°C in a high alumina crucible (99.8%  $\text{Al}_2\text{O}_3$ ). The slags were melted at 1500°C for about 1 hour. The melt was then quenched by pouring into a platinum mold. If the melt was unable to be poured, then the melt was air cooled in the crucible. The poured slag was annealed for one hour at about 500°C and then the furnace was turned off to cool to room temperature.

**Slag Dissolution.** Some of the slags made were dissolved and analyzed to check the mass balance. The dissolution process used to determine the bulk compositions of the slags and INEL soil consists of a Parr bomb dissolution step and a hot plate digestion step. The Parr bomb step is used for those samples that require the determination of B and Si along with other components which are soluble in  $\text{HF-HNO}_3$ . A 50-100 mg finely divided sample is treated with 8 mL of  $\text{H}_2\text{O}$ , 5 mL of conc.  $\text{HNO}_3$ , and 0.5 mL of conc. HF in a Teflon cup. This cup is sealed in a Parr Bomb and heated (typically overnight) to 140°C in a laboratory oven. After cooling, this solution is diluted to known volume and analyzed by ICP-MS.

The hot plate digestion step is applied to those materials that require rare earths and actinide (or actinide surrogate such as Ce) measurements. The solution from the Parr bomb step is filtered through a Whitman #42 paper, and the filtrate is collected in a volumetric flask. The filter paper and residue are rinsed with deionized water, then placed in a tared platinum crucible. The filter paper is then burned in a 600°C muffle furnace. The residue is moistened with  $\text{H}_2\text{O}$  and a few mL of  $\text{HClO}_4$ . The solution is heated on a hot plate in a hood until the residue dissolves. This solution is then added to the volumetric flask containing the filtrate, diluted to volume, and submitted for ICP-MS analysis.

### Chemical Durability Tests

Each slag was thoroughly tested for durability as shown by the test matrix in Table III, and these tests are described in the following paragraphs.

TCLP Test. The EPA Toxicity Characteristic Leaching Procedure (TCLP) [4] was used to determine the leachability of arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Leachate concentrations were measured after glassy slag powders were reacted for 18 hours at 22°C in a sodium acetate buffer solution. This test satisfies the EPA regulatory requirements for RCRA controlled toxic metals and allows the performance of the glassy slag in the TCLP test to be compared to that of other waste forms.

PCT-Type Test. A static powder test similar to the Product Consistency Test (PCT) [5] was used to evaluate the relative durability of the glassy slags by measuring the concentrations of the elements released from the crushed glassy slags (75-150  $\mu\text{m}$ ) to the solution at 90°C. This test allowed the durability of glassy slag to be compared with that of high-level nuclear waste (HLW) glasses that have been tested extensively and have a large durability data base accumulated.

Vapor Hydration Test. The ANL vapor hydration test [6] was utilized as an acceleration test to measure the durability of the glassy slags in saturated water vapor at 200°C. Durability was measured as a function of (1) the rate and amount of secondary alteration phase formation on the surface of the glassy slags and (2) the thickness of the altered surface layers surrounding the samples, as measured in cross section. This information provides insight regarding the long-term durability of glassy slags and allows a comparison with the durability of HLW glasses.

Monoliths were used in the vapor hydration tests. Surfaces of the slag samples were polished to a 600 grit finish, and the samples were ultrasonically cleaned in a methanol bath. Tests were initiated by suspending sample monoliths from Teflon threads which were then attached, in pairs, to a stainless steel support rod. The entire sample-Teflon thread-support rod assembly was next inserted into the inside of a stainless steel reaction vessel having a volume of 21.4 mL. A predetermined volume of water (0.25 mL) was added to each vessel in an amount sufficient to saturate the vessel atmosphere with water vapor after heating to the appropriate experimental temperature, but insufficient to cause refluxing of water between the samples and the fluid collected in the bottom of the vessels. After the water had been added, the vessels were hermetically sealed and inserted into a 200°C oven that was controlled to  $\pm 2^\circ\text{C}$  [6].

#### Analyses of Solutions and Solids

Solution Analyses. Cations and radionuclides were analyzed with ICP-MS with an accuracy of  $\pm 10\%$  for major elements and  $\pm 50\%$  for radionuclides and minor elements. Anions were analyzed with ion chromatography with an accuracy of about 50%. The pH was analyzed with an ion selective electrode.

Solids Analyses: X-Ray Diffraction (XRD) Analysis. The as-melted slag powders were analyzed with a Philips Powder Diffractometer (with theta-compensating Slit) and  $\text{CuK}$  radiation. The scan range was from 10 to 80 degrees (2 theta), with a stepping interval of 0.05 degree and a 2-second count time. Samples were placed in a low-background quartz holder (from Gem Dugout) with a depression 16 mm in diameter and 0.2 mm deep. The sample holder holds about 0.1 g of powdered slag (<75  $\mu\text{m}$ ).

Solids Analyses: Scanning Electron Microscopy (SEM). Spectra and images were collected on a Topcon ABT60 SEM at 15 kV with a Princeton Gamma-Tech (PGT) energy-dispersive X-ray spectrometer (EDS) on both as-melted and reacted slags. To prepare samples from the PCT tests, many slag chips were embedded in a room-temperature-curing epoxy, then cross sectioned and polished to a 600 grit finish. Monoliths from the vapor hydration tests were either mounted directly on an aluminum mounting stub and examined in the SEM or mounted in epoxy and cross sectioned for layer thickness measurements.

Solids Analyses: Transmission Electron Microscopy (TEM). The reacted glassy slags were examined in a JEOL 2000FXII TEM operated at 200 kV and equipped with two EDS detectors and an electron energy loss spectrometer. Particles of slag were embedded in epoxy and sectioned by ultramicrotome.

## RESULTS AND DISCUSSION

### Evaluation of Unreacted Slags

The characterization of the unreacted glassy slags include the study of morphology, element distribution among different phases, and the identification of these phases. This knowledge will enable us to better understand the corrosion behavior, the ability to retain hazardous/radioactive elements, and optimized formulation of the glassy slag waste form.

As-melted slags were examined using XRD, SEM/EDS, and TEM/EDS. The unaltered slag waste form is composed of both crystalline and glassy materials. The texture of the slag can best be described as porphyritic, with relatively coarse-grained crystalline phenocrysts suspended in a predominantly glassy matrix. The distribution between glassy and crystalline phases is generally nonuniform, with both glass- and crystalline-rich regions occurring in most samples (Fig. 1) of a glassy slag. Sample ANL-M3 was especially heterogeneous, with porphyritic regions separated by entirely glassy regions of the samples (Fig. 1a). The proportions of crystalline material are given in Table IV. These proportions were estimated from observations of a single sample of each composition, thus, sample heterogeneity may result in significant variations in these estimates. The coarse-grained primary crystalline phases exhibited a variety of habits, including blocky, trigonal, lath, and round shaped crystals (Figs. 1 and 2).

PLACE FIGURE 1 HERE

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Of key interest in this study, is how the hazardous components are partitioned between the glassy and crystalline phases of the melt and how they behave during the alteration of glassy slags. The elements of interest are the hazardous metals Cr, Ni, and Pb, and Ce used in this study as a surrogate for Pu.

The elemental compositions of the glassy regions were fairly consistent, with variations resulting from different amounts of major glass constituents present, as shown in Table V. All glass matrix regions were dominated by Si, with lesser amounts of Al, Ca, Fe, and K. These five elements were present in all samples examined. Cerium

was detected as a minor constituent in the glass phases in slag compositions ANL-7, ANL-M8, ANL-M10, ANL-M11, and ANL-M12. In addition, the glass phases of ANL-8 and ANL-M11 contained Pb. The EDS spectra peaks for additional constituents, Ti, Mg and Na were barely detectable. A typical EDS spectrum from TEM of the glass phase in a glassy slag is shown in Fig. 3a. The presence of Ce in the glass phase of ANL-M8 was further verified by the EELS spectrum (Fig. 3b) where the characteristic  $M_4$  and  $M_5$  peaks of Ce are clearly identified. Another interesting observation from Table V is that  $SiO_2$  and  $Al_2O_3$  are concentrated in the glass phase. The total wt% of  $SiO_2$  and  $Al_2O_3$  in glass phase is between 69 to 79%. A glass with such high content of silica and alumina is usually very durable. This will offer an explanation for the observed superior durability discussed below and this good durability of the glass phase means that the Ce (surrogate for radionuclides) and Pb release from the slag is minimal.

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Table V also indicates that Cr and Ni are partitioned almost exclusively into the Fe-rich crystals during the slag solidification process. Because the Fe-rich crystals are relatively resistant to chemical attack, release of Ni and Cr to the environment should be minimal during alteration of the slag waste.

The primary crystalline phases appear to be Fe-rich spinel group minerals that contain variable amounts of Cr, and lesser amounts of Ni, Al, Ca, and Ti as shown in Table V. TEM was utilized for the identification of the crystals. Convergent beam electron diffraction was used to examine the overall symmetry of the crystalline phases. Zone axis patterns with four fold symmetry suggested that the phase was cubic, and therefore probably a spinel and the electron diffraction of the most abundant crystals matches with spinel iron oxide (maghemite). Figure 4a is the EDS spectrum of a Fe-Cr-Ni crystalline phase, and Fig. 4b is the selected area electron diffraction (SAED) pattern taken down the  $\langle 101 \rangle$  zone. This phase is identified as a spinel phase. This is considered as consistent with the XRD analysis on powdered glassy slags, which suggest the presence of spinel group minerals including maghemite ( $\gamma-Fe_2O_3$ ), trevorite ( $NiFeO_4$ ), and chromite ( $FeCr_2O_4$ ).

PLACE FIGURE 4 HERE

#### Chemical Durability of Glassy Slags

The results of the TCLP analyses are shown in Fig. 5. The measured concentrations of Ag, As, Ba, Cd, Cr, Hg, Pb, and Se were at least a factor of 40 below the regulatory levels of the EPA TCLP test for all the glassy slags. Most of these toxic elements were detected in the TCLP leachates in ppb range (Fig. 5). These low TCLP concentrations occurred despite the fact that hazardous elements, such as Cr and Pb, were as high as 7 and 3%, respectively, in our slags, while in most other studies reported, their levels in the waste forms were only a few hundred ppm [7]. There is no TCLP limit available for Ni, but all the slags pass the more restrictive land disposal limit of 0.32 ppm [8] even though the slags contain as high as 4 wt% Ni.

The 28-day PCT results, shown in Fig. 6, indicate that the slags with high metal loadings have chemical durabilities (as determined by the release of silica, sodium, and potassium into solution) similar to or

better than high-level nuclear waste glasses such as SRL 131, SRL 165, SRL 202U, SF6, SF10, TC-13, WVCM59, and WVCM62 [9].

The slag samples reacted under PCT test conditions were examined with both SEM and TEM to characterize the extent of reaction. None of the samples examined showed any indication of glass dissolution or reaction product formation. Slag ANL-M8 in the "as-melted" and reacted states were compared to verify this conclusion (Fig. 2). Formation of a reaction layer would result in the observation of contrast differences in the SEM image due to changes in density and composition. Also, EDS analysis might indicate a change in composition. Neither of these changes were observed. Glass dissolution would result in a preferential loss of glass compared to the crystalline phase. This would cause the sample surface to be rich in crystalline material with void intrusions where the glass had been present. Such voids were not observed. The TEM micrographs in Fig. 7 may show only slight evidence of slag reaction with water (Fig. 7a), but the evidence is hard to see in Fig. 7b, taken after the sample had reacted in water for seven days under PCT test conditions. More detailed TEM examinations are in progress to investigate these reactions.

The behavior of slags in vapor hydration tests at 200°C in saturated water vapor provides insight on the long-term durability of the waste form. Optical and SEM/EDS examination of the reacted samples from the 28-day vapor hydration tests indicate the development of patches of green-grey to rust-colored discoloration and the formation of dispersed, very fine-grained, white precipitates. Alteration phases that were tentatively identified on these samples include clays with compositions consistent with nontronite and/or nontronite-illite mixtures, calcite-dolomite [ $\text{CaCO}_3\text{-CaMg}(\text{CO}_3)_2$ ], anhydrite [ $\text{CaSO}_4$ ], and unidentified Ca-Si spheres and Ca-P-Si fibers. Several Fe-, Si-, and Cu-rich phases were also located, with the Cu-rich phases containing notable quantities of Fe, Sn, Pb, Zn, and Cr.

The overall appearance of the reacted sample surfaces and the composition of the alteration phases suggest that the Fe-rich crystalline phases are more resistant to chemical attack than is the glass matrix, although both the glass and crystalline phases display very little evidence of chemical corrosion even under these aggressive conditions. Alteration of the slag surface under vapor hydration test for 28 days was less than 1  $\mu\text{m}$ . By contrast, SRL 202 glass, a high-level waste glass, had developed reaction layer thicknesses of about 20  $\mu\text{m}$  under identical conditions after 21 days [10]. These comparisons suggest that glassy slags are more resistant to corrosion under these test conditions than high level nuclear waste glasses.

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## CONCLUSIONS

The slags produced in this project represent a waste form that contains both glass and crystalline phases. The crystalline phases may account for more than 80% of the total volume of slags having high metal loadings. Slags may be formulated in such a way that both the



glass and crystalline phases are very durable. The Ni- and Cr-spinel phases identified incorporate toxic elements and are very stable and durable, and show negligible leaching of hazardous Cr and Ni. As a result of crystalline phase formation, the glass phase in the slag becomes enriched in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and may account for more than 80 wt% of the glass phase. The glass phases in the slags generated in this program were observed to be very durable. This is important because the glass phase serves as a durable host for radionuclides and other hazardous elements not incorporated into crystalline phases. These tests showed that up to 84 wt% metal oxides (Fe, Ni, and Cr) can be loaded into a glassy slag to produce a processable and highly durable final waste form with zero purchased additives. Therefore, utilizing glassy slag waste forms allows the MAWS approach to be applied to a much wider range of waste streams than those simply amenable to homogenous glass waste forms and it may also offer larger volume reduction and overall remediation cost savings.

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Table II. Slag compositions in terms of (soil + simulated waste metals) as mixed, wt%

	Carbon Steel	Stainless Steel	Soil	Aluminum	Lead	CeO <sub>2</sub>	Sand
ANL-M1	62.1		37.9				
ANL-M2	73.7		26.3				
ANL-M3		15.0	85.0				
ANL-M4		30.0	70.0				
ANL-M5	50.0		50.0			1.0	
ANL-M6	54.0		20.0	5.0		1.0	20.0
ANL-M7	47.0	24.0	28.0			1.0	
ANL-M8	39.9	17.1	34.9	4.7	2.0	1.1	
ANL-M9	40.0	15.0	45.0			1.0	
ANL-M10	45.0	10.0	44.0			1.0	
ANL-M11	43.0	10.0	44.0		2.0	1.0	
ANL-M12	45.0 (2% Cl)	10.0	44.0			1.0	
ANL-M13	47.0	8.0	44.0			1.0	
ANL-M14		10.0	89.0			1.0	
ANL-M15	49.0	10.0	38.0		2.0	1.0	
ANL-M16	69.0		30.0			1.0	

Table III. Testing performed for glassy slags

Melts	PCT Tests			TCLP	Vapor Tests	
	7	28	91		7	28
ANL-M1	Y	Y	Y	Y	Y	Y
ANL-M2	Y	Y	Y	Y	Y	N
ANL-M3	Y	Y	Y	Y	Y	Y
ANL-M4	Y	Y	Y	Y	N	N
ANL-M5	Y	Y	Y	Y	N	N
ANL-M6	Y	Y	Y	Y	N	N
ANL-M7	Y	Y	Y	Y	N	N
ANL-M8	Y	Y	Y	Y	N	N
ANL-M9	Y	Y	Y	Y	N	N
ANL-M10	Y	Y	Y	Y	N	N
ANL-M11	Y	Y	Y	Y	Y	Y
ANL-M12	Y	Y	Y	Y	Y	N
ANL-M13	Y	Y	Y	Y	Y	Y
ANL-M14	Y	Y	Y	Y	N	N
ANL-M15	Y	Y	Y	Y	N	N
ANL-M16	Y	Y	Y	Y	N	N

Y = completed; N = not scheduled.

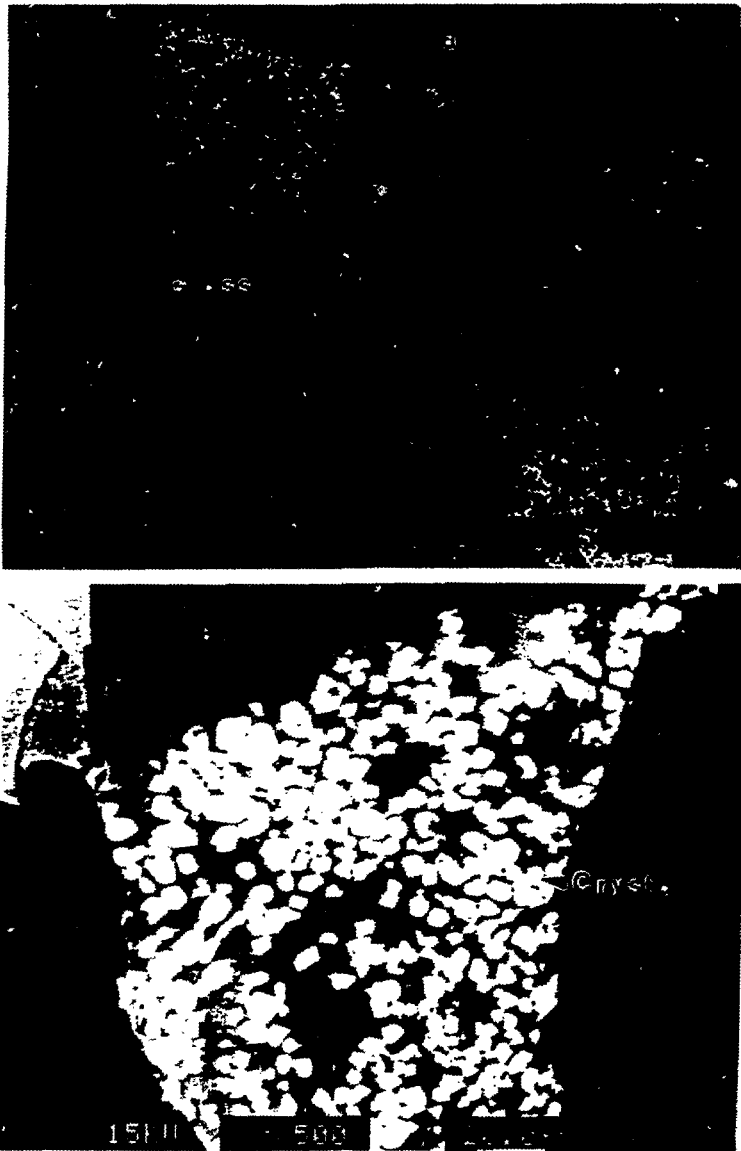
Table IV. Volume estimates of slags

Slag ID	Volume % Crystals
ANL-M1	80
ANL-M2	80
ANL-M3	20
ANL-M11	50
ANL-M12	70
ANL-M13	70

Table V. SEM semiquantitative EDS analysis of glassy slags. Oxide weight %  $\pm 10\%$ .

Melt		Al <sub>2</sub> O <sub>3</sub>	CaO	CeO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	NiO	PbO	SiO <sub>2</sub>	(SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> )
ANL-M1	Glass Crystal	13 4	7 -	- -	- -	13 96	2 -	- -	- -	66 -	(79)
ANL-M4	Glass Crystal	10 4	8 -	- -	- 16	9 68	2 -	- 9	- -	67 3	(77)
ANL-M7	Glass Crystal	13 5	7 -	3 -	- 6	9 88	2 -	- -	- -	66 2	(79)
ANL-M6	Glass Crystal	16 11	5 -	1 -	- 6	15 80	2 -	- 3	7 -	53 -	(69)
ANL-M10	Glass Crystal	11 4	8 -	1 -	- 3	16 92	2 -	- 1	- -	62 -	(73)
ANL-M11	Glass Crystal	13 7	7 -	1 -	- 8	10 81	1 -	- 2	8 -	62 2	(75)
ANL-M12	Glass Crystal	12 5	6 -	4 -	- 6	19 88	1 -	- 2	- -	57 -	(69)

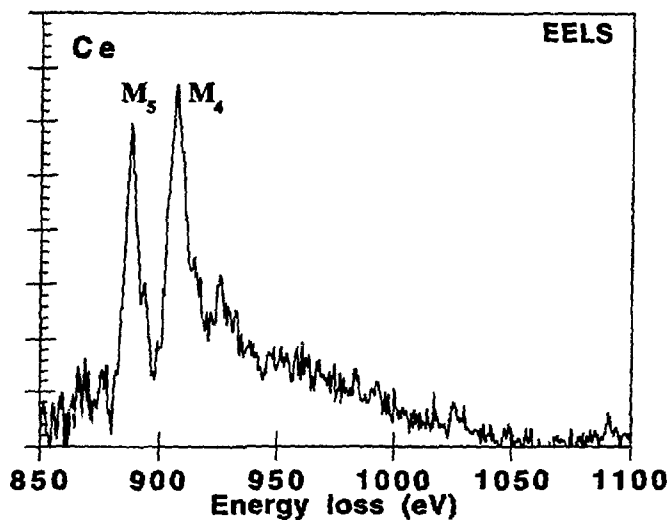
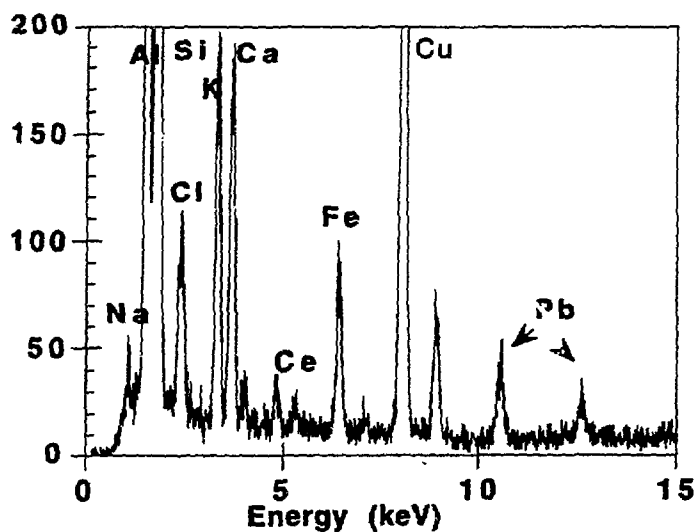




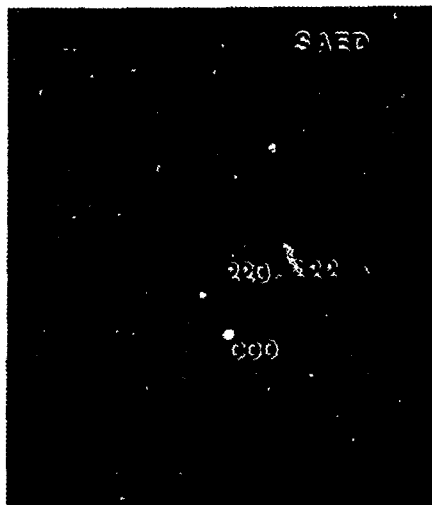
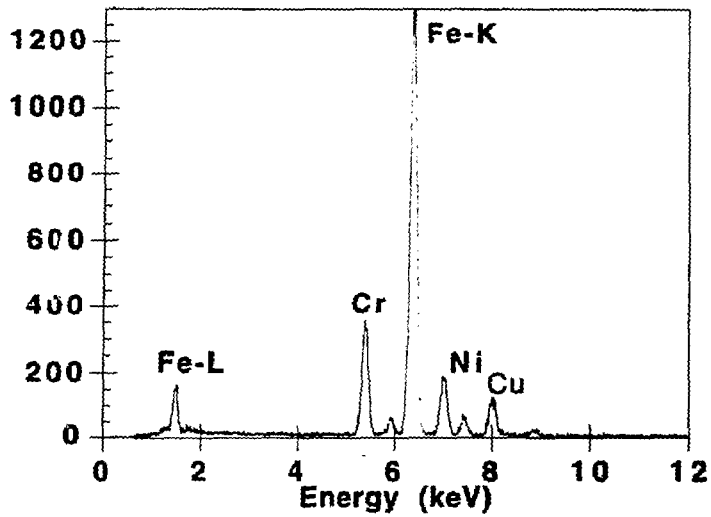
**Fig.1 SEM micrographs of the cross sections of glassy slag ANL-M3 (a) and ANL-M4 (b), showing the nonuniform distribution of crystalline phases.**



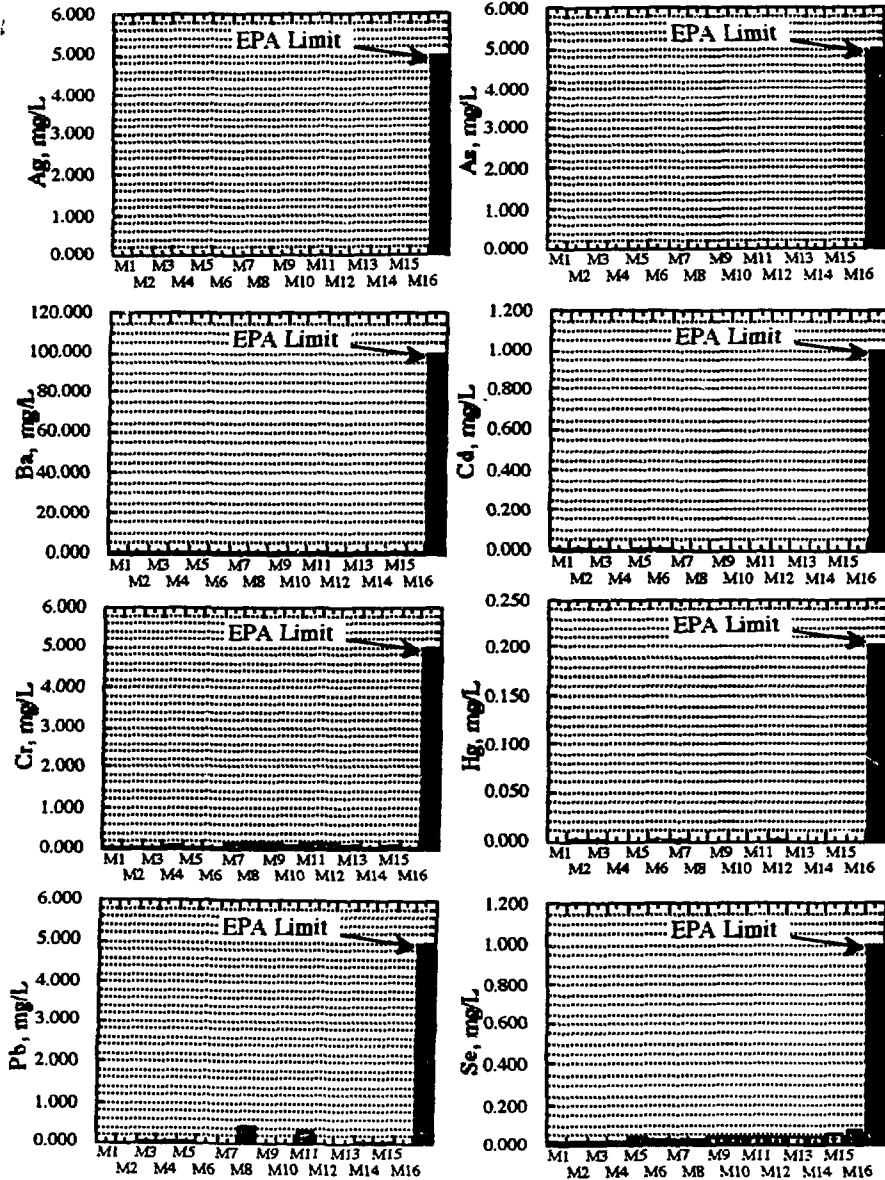
**Fig.2 SEM micrographs of glassy slag ANL-M8 in the state of "as-melted" (a) and after 7-day PCT test (b), showing no evidence of slag reaction with water.**



**Fig.3 (a) EDS spectrum of the glass phase of ANL-M8, showing the presence of Ce and Pb.**  
**(b) EELS spectrum of the glass phase of ANL-M8, showing the characteristic peaks, M<sub>4</sub> and M<sub>5</sub> of Ce.**

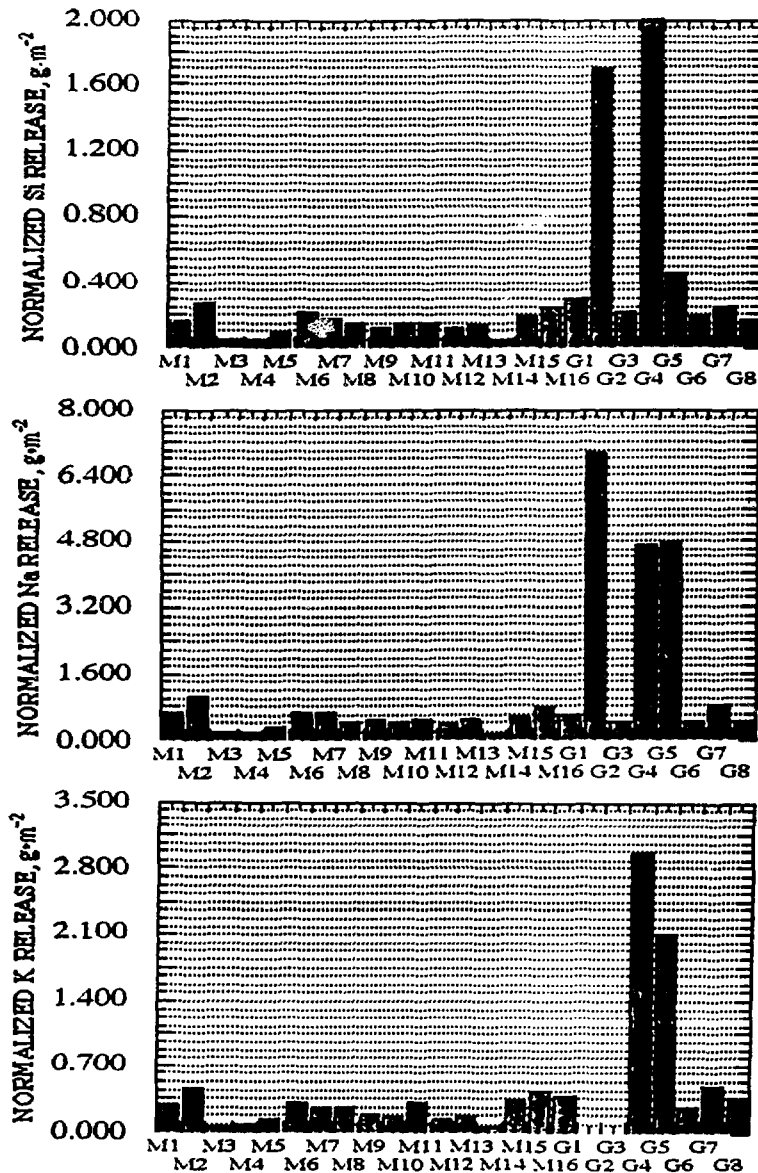


**Fig.4 (a) EDS spectrum of a spinel phase of ANL-M8, showing the presence of Ni and Cr.**  
**(b) The SAED pattern of the Ni-Cr spinel phase taken down the  $\langle 101 \rangle$  zone axis.**



**Fig.5 Comparison the TCLP leachate concentrations of glassy slags with the EPA TCLP limits on the hazardous elements.**

Label explanation: M = ANL-M, i.e., M1 = ANL-M1.



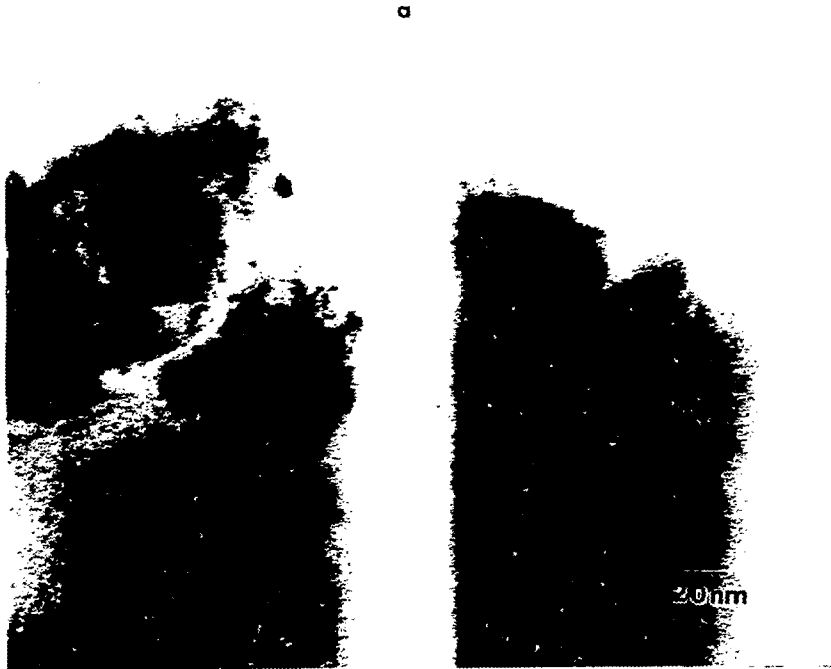
**GLASSY SLAGS:**

- M1 - ANL-M1
- M2 - ANL-M2
- M3 - ANL-M3
- M4 - ANL-M4
- M5 - ANL-M5
- M6 - ANL-M6
- M7 - ANL-M7
- M8 - ANL-M8
- M9 - ANL-M9
- M10- ANL-M10
- M11- ANL-M11
- M12- ANL-M12
- M13- ANL-M13
- M14- ANL-M14
- M15- ANL-M15
- M16- ANL-M16

**HIGH - LEVEL NUCLEAR WASTE GLASSES:**

- G1 - SRL-202U
- G2 - SRL-131
- G3 - SRL-165
- G4 - SF6
- G5 - TC-13
- G6 - WVCM62
- G7 - WVCM59
- G8 - SF10

**Fig.6 Comparison of 28-day PCT test results of glassy slags with these of high-level nuclear waste glasses in terms of release of Si, Na, and K from waste forms to solutions.**



**Fig.7** TEM micrographs of ANL-M8 after 7-day PCT tests.