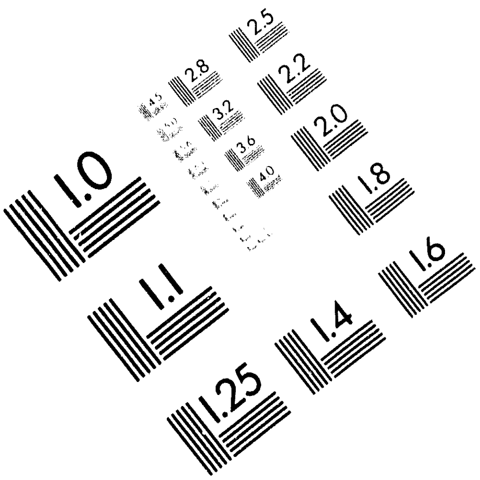

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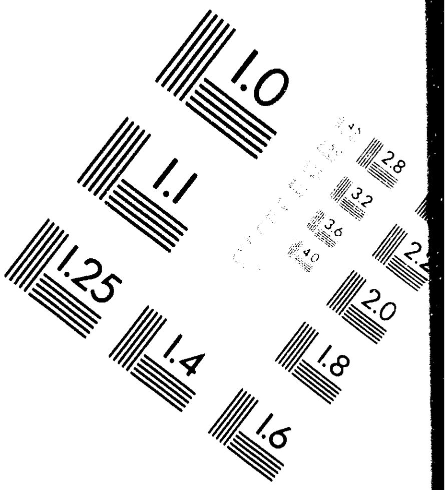

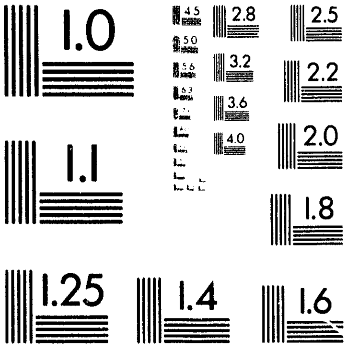

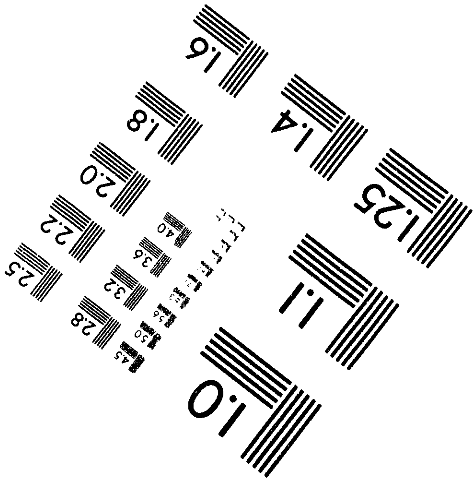

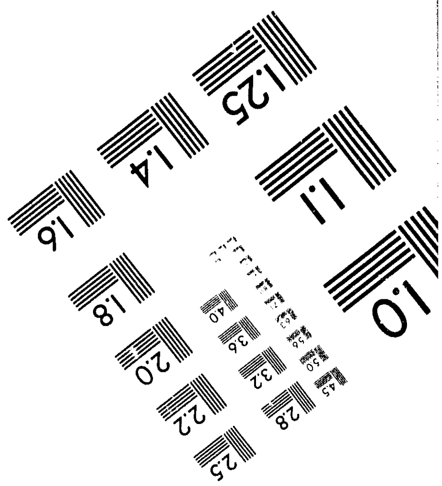

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GLASSY SLAG - A COMPLEMENTARY WASTE FORM TO HOMOGENEOUS GLASS FOR THE IMPLEMENTATION OF MAWS IN TREATING DOE LOW-LEVEL/MIXED WASTES

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GLASSY SLAG - A COMPLEMENTARY WASTE FORM TO HOMOGENEOUS GLASS FOR THE IMPLEMENTATION OF MAWS IN TREATING DOE LOW-LEVEL/MIXED WASTES

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ABSTRACT

Glassy slag waste forms are being developed to complement glass waste forms in implementing the Minimum Additive Waste Stabilization (MAWS) Program for supporting DOE's environmental restoration efforts. These glassy slags are composed of various metal oxide crystalline phases embedded in an alumino-silicate glass phase. The slags are appropriate final waste forms for waste streams that contain large amounts of scrap metals and elements with low solubilities in glass, and that have low-flux contents. Homogeneous glass waste forms are appropriate for wastes with sufficient fluxes and low metal contents. Therefore, utilization of both glass and glassy slag waste forms will make vitrification technology applicable to the treatment of a much larger range of radioactive and mixed wastes. The MAWS approach was applied to glassy slags by blending multiple waste streams to produce the final waste form, minimizing overall waste form volume and reducing costs. The crystalline oxide phases formed in the glassy slags can be specially formulated so that they are very durable and contain hazardous and radioactive elements in their lattice structures. The Structural Bond Strength (SBS) Model was used to predict the chemical durability of the product from the slag composition so that optimized slag compositions could be obtained with a limited number of crucible melts and testing.

I. INTRODUCTION

Vitrification to produce borosilicate glasses is the best demonstrated available technology within the DOE complex for treatment of low-volume, high-level radioactive wastes (HLW) that have low waste loading and high treatment costs, where vitrification is justifiable because of the small volume and high risk associated with the HLW. The MAWS concept [1] provides an environmentally sound, cost-effective alternative for the vitrification of the vast amounts of low-level radioactive and mixed wastes that exist within the DOE complex. The MAWS approach uses multiple waste streams as a substitute for glass-forming additives that would otherwise be necessary to produce high-quality waste forms. The substituting of other waste streams for glass-forming additives lowers the overall waste form volume and cost for disposal. The first pilot-scale demonstration and evaluation of a complete vitrification system using the MAWS approach is being implemented at Fernald, Ohio; glass is produced as the final waste form [2].

Glass is a relatively homogeneous, amorphous solid without long-range order. A properly formulated glass waste form can be relatively easy to produce, and it can possess a high resistance to aqueous corrosion. In addition, the glass matrix can have powerful solvating properties applicable to a wide range and large amounts of hazardous and radioactive components. However, two limitations for the production of glass final waste forms restrict their application to the MAWS approach: (1) a sufficient amount of fluxing components (such as alkalis, boron, or alkaline earths) is required to attain a processible melt viscosity at a practical temperature, and (2) the solubilities of many metal waste components in the glass are low, so waste loadings may be unacceptably small. Many DOE wastes, as discussed in the next section, exhibit these two limitations, which lead to processing difficulties and deterioration of glass waste form durability under repository-relevant conditions.

In Sections III and IV, we describe the characteristics of glassy slags that make them attractive for disposing of these DOE wastes. Section V summarizes the current status in the development of glassy slags.

II. DOE WASTES SUITABLE FOR GLASSY SLAGS AND THE VITRIFICATION PROCESS

Many DOE sites have large volumes of wastes that contain large amounts of scrap metals (e.g., metals constitute 22 wt% of the buried wastes at Idaho National Engineering Laboratory's Radioactive Waste Management Complex) and metal oxides of Cr, Ni, Ti, and Fe (e.g., the 16-million kilograms of K-25 pond sludge/soil at the Oak Ridge site contains about 25 wt% iron oxides, 20 wt% alumina, and 20 wt% calcium oxides). These wastes typically contain only small amounts of fluxing components. Because these metal oxides have relatively low solubilities in glass, moderate loadings of these waste streams can result in the formation of crystalline phases during vitrification. This uncontrolled crystallization in glass melts may lead to difficulties in glass processing and uncertainties in glass durability. If this two-phase material is not an acceptable waste form, expensive additives must be purchased to dilute the metal oxides. This increases the final waste form volume and treatment costs.

The vitrification process uses high temperatures (typically between 1100 and 3000°C) to chemically incorporate wastes into a stable amorphous liquid. If this liquid is cooled down to become a solid without crystallization, the solid freezes the unordered liquid and becomes a glass waste form that is amorphous. Crystalline phases may be either thermodynamically unstable or kinetically unable to form during the cooling down period. With high metal wastes, the low solubilities of metals make the crystalline phase formation both thermodynamically and kinetically favorable during the cooling down period. There are two possible scenarios: either crystallization in a glass melt where sufficient fluxing elements exist or a controlled crystallization in a glassy slag melt where metal oxides are abundant and fluxes are deficient. The crystallization process in glass melts is undesirable and can result in: (1) high viscosity, making glass flow difficult; (2) precipitation of crystals, leading to clogging of the melter; (3) formation of crystals that are very soluble in water, such as the lithium phosphate phases observed in West Valley nuclear waste glass [4]; and (4) enrichment of fluxes in the vitreous phase, leading to decreased durability of glasses.

In contract to homogeneous glass, the crystallization is a controlled and preferred process in glassy slags. The high viscosity due to crystallization is much less of a concern because a plasma centrifugal furnace is used for the production of glassy slags. The crystallization is controlled by the slag formulations so that only stable and durable crystals form. The wastes treated with glassy slags usually contain small amounts of fluxes, and there is less concern of forming a soluble vitreous phase in the slags. By contrast, the crystallization process expels SiO_2 and Al_2O_3 from the crystalline phases, resulting in a SiO_2- and Al_2O_3-rich vitreous matrix that is very durable; this will be discussed in more detail later.

Glassy slag waste forms are excellent candidates for high metal waste streams because these slags will accept waste streams with high metal loadings and low flux contents without sacrificing product durability, corrosion resistance, or processibility. The MAWS approach is, therefore, also being evaluated with glassy slags in which crystalline metal oxide phases are dispersed throughout a glassy matrix [5].

III. THE RELATIONSHIP BETWEEN GLASSY SLAGS AND HOMOGENEOUS GLASSES

Both homogeneous glasses and glassy slags have been identified as having the potential to yield environmentally sound waste forms. The relationship between the two distinct regions of the compositional envelope for the glass and glassy slag is illustrated in Fig. 1. As shown, the homogeneous glass region is more amenable to lower temperature melters, while the glassy slag region is better suited to high-temperature processing. The glass region contains mostly network-formers that are "structure making" components, such as SiO_2, Al_2O_3, ZrO_2, and "fluxes," such as alkalis and boron with only small amounts of "intermediates" or crystal formers (such as iron, nickel, and chromium oxides). This glass region is being investigated at the Catholic University of America. The glassy slag region, which contains "structure making" components and higher quantities of "intermediates" (metal oxides) with low concentrations of fluxing agents, is being investigated at ANL. As shown in Fig. 1, the slag region is deficient in fluxes and rich in metal oxides; this condition favors crystallization and produces both durable vitreous and crystalline phases. The glass region in Fig. 1 favors formation of amorphous solids and discourages crystalline phase formation. Thus, glassy slag is good for waste streams with high metal contents and with low flux (alkalis and boron) contents, while homogeneous glass is suitable for waste streams with low metal content and sufficient flux contents.

IV. CHARACTERISTICS OF GLASSY SLAG WASTE FORMS

A. Production

Glassy slags have been produced at ANL by melting together soils from the Idaho National Engineering Laboratory with metal oxides that are typical of those in waste steel scrap, tools, and equipment. The highest loading was 84 wt% of metal oxides. A total waste loading of 100% was achieved. Since the soils were meant to be typical of soils contaminated with actinides, cerium, as CeO_2, was added to some slags as a surrogate for plutonium. All slags were melted at 1500°C. Two typical slag compositions are shown in Table 1 (discussed later).

Slags with compositions similar to those developed through laboratory crucible melts were also successfully produced at Ukiah, California, in the Retech 1.5-ft dia. plasma centrifugal furnace (PCF) by MSE, Inc. [6]. These semi-continuous bench-scale melts demonstrated the potential of producing glassy slag waste forms by this high-temperature melting technique. These tests were the initial feasibility studies for this equipment. The processing requirements imposed by this type of vitrifier on viscosities, electrical conductivities, and other processing parameters were much less stringent than those for producing homogeneous glass waste forms in other types of vitrifiers.

The slags made in small laboratory crucibles simulated many aspects of the slags produced in the PCF. The crucible and PCF slags had similar glass and crystalline phases, and they exhibited similar chemical durability in terms of normalized release rates of the major components of the slags in leach tests. Although the slags produced in the PCF furnace using actual metals were usually less oxidized, this difference had little effect on the long-term corrosion behavior. The only difference observed was the normalized release of cerium, but this difference was transitory and disappeared after 28 days in leach tests. The organic content of both slags was very low, and the leachates of the slags showed total organic contents of only a few milligrams per liter [6]. Over 99.99% total organic destruction in slags has been demonstrated by Kujawi and Whitworth [3].

B. Morphology

The glassy slags produced in this study were composed of various crystalline and metal oxide phases embedded in a silicate glass phase; a typical slag is shown in Fig. 2. The crystals exhibited a variety of habits, including blocky, trigonal, lath, and rounded crystals. The shapes, sizes, amounts, and nature of these crystals depended on the slag compositions and heat treatment during the production [6]. The volume fraction of the crystalline phases was as much as 80%. The crystalline oxide phases formed in the glassy slags were specially formulated so that they are very durable and contain most of the hazardous and radioactive elements in their lattice structures. For this reason, there is no need of efforts to avoid crystalline phase formation, as is the case for homogeneous glasses.

C. Solid Characteristics

Glassy slags were characterized to identify the distribution of radioactive/hazardous materials among the glass and crystal phases. As-melted slags were examined using X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). Analysis of the slags indicated the presence of spinel-group minerals, including magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and solid solutions of magnetite with chromium and nickel. The types and amounts of crystalline phases present depend on the metal-waste loadings. Hazardous elements, such as chromium and nickel, are incorporated into crystalline phases. The glass phase consists mainly of structure-making oxides, such as SiO_2 and Al_2O_3 with small amounts of the oxides of Fe, Ca, Pb, K, and Ce. The composition of the glass phase depended on both the materials charged and on the phases crystallized. Because cerium and lead were mainly in the glass phase in these slags, the ability to retain cerium and lead is determined by the durability of the glass phase, while the retention of hazardous elements, such as nickel and chromium, depends on the stability of the crystalline phases.

The recent efforts to develop glassy slags have been directed toward the formation of crystals that sequester actinides in their lattice structures. For example, uranium and cerium were found to be preferentially concentrated in zirconalite [7], which incorporated more than 10 wt% uranium oxide and 7 wt% cerium oxide in the lattice. This finding strongly suggests that zirconalite will also sequester plutonium and other transuranic elements. Plutonium-doped slags are also being made at ANL. If most of the hazardous elements and radionuclides can be incorporated into a crystalline phase such as zirconalite, the emphasis on making a durable glass phase in the slags can be reduced, and then waste streams with high alkali contents can also be converted into glassy slags.

D. Chemical Durability

The chemical durability of the glassy slag was evaluated using the experience and methods accumulated in the testing of HLW glasses. The test methods included the EPA Toxicity Characteristic Leaching Procedure (TCLP) [8], the Product Consistency Test (PCT) [9], and the ANL vapor hydration test [10]. The TCLP was used to show that the slags can satisfy RCRA requirements controlling toxic metals. The PCT was used to demonstrate the chemical durability of slags related to HLW glasses. The vapor hydration test was used to provide insight into the long-term durability of slags. Leachate solutions from these tests were analyzed for cations using inductively coupled plasma-mass spectroscopy (ICP-MS), anions using ion chromatography, and pH using a pH meter. The reacted solids were characterized with optical microscopy, SEM/EDS, and transmission electron microscopy (TEM).

The results from these tests can be summarized as follows. The hazardous element concentrations in leachates from the slags tested by the TCLP were at least a factor of 40 below the regulatory limits [4]. The PCT results indicated that the slags with high metal loadings have chemical durabilities (as determined by the release rate of silicon into solution) better than HLW glasses, such as SRL 165, SRL 131, and WVCM62 [11]. These results are shown in Table 2, where the normalized silicon releases of glassy slags and high-level nuclear waste glasses are compared. The least durable slag composition, ANL-M2, which had a metal loading of about 80%, was at least four times more durable than SRL 131 and had a durability similar to the other HLW glasses. The normalized silicon release rate (normalized release divided by test duration) for ANL-M2 is 0.036 $g/m^2/day$, which is much lower than the 0.17 $g/m^2/day$ for SRL 131. The normalized silicon release rates for HLW glasses SRL 165 and WVCM62 are 0.030 and 0.022 $g/m^2/day$, respectively, while the rates for slags ANL-M3 and ANL-M14 are 0.0048 and 0.0047 $g/m^2/day$, respectively. Also note that the waste loading for HLW glasses is usually less than 30%, while the slags can be made of 100% wastes (i.e., waste metals plus contaminated soil).

The TEM examination of slags reacted for 91 days in PCT tests at 90°C indicated an absence of, or at most a limited formation of, alteration phases, as shown in Fig. 3, and similar compositions of the slags before and after testing

[4]. Figure 3 also shows that the vitreous and crystalline phases remained in contact in spite of the harsh sectioning process. (The TEM sample was sectioned in a microtome to a thickness of about 100 nm in order to be transparent to electrons.) This finding indicates that these boundary regions will not experience preferential dissolution due to high-permeability fractures.

The slags reacted in a saturated water vapor environment at 200°C for 28 days showed surface alteration layers of less than one micrometer in thickness. By comparison, SRL 202 glass, a likely composition to be produced in the Defense Waste Processing Facility at the Savannah River Site, would have developed surface alteration layers with thickness of about 20 μm after 21 days at 200°C [12]. This result indicates that glassy slags are expected to have better long-term durability than the HLW glasses.

The superior chemical durability of the glassy slags is due to the crystalline and glass phases when the overall composition is optimized. Glass, by definition, is metastable and will transform eventually into an assemblage of more stable crystalline phases when in contact with water and water vapor [13]. However, the spinel phases identified in the glassy slags are considerably more stable than glasses and have lower solubilities in groundwaters. Phase stability is an important reason why very little alteration was seen on slags exposed to very severe vapor hydration test conditions (200°C and saturated water vapor) and to 91-day testing with the PCT.

Table 1 shows the typical compositions of glassy slags and their element distributions between vitreous and crystalline phases. The first column shows the initial formulation compositions. The second column is the typical composition of the vitreous phases in the slags. The third column is the typical composition of the crystalline phases in the slags. The fourth column shows typical HLW glass compositions.

As shown in Table 1, the crystalline phases formed in these slags incorporate the hazardous elements, nickel and chromium. As a result of crystalline phase formation, the glass phases of the slags became enriched in structure-making oxides such as SiO_2 and Al_2O_3 (typically about 70 wt% oxide). This enrichment results in high chemical durability of the glass portion of the waste form, where the lead and chromium are immobilized. The superior chemical durabilities of the glass phase in the slags can be recognized by comparing the acceptable HLW glass compositions of SRL 131 and WVCM50 with the vitreous phase compositions of the slags in Table 1. The vitreous phases in slags have much more structure-making components, SiO_2 and Al_2O_3, than either SRL 131 or WVCM50. These observations indicate that both the crystalline and glass phases can serve as stable hosts for radionuclides and hazardous elements.

V. CURRENT STATUS IN THE DEVELOPMENT OF GLASSY SLAGS

The development of the glassy slag waste forms for the MAWS Program was initiated in 1993 at ANL. The 1993 accomplishments include:

- The MAWS approach was demonstrated to be applicable to high-metal-content waste streams using glassy slag as the final waste form. By using contaminated soils rather than glass-forming additives, waste loadings up to 100% were achieved.

- Glassy slags with compositions developed in crucible melts at ANL were successfully produced in the pilot-scale Retech PCF by MSE Inc. at Ukiah, California [5]. Detailed examinations of these materials showed that the crucible melts and PCF melter produced similar glass and crystalline phases. The glassy slags exhibited similar chemical durability in terms of normalized releases of the major components of the slags in standard leach tests.

- The distribution of hazardous and radioactive components among the vitreous and crystalline phases was determined. The results showed that both crystalline and vitreous phase can serve as stable hosts for radioactive and toxic elements. The slag formulations were developed in such a way that both crystalline and vitreous phases are very stable and have low water solubilities.

- The chemical durabilities of glassy slags were demonstrated to be better than candidate high-level waste glasses. Concentrations of hazardous elements in leachates from TCLP tests were orders of magnitude lower than the RCRA and Land Disposal limits.

- The Structural Bond Strength model was used to guide this work, with the result that the number of crucible melts needed to identify suitable formulations was greatly reduced [5]. This decreased the development time and costs at both ANL and MSE.

This program is ongoing at ANL in 1994. The current tasks include:

- Develop the composition envelope for waste streams that can be disposed by glassy slag. This effort complements a parallel MAWS Program to develop the compositional envelope for glass waste forms.

- Melt and test DOE wastes and plutonium-doped surrogate wastes to shorten the time for process commercialization. These tests will add to the data obtained from our simulated slag tests and provide information on plutonium behavior in glassy slags that simulate a wide range of DOE wastes.

- Formulate the slag composition in such a way that a durable crystal phase is formed, but in addition, these phases sequester radionuclides, especially actinides, and hazardous elements.

- Characterize fully the slags to identify the distribution of hazardous elements and radionuclides among vitreous and crystalline phases.

- Test the selected slags extensively to provide data and understanding for the long-term performance of the slag waste forms.

- Continue to utilize the SBS model to expedite the development of suitable slag formulations, compare this model with other available models, and improve the model if needed.

VI. CONCLUSIONS

Utilization of glassy slag waste forms allows MAWS technology to be applied to a much wider range of waste streams than those amenable to glass waste forms. The initial work at ANL has indicated that glassy slags are good final waste forms because of (1) their high chemical durability (when properly formulated); (2) their ability to incorporate large amounts of metal oxides; (3) their ability to incorporate waste streams having low contents of flux components; and (4) their less stringent requirements on processing parameters, such as viscosities, compared to glass waste forms. In addition, their production requires little or no purchased additives, which means greater waste volume reduction and treatment cost savings. Because the high temperatures in the slag-making furnaces can destroy organic materials, this technology should be able to treat wastes containing large amounts of toxic organic contaminants.

The slags produced in this project at ANL represent a class of waste forms that contains significant amounts of both vitreous and crystalline phases. The crystalline phases may account for up to 80% of the total volume of slags having high metal loadings. Slags may be formulated in such a way that both crystalline and glass phases are very durable. Alternatively, slags can be made such that most of the hazardous and radioactive compounds are concentrated in crystalline phases. If most of the hazardous and radioactive compounds are contained in highly durable crystalline phases, the durability of the vitreous phase would be of less concern, and it may then be possible to convert high alkali waste streams into durable glassy slags. Slag compositions developed through crucible melts were also produced in the Retech bench-scale PCF, with up to 100% waste loadings. These successful campaigns demonstrated the processibility of glassy slag.

Glassy slag waste forms are being developed to complement, not to replace, glass waste forms in implementing the MAWS Program in support DOE's environmental restoration efforts. Utilization of both glass and glassy slag waste forms will make vitrification technology applicable to the disposal of a much larger range of nuclear and mixed wastes.

VII. ACKNOWLEDGMENTS

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Table 1. Element Redistribution in Glassy Slag (wt%)

Oxides	Initial Formulation	Glass	Crystal	HLW Glass
	ANL-M8			SRL 131
Al_2O_3	10	16	11	4
CaO	2	5	0	1
CeO_2	1	1	0	0
Cr_2O_3	4	0	6	0
Fe_2O_3	62	15	80	14
K_2O	1	2	0	16*
NiO	2	0	3	2
PbO	2	7	0	0
SiO_2	15	53	0	44
	ANL-M10			WVCM50
Al_2O_3	6	11	4	10
CaO	2	8	0	1
CeO_2	1	2	0	0
Cr_2O_3	2	0	4	0.1
Fe_2O_3	66	16	90	12
K_2O	1	2	0	12*
NiO	1	0	2	0.3
SiO_2	20	62	0	40

*Total alkalis.

Table 2. Normalized Silicon Release Rates ($g/m^2/day$) for ANL Slags and HLW Glasses in 7-Day PCT Tests

ANL Slags	$g/m^2/day$	HLW Glasses	$g/m^2/day$
M1	0.0202	SRL 202U	0.0373
M2	0.0362	SRL 131	0.1716
M3	0.0048	SRL 165	0.0297
M4	0.0067	SF6	0.1817
M5	0.0117	TC-13	0.567
M6	0.0129	SF10	0.0223
M7	0.0229	WVCM59	0.0241
M8	0.0130	WVCM62	0.0216
M9	0.0152		
M10	0.0146		
M11	0.0113		
M12	0.0128		
M13	0.0126		
M14	0.0047		
M15	0.0123		
M16	0.0206		

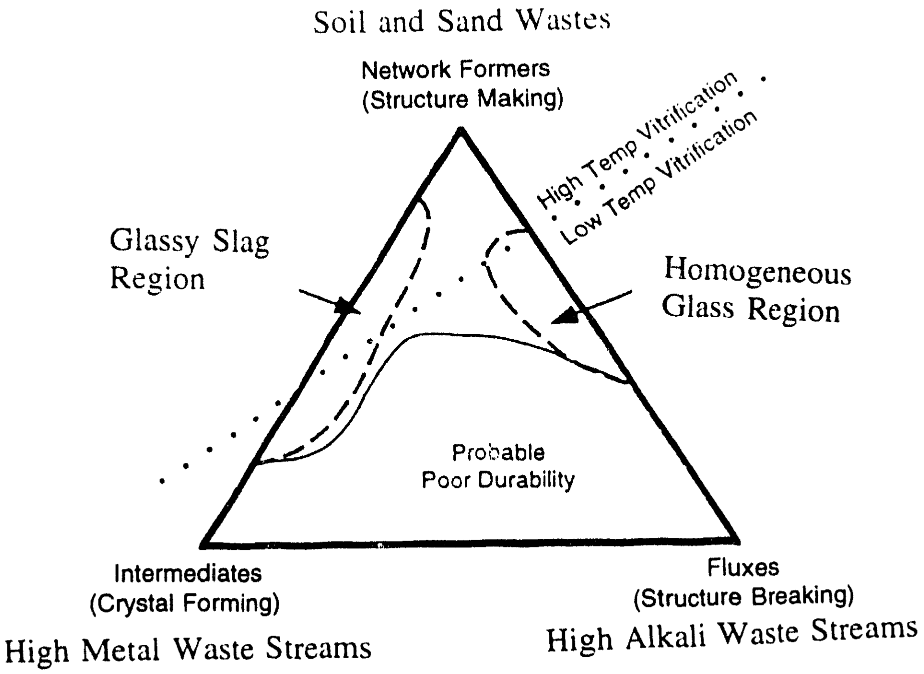

Fig. 1. MAWS compositional envelope showing the relationship between glassy slag waste forms and homogeneous glass waste forms.

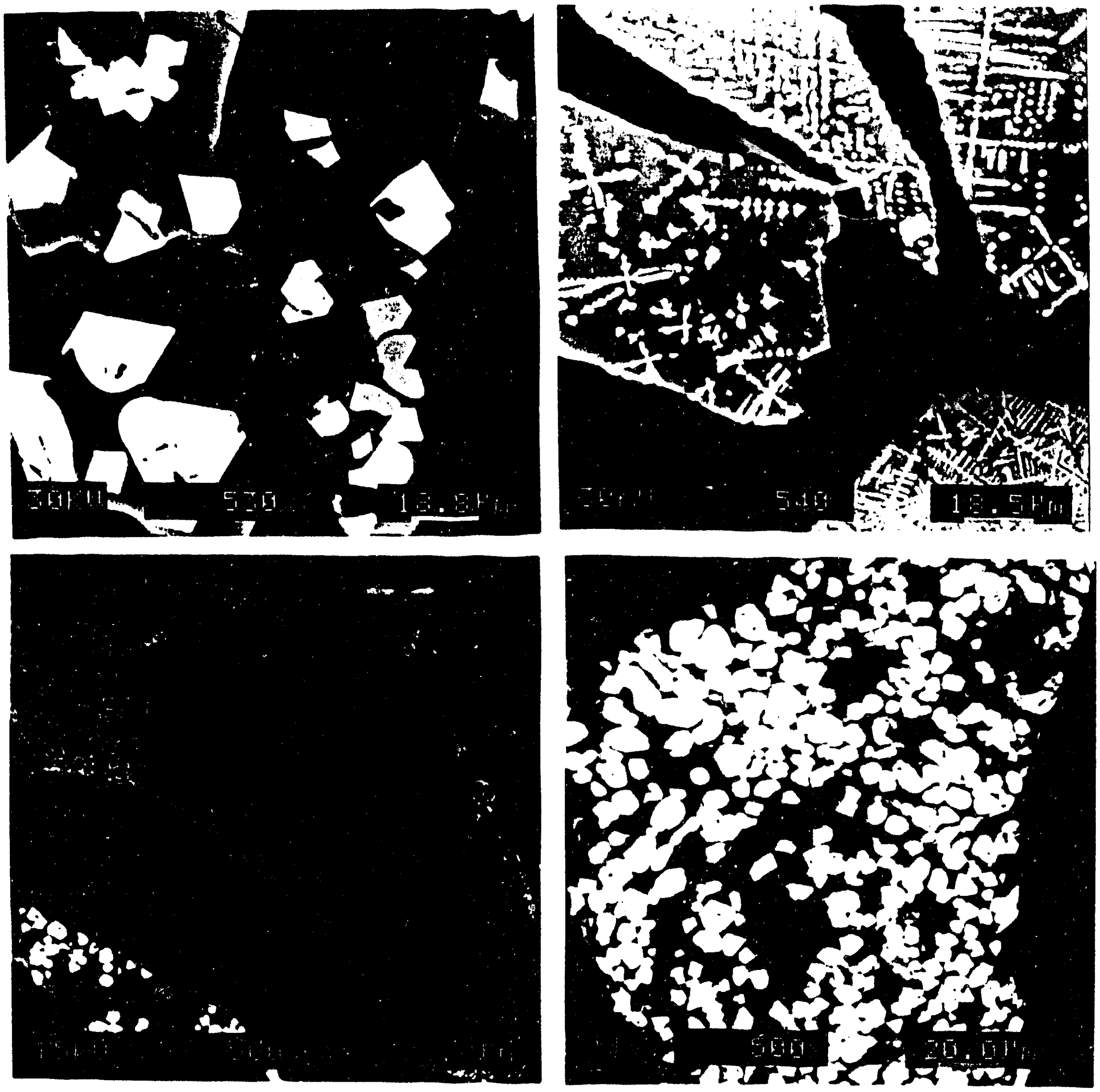

Fig. 2. SEM micrographs of glassy slag waste forms. The bright crystals in various shapes and sizes are dispersed in a dark silicate glass matrix.

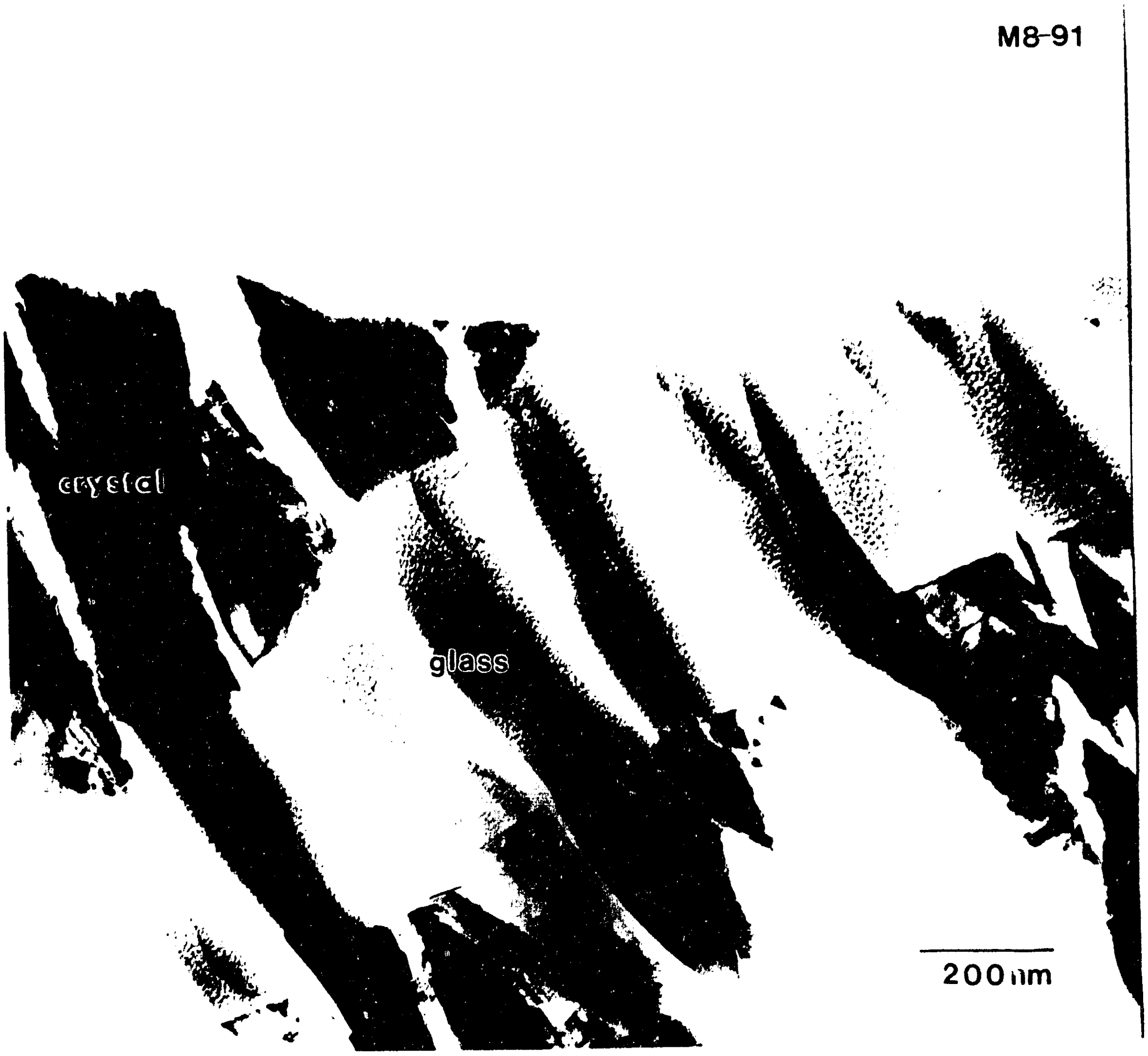

Fig. 3. TEM micrograph of glass slag corrosion after 91-day PCT (the water-slag interaction front is the upper edge of the micrograph). Little evidence of slag corrosion. The crystal-glass interface has remained intact after the sample was cut into a thickness of less than 1 μm.

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