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GLASSY SLAGS FOR MINIMUM ADDITIVE WASTE STABILIZATION
INTERIM PROGRESS REPORT, MAY 1993 - FEBRUARY 1994

by

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Chemical Technology Division

May 1994

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ABSTRACT

Glassy slag waste forms are being developed to complement glass waste forms in implementing Minimum Additive Waste Stabilization (MAWS) for supporting DOE's environmental restoration efforts. The glassy slag waste form is composed of various crystalline and metal oxide phases embedded in a silicate glass phase. The MAWS approach was adopted by blending multiple waste streams to achieve up to 100% waste loadings. The crystalline phases, such as spinels, are very durable and contain hazardous and radioactive elements in their lattice structures. These crystalline phases may account for up to 80% of the total volume of slags having over 80% metal loading. The structural bond strength model was used to quantify the correlation between glassy slag composition and chemical durability so that optimized slag compositions were obtained with limited crucible melting and testing. Slag compositions developed through crucible melts were also successfully generated in a pilot-scale Retech plasma centrifugal furnace at Ukiah, California.

Utilization of glassy slag waste forms allows the MAWS approach to be applied to a much wider range of waste streams than 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; (2) their ability to incorporate large amounts of metal oxides; (3) their ability to incorporate waste streams having low contents of flux components; (4) their less stringent requirements on processing parameters, compared to glass waste forms; and (5) their low requirements for purchased additives, which means greater waste volume reduction and treatment cost savings.

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SUMMARY

The Minimum Additive Waste Stabilization (MAWS) approach is being evaluated using glassy slags as a final waste form, in which crystalline metal oxide phases are dispersed through a glassy matrix. This new waste form can incorporate high-metal-content waste streams (both metallic and metal oxide wastes) that are not amenable to the formation of a homogeneous glass waste form.

To develop final waste forms for high-metal-content waste streams, glassy slags have been produced by melting soils from Idaho National Engineering Laboratory (INEL) with metal oxides in crucibles. The melts simulate the treatment of waste streams that contain metals such as contaminated carbon steel and stainless steel scrap, tools, and equipment. This laboratory work was coordinated with work at MSE, Inc., to prepare slags in a prototype plasma centrifugal furnace (PCF). Slags with metal oxide contents up to 84 wt % were prepared by melting the materials at 1500°C.

The glassy slags produced at Argonne National Laboratory (ANL) and MSE were characterized by identifying the distribution of radioactive/hazardous materials among the crystalline and glass phases. As-melted slags were thoroughly examined by using X-ray diffraction (XRD), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), and transmission electron microscopy (TEM). The types and amounts of crystalline phases present depended on the metal-waste loadings. Analysis indicates the presence of spinel group minerals, including maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and solid solutions of magnetite (Fe_3O_4) with NiO , Cr_2O_3 , and Al_2O_3 . Further verification of the presence of trevorite (NiFe_2O_4) and chromite (FeCr_2O_4) phases is required. Hazardous elements, such as Cr and Ni, were incorporated into the crystalline spinel phases. The glass phase consisted mainly of network-making oxides, such as SiO_2 and Al_2O_3 , with small amounts of Fe, Ca, Pb, K, and Ce as oxides. The composition of the glass phase depends on both the materials that are melted and on the phases that crystallize. The ability of the slags to retain Pb and Ce (the latter was used as a surrogate for Pu) was determined by the durability of the glass phase, while the retention of hazardous elements, such as Ni and Cr, depended on the stability of the crystalline phases. The crystalline and glass phases were found to remain tightly bound even after the severe conditions of the tests and sectioning for TEM samples, indicating the high mechanical integrity of the waste form.

The chemical durability of the glassy slag was evaluated using the experience and methods accumulated in the testing of high-level waste (HLW) glasses. The Toxicity Characteristic Leaching Procedure (TCLP) was used to show that the slags can satisfy U.S. Environmental Protection Agency (EPA) regulatory requirements for the containment of toxic metals. A Product Consistency Test (PCT) demonstrated the slags' ability to contain radioactive components. An ANL vapor hydration test provided insight into long-term durability of the slags.

The hazardous element concentrations of the slags in the EPA TCLP tests were at least a factor of 40 below the regulatory limits. The PCT results indicate that the slags have chemical durabilities better than HLW glasses such as SRL 200, SRL 165, SRL 131, and WVCM62. The normalized release rate of silicon for glassy slags was as low as $0.0048 \text{ g/m}^2/\text{day}$, while the rates for SRL 165, SRL 131, and WVCM62 were 0.030, 0.170, and $0.022 \text{ g/m}^2/\text{day}$, respectively. The slags reacted in a saturated water vapor environment at 200°C for 28 days showed surface alteration layers less than $1 \mu\text{m}$ thick, while SRL 202 glass developed surface alteration layers about $20 \mu\text{m}$ thick after reacting for 21 days. This indicates that the glassy slags studied in this work have better long-term durability than the HLW glasses.

Slag compositions developed through crucible melts were also successfully produced by MSE in a Retech PCF at Ukiah, California. This type of high-temperature vitrifier represents one potential means of treating wastes. The Retech tests were the initial feasibility studies on conducting the process in semicontinuous bench-scale equipment. The glassy slags produced at ANL were generally found to be similar to the slags produced in the PCF. The laboratory crucible melts produced glass and crystalline phases similar to those in the PCF slags. They exhibited similar chemical durability in terms of normalized release rates of the major components of the slags. Although the slags produced in the PCF using actual melts were usually less oxidized, this difference was found to have little effect on the corrosion behavior of the major components of the slags. A difference was observed in the normalized release of cerium between crucible slags and PCF slags, but this difference was transitory.

MSE also produced several slags during the Buried Waste Integrated Demonstration (BWID) Project. The normalized release of major elements from the BWID slags was usually less than the release from ANL slags (as measured by short-term PCT tests) for the following reasons. (1) The ANL slags had metal loadings up to 80%, while the highest metal loadings for BWID slags was 50%. (2) The simulated metals loaded into ANL slags were limited mostly to carbon and stainless steel, while BWID slags also included metallic aluminum, which is known to improve waste form durability. (3) The overall content of SiO_2 and Al_2O_3 (glass network formers) in BWID formulations was as high as 60% (50% SiO_2 and 10% Al_2O_3), while ANL slags usually had only about 20% of these oxides, which are also known to improve durability. However, the cerium release from ANL slags was usually 10 times less than for BWID slags. The observed difference may be due to the fact that the BWID slags were tested in stainless steel vessels, so 90% of the cerium released from the slags was deposited on the walls of the vessels. The ANL slags were tested in Teflon vessels, so the deposition (if any) of cerium precipitates was mainly on the slag surface.

Cerium was used as a surrogate for plutonium in this study because the thermal, chemical, and thermodynamic properties of cerium have been shown to most closely simulate those of plutonium in a high-temperature environment such as a glass melt. However, the accuracy with which cerium simulates the corrosion behavior of plutonium under repository-relevant conditions needs further investigation. This is especially important when comparing the leaching behavior of plutonium and cerium over a range of redox conditions.

The structural bond strength (SBS) model was used to quantify the correlation between the composition of the glassy slag and its chemical durability. This quantification helped in selecting a range of slag compositions that have high waste loadings and acceptable chemical durabilities. Use of this model reduced the number of crucible melts and durability tests required to determine acceptable composition ranges and reduced the time and cost needed for the development of a slag composition envelope. This model can be a guide for optimizing formulations in the absence of a durability data base for the glassy slags.

This model assumes that the strength of the bonds between atoms in the waste forms is the predominant factor controlling the composition dependence of slag properties. The values of the binding strength of the bonds in the glass are derived from the known heats of formation of these bonds on the basis of four simple structural rules. The application of this model in the slag composition development will shorten development time and reduce costs. The relative durabilities of the slag formulations predicted by the SBS model agree well with the order measured in the PCT tests.

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.

1.0 INTRODUCTION

Vitrification is currently the best demonstrated available technology (BDAT) for the disposal of high-level nuclear wastes. An innovative vitrification approach known as minimum additive waste stabilization (MAWS) is being developed in which glass is used as the final waste form. This approach is being used at the U.S. Department of Energy site at Fernald, Ohio, to treat low-level and mixed waste streams [1]. In the MAWS approach, the available waste streams are utilized as resources for the glass-making process, and multiple waste streams are blended to minimize the need for the purchased additives usually required for stabilization. The goal of the MAWS approach is to achieve maximum reduction in waste volume and maximum cost savings. Glass waste forms are resistant to aqueous corrosion, can incorporate a wide range of hazardous and radioactive components, and are easily processed. However, the process of producing glass final waste forms has two limitations that restrict the application of the MAWS approach: (1) the quantity of fluxing components, such as alkalis, boron, or alkaline earths, must be sufficient to attain a processible melt viscosity at a practical temperature, and (2) the solubilities of many metal oxides in the glass are low, so loadings of wastes with high metal contents may be unacceptably small.

A homogeneous glass waste form may not be appropriate for all DOE waste streams. Many DOE sites have high-volume waste streams that contain large amounts of scrap metals, as well as the oxides of Cr, Ni, Ti, Fe, Ca, and Mg, but only small amounts of flux components. For example, 22 wt % of the buried wastes at the Idaho National Engineering Laboratory (INEL) Radioactive Waste Management Complex (RWMC) is metals [2], and the 16 million kilograms of pond sludge/soil at the K-25 site at Oak Ridge, Tennessee, contains about 25 wt % Fe, 20 wt % Al, and 20 wt % Ca. Glass waste forms cannot be produced from these high-metal-content waste streams because even moderate loadings will result in the formation of crystalline precipitates during the usual vitrification process. The crystalline phases complicate glass processing and lead to uncertainties in glass durability. Vitrification of such waste streams to produce glass waste forms will require the addition of large amounts of expensive purchased additives and a significant reduction in waste loadings. Low waste loadings and large amounts of additives can substantially limit the net volume reduction and increase remediation 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 formation of crystalline phases 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; and (4) enrichment of fluxes in the vitreous phase, leading to decreased durability of glasses.

In contrast to homogeneous glass, the crystallization is a controlled and preferred process in glassy slags. The high viscosity resulting from crystallization is much less of a concern because a PCF is used to produce 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 likelihood 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.

The objective of this project is to support DOE's effort to apply the MAWS approach to the remediation of wastes across the DOE complex. The specific objective is to expand the compositional envelope within which durable waste forms can be produced by using glassy slags to stabilize wastes. The use of glassy slags will expand the range of waste streams that can be treated using the MAWS approach to include streams containing large amounts of scrap metals and metal compounds and small amounts of flux components. This work focuses on blending soils requiring remediation with scrap metals to produce a durable glassy slag waste form. The glassy slags produced are being characterized and tested to determine the limits on blending scrap metals into glassy slags, to identify the distribution of hazardous and radionuclide constituents between glass and crystalline phases within the glassy slags, and to assess the long-term durabilities of the waste forms.

This report summarizes the work performed at Argonne National Laboratory (ANL) during the period May 1993 to February 1994. This initial work, which constituted proof of principle, included preparing glassy slags that have high waste metal loadings, characterizing and testing these slags* to show that they have acceptable durability, applying a structural bond strength (SBS) model to facilitate the development of slag formulations, and recommending formulations to be produced at pilot scale in a Retech plasma centrifugal furnace (PCF) [2] by MSE, Inc., at Ukiah, California.

*The term "glassy slag" is used interchangeably with "slag" in this report.

2.0 APPROACH AND METHODOLOGY

2.1 Approach

2.1.1 Selection of Waste Streams

The initial work focused on development of slag compositions with high metal loadings and acceptable chemical durabilities, i.e., the ability to resist corrosion by groundwater. The wastes considered in this initial study are large-volume, mixed wastes, such as scrap metals and contaminated equipment. These wastes can cause devitrification and significantly affect the chemical durability of the resulting glass. Three major metals, Cr, Ni, and Fe, were selected for this scoping study; they represent the major metal wastes that need remediation at DOE sites. The Fe, Cr, and Ni contained in carbon steel scrap (99 wt % Fe) and stainless steel scrap (1.1 wt % Al, 19.02 wt % Cr, 68.35 wt % Fe, 1.38 wt % Mn, 9.28 wt % Ni, and 0.87 wt % Si) constitute about 80% of the metallic waste at the RWMC of INEL, as shown in Table 1. Because the maximum solubilities in borosilicate glass are only about 20 wt % for Fe_2O_3 , 3 wt % for Cr_2O_3 , and 3 wt % for NiO , these wastes would produce glass waste forms with low waste loadings. However, these wastes are suitable for immobilization in slags because, as shown in this study, they can be made into durable glassy slags containing up to 84% Fe_2O_3 (Table 2).

Table 1. Nominal RWMC Buried Waste Composition [2]

Waste Component	wt %
Carbon Steel	15
Stainless Steel	2.5
Lead	1
Aluminum	1.5
Plastic	0.5
Paper	6
Cloth	6
Sludge	7.5
Glass	3
Brick	3
Concrete	4
INEL Soil	40
Water	10

Table 2. Compositions of ANL Slag Formulations and INEL Soil, Oxide wt %^a

Oxides	M1	M2	M3	M4	M5	M6	M7	M8
Al ₂ O ₃	3.1	2.0	9.9	7.8	4.3	9.2	2.3	10.1
BaO	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0
CaO	2.1	1.4	6.8	5.4	2.9	1.1	1.6	1.9
CeO ₂	0.0	0.0	0.0	0.0	1.1	0.8	1.1	1.0
Cr ₂ O ₃	0.0	0.0	3.8	7.2	0.0	0.0	4.4	4.0
Fe ₂ O ₃	76.2	84.5	17.5	28.6	65.7	63.5	74.6	62.0
K ₂ O	0.6	0.4	2.1	1.6	0.9	0.3	0.5	0.6
MgO	0.6	0.4	2.0	1.6	0.8	0.3	0.5	0.5
MnO ₂	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0
Na ₂ O	0.3	0.2	1.0	0.8	0.4	0.2	0.2	0.3
NiO	0.0	0.0	1.6	3.1	0.0	0.0	1.8	2.0
PbO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.2
Sb ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SiO ₂	16.8	10.9	54.4	43.1	23.4	24.4	12.8	15.1
TiO ₂	0.2	0.1	0.6	0.5	0.3	0.1	0.1	0.2
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^aThe following oxides were not measured in the slags: As₂O₃, B₂O₃, CoO, CuO, Li₂O, MoO₃, SeO₂, SnO₂, SrO, Tl₂O₃, V₂O₃, ZnO, and ZrO₂.

Table 2 (Contd.)

Oxides	M9	M10	M11	M12	M13	M14	M15	M16	INEL SOIL
Al ₂ O ₃	3.8	3.7	3.7	3.7	3.7	10.0	3.1	2.3	12.1
BaO	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1
CaO	2.6	2.6	2.6	2.6	2.5	6.9	2.1	1.6	8.4
CeO ₂	1.1	0.9	0.9	0.9	0.9	1.2	0.9	0.8	0.0
Cr ₂ O ₃	3.7	2.5	2.5	2.5	2.0	3.3	2.4	0.0	0.0
Fe ₂ O ₃	64.4	66.8	64.9	66.8	67.7	16.1	69.8	81.2	5.4
K ₂ O	0.8	0.8	0.8	0.8	0.8	2.1	0.6	0.5	2.5
MgO	0.7	0.7	0.7	0.7	0.7	2.0	0.6	0.5	2.4
MnO ₂	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1
Na ₂ O	0.4	0.4	0.4	0.4	0.4	1.0	0.3	0.2	1.2
NiO	1.6	1.1	1.1	1.1	0.8	1.4	1.0	0.0	0.0
PbO	0.0	0.0	1.8	0.0	0.0	0.0	2.0	0.0	0.0
Sb ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
SiO ₂	20.6	20.3	20.3	20.3	20.2	55.0	16.9	12.7	66.7
TiO ₂	0.2	0.2	0.2	0.2	0.2	0.6	0.2	0.1	0.7
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

In the feasibility study stage, uncontaminated INEL soil was used, and the scrap metals were simulated by using the pure metal oxides Fe_2O_3 , Cr_2O_3 , and NiO . Plutonium-doped and actual DOE wastes will be used in the later phases of this project.

2.1.2 Time Constraints

Efforts were focused on blending multiple waste streams having high metal loadings to produce a product with high durability. The project called for ANL to provide MSE with eight formulations for testing in a PCF within three months after the initiation of the project. However, no data base on the durability of glassy slags existed. With this lack of data and the tight schedule, the conventional approach--multiple cycles of formulation-melting-testing-formulation--would not be practical, because the time needed for several cycles would be too long. Instead, we used the SBS model [3-5] to predict the relationship between formulation and durability, which reduced the number of test cycles required to develop suitable formulations to just one. This model is described in Section 3.5.

2.2 Materials and Methods

The operations performed at ANL included soil characterization, glass melting, durability testing on glassy slag waste forms, analyses of elemental composition, determinations of the Fe(II)/Fe(III) ratio of the glassy slags, analyses of leachates, and analyses of solids by means of optical microscopy, scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS), transmission electron spectroscopy (TEM), and X-ray diffraction spectroscopy (XRD).

2.2.1 Characterization of Soil from Idaho National Engineering Laboratory

Because INEL soil is a good source of SiO_2 and Al_2O_3 , it was used as an additive in the slag formulation to demonstrate high waste loading while maintaining acceptable chemical durability. The soil was first dried at 500°C for about 18 h, with 16.3% of the weight lost. The dried INEL soil was next dried at 1100°C for another 8 h, with an additional 5.9% weight loss. These weight losses were attributed to the loss of water, organics, and other volatile materials. The INEL soil composition was analyzed at ANL, and the elemental composition after drying is shown in the rightmost column of Table 2. The soil also contained 10 to 100 ppm (by weight) of Ag, As, Cd, Hg, and Se, but these amounts are shown as 0.0 in Table 2.

2.2.2 Preparation and Analysis of Glassy Slags

Three types of glassy slags were studied in this project. The first type is represented by 16 slags made in crucibles at ANL; these are designated as "ANL-M#." These ANL slags, which are the focus of this report, were made to explore optimized formulations for high metal loading, acceptable durability, and ease of processing. They were also extensively characterized in terms of morphology, identities of the phases in the slag matrix, and their chemical durabilities. The second group of slags was made at Ukiah, California, in a pilot-scale Retech PCF. The Retech, Inc., facility is operated by MSE, Inc., of Butte,

Montana. These PCF slags were made on the basis of formulations provided by ANL and are designated as "MAWS-#." This group of slags was made to demonstrate the processibility of ANL slags and to assess how well crucible melts can simulate slags made in the PCF. The third group of slags was made by MSE during the Buried Waste Integrated Demonstration (BWID) Project in a Retech PCF at Butte, Montana, and designated as "BWID-#." (The MSE designation for these slags is also noted in this report.) The BWID slags, which usually had lower metal loadings than ANL slags, were tested at ANL to assess their long-term chemical durabilities.

2.2.2.1 ANL Slag Preparation

Glassy slags were produced in crucibles by melting undried INEL soil with metal oxides (such as Fe_2O_3 , Cr_2O_3 , and NiO) to simulate high-metal-content waste streams, such as those containing contaminated carbon steel and stainless steel scrap, tools, and equipment. Two slags were also made in which additional Al_2O_3 was used to simulate scrap aluminum metal. Three slags were made with PbO to determine how lead is partitioned in slags. One slag was made with SiO_2 to determine if sand can improve slag durability. (Some DOE sites, such as the Oak Ridge site, have waste sands.) Twelve slags were made with CeO_2 , which served as a surrogate for plutonium. The formulations in terms of INEL soil and waste metals are shown in Table 3. The highest metal loading was 74 wt % (slag ANL-M2). Because the INEL soil we used contains 22 wt % volatile materials, the actual metal loading is 78 wt % in terms of dried INEL soil. This translates into a 84 wt % metal oxide loading (Table 2). All these melts contain 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 the mixture of chemicals and INEL soil was ball milled for more than 4 h to ensure complete mixing. The mixture, contained in a high-alumina crucible (99.8% Al_2O_3), was then put into a furnace preheated to about 800°C. The temperature of the furnace was then quickly raised to 1500°C. The molten slag was kept at 1500°C for 40 min to 1 h. If the melt was pourable, it was quenched by pouring it into a platinum mold. The poured slag was annealed for 1 h at about 500°C; then the furnace was turned off to cool to room temperature. If the melt was not pourable, it was air cooled in the melt crucible.

Sixteen slags were produced, with compositions (Table 2) for investigating the following issues:

- High loading of carbon steel (ANL-M1, -M2, -M5, -M16),
- Loading of stainless steel (ANL-M3, -M4, -M14),
- Loading of both carbon steel and stainless steel (ANL-M7, -M9, -M10, -M13),

Table 3. Slag Compositions in Terms of Soil and Simulated Waste Metals, wt % As Mixed

	Carbon Steel	Stainless Steel	Soil	Aluminum	Lead	CeO ₂	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	

- Effect of 2% lead on slag properties when slag already contains carbon steel and stainless steel (ANL-M8, -M11, -M15),
- Effect of 2% chlorine, added as FeCl₃ (ANL-M12), and
- Effect of aluminum and sand (ANL-M6).

2.2.2.2 Slag Dissolution

Some of the slags were dissolved and analyzed to determine their bulk composition. The dissolution process consisted of Parr bomb dissolution followed in some cases by hot plate digestion. The Parr bomb step was used for samples containing B, Si, and

other components soluble in HF-HNO₃. A 50-100 mg, finely divided sample was treated with 8 mL of H₂O, 5 mL of concentrated HNO₃, and 0.5 mL of concentrated HF in a Teflon cup. This cup was sealed in a Parr bomb and heated (typically overnight) to 140°C in a laboratory oven. After cooling, this solution was diluted to a known volume and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

The hot plate digestion step was applied to samples containing rare earths and actinides. The solution from the Parr bomb step was filtered through a Whitman #42 paper, and the filtrate was collected in a volumetric flask. The filter paper and residue were rinsed with water and then placed in a tared platinum crucible. The filter paper was then burned in a muffle furnace by raising the temperature to 600°C. The residue was moistened with water and a few milliliters of HClO₄. This solution was heated on a hot plate in a hood until the residue dissolved. This solution was added to the volumetric flask containing the filtrate, diluted to volume, and analyzed by ICP-MS.

For slags ANL-M1, -M4, -M7, and -M8, only Parr bomb dissolution was used. The compositions as analyzed (Table 4) were in general agreement with the formulated compositions, except that the amounts of analyzed CeO₂ in the glassy slags were lower, possibly due to the limited solubility of cerium in the HF-HNO₃ solution. Slags ANL-M10, -M11, and -M12 were dissolved by using both the Parr bomb and hot plate digestion. For these slags, the results for cerium (Table 4) show good agreement with the cerium content of the feed materials (Table 2). Overall, there is good agreement between the analyzed compositions in Table 4 and the feed compositions in Table 2, indicating that little material was lost during melting. The aluminum content in Table 4 is usually higher than that in the feed composition; this is probably due to partial dissolution of the aluminum crucible during melting. The silicon analyses of the slags are in general agreement with the silicon content of the feed, except for ANL-M12, where a much lower value was reported for the melted slag. The iron analyses were usually in close agreement, except for ANL-M12, where a higher value is reported for the melted slag. An error in the iron analysis will be reflected in reported amounts of other elements, particularly those with high values (such as silica), when the composition is normalized. The abnormal results for ANL-M12 may be due to the extra 2% chlorine introduced into the melt or to an improper dissolution operation in which silicon was lost during the HF-HNO₃ treatment. Since only a few slags were analyzed and since there is good agreement between formulation values in Table 2 and the analyzed values in Table 4, the formulation values in Table 2 were used for all calculations in this report.

The organic content of the slags was found to be very low, and the leachates of the slags showed total organic contents of only a few parts per million. The total organic compound destruction during the slag-making process in the PCF was reported to be better than 99.99% [2].

Table 4. Analyzed Slag Compositions, wt %

	ANL-M1	ANL-M4	ANL-M7	ANL-M8	ANL-M10	ANL-M11	ANL-M12
Al ₂ O ₃	6.39	10.8	4.73	12.0	6.29	9.15	5.74
BaO	0.03	0.08	0.02	0.02	0.04	0.04	0.02
CaO	1.85	5.05	1.00	1.50	21.9	2.33	1.27
CeO ₂			0.14	0.43	0.87	0.84	1.02
Cr ₂ O ₃		3.96	3.68	3.26	1.87	1.92	2.21
CuO		0.01			0.01		
Fe ₂ O ₃	72.6	25.2	77.5	62.0	65.8	61.5	74.7
K ₂ O	0.66	1.90	0.39	0.58	0.43	0.79	0.43
MgO	0.64	1.52	0.41	0.56	0.80	0.81	0.46
MnO ₂	0.06	0.07	0.03	0.04	0.04	0.04	0.04
Na ₂ O	0.42	0.88	0.20	0.35	0.33	0.40	0.32
NiO	0.05	2.28	1.98	2.14	1.05	1.09	1.28
PbO				1.91		1.61	0.02
SiO ₂	17.04	47.73	9.84	14.92	20.04	19.21	12.32
SrO	0.01	0.02		0.01	0.01	0.01	0.01
TiO ₂	0.18	0.46	0.11	0.14	0.22	0.21	0.13
V ₂ O ₃		0.02		0.02	0.01	0.01	0.01
ZnO		0.03	0.02	0.02	0.02	0.01	0.01
ZrO ₂	0.01	0.03			0.01	0.01	0.01

2.2.2.3 Fe(II)/Fe(III) Ratio Analysis of Slags

Because the redox states of the elements in the slag affect its durability, the Fe(II)/Fe(III) ratios of selected glassy slags were analyzed. The Fe(II) content was obtained by first dissolving the slag in a hot, oxygen-free H₂SO₄-HF solution, then immediately titrating the resulting solution with standardized K₂Cr₂O₇ solution. When two samples of standard Mohr salt [Fe(NH₄)₂(SO₄)₂•6H₂O] were treated in the same way, the recovery of Fe(II) was found to be 99.37% and 99.2%. The Fe(III) content was calculated as the difference of the Fe(II) value obtained by the method just described and the total Fe measured by means of the Parr bomb and hot plate digestion process. The Fe(II)/Fe(III) ratios for the crucible slags are 0.40, 0.21, 0.36, 0.39, 0.34, 0.36, and 0.32 for ANL-M1, ANL-M4, ANL-M7, ANL-M8, ANL-M10, ANL-M11, and ANL-M12, respectively. The Fe(II)/Fe(III) ratios for four BWID glassy slags [2] produced in the PCF are 1.69, 1.63, 1.59,

and 0.924 for 92-BWID-2 (sample #1), 92-BWID-2 (sample #2), 93-BWID-1, and 93-BWID-3, respectively. These results indicate that the PCF produces more reduced slags (i.e., the metal oxides in the PCF slags are at lower oxidation states) than the crucible melts.

2.2.3 Durability Tests

The measure of the chemical durability of a glassy slag is its ability to resist corrosion when in contact with an aqueous solution or water vapor. The durability of the slags was determined by three tests--the Toxicity Characteristic Leaching Procedure (TCLP), a modified Product Consistency Test (PCT), and ANL vapor hydration tests--which are described in the following paragraphs. The detailed test matrix for each slag is shown in Table 5.

2.2.3.1 Toxicity Characteristic Leaching Procedure Test

The U.S. Environmental Protection Agency's (EPA's) TCLP test [6] was used to determine the leachability of Ag, As, Ba, Cd, Cr, Hg, Pb, and Se by measuring the leachate concentrations obtained after glassy slag powder had reacted in a sodium acetate buffer solution at 22°C for 18 h. The purpose of using this test is to satisfy the EPA regulatory requirements for toxic metals controlled under the Resource Conservation and Recovery Act (RCRA) and to compare the performance of the glassy slag to that of other waste forms.

2.2.3.2 Product Consistency Test

A static powder test similar to the PCT [7] 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 μm) to the solution at 90°C. These tests were performed in deionized water in Teflon vessels. (The BWID slags were tested in 304L stainless steel vessels.) The ratio of the surface area of the slag to the volume of leachant (SA/V) was usually 2000 m^{-1} , except for the BWID slags, for which a higher SA/V of 20,000 m^{-1} was also used. The results from this test allowed a comparison of the durability of glassy slag to that of high-level waste (HLW) glasses, which have been tested extensively and have a large durability data base.

2.2.3.3 Vapor Hydration Test

The ANL vapor hydration test [8,9] was used as an accelerated corrosion test to measure the long-term durability of the glassy slags. This test is performed in saturated water vapor at 200°C. Durability is measured by the rate of formation of secondary alteration phases on the surface of the glassy slags, and the thickness of the altered surface layers on the samples was measured in cross section. This information provides insight into the long-term durability of glassy slags and provides another measure of the durability of HLW glasses.

Table 5. Durability Testing Performed on Glassy Slags^a

Slag	PCT Tests			TCLP	Vapor Tests	
	7 Days	28 Days	91 Days		7 Days	28 Days
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

^aY = completed; N = not scheduled.

For the vapor hydration tests, cylinders 10 mm in diameter were cut from solidified slag casts. These cylinders were sectioned into 1-mm thick circular disks, which were notched at either end of a diameter to allow supporting threads to be attached. The samples were polished to a 600-grit finish and ultrasonically cleaned in a methanol bath. The slags having a high proportion of crystalline phases tended to fracture during cutting and polishing because of their brittleness. All samples were examined by optical microscopy before the vapor hydration tests.

Tests were initiated by suspending the sample disks from Teflon threads, which were then attached to a stainless steel support rod (Fig. 1). Two disks were used for each test. The entire sample/thread/support rod assembly was placed in a stainless

steel reaction vessel. A predetermined volume of water (0.25 mL) was added to each vessel; this amount was sufficient to saturate the vessel atmosphere with water vapor after heating to the appropriate experimental temperature, but not sufficient to result in refluxing of water between the samples and the fluid in the bottom of the vessel.

After the water was added, the vessels were hermetically sealed and inserted into a 200°C oven that was controlled to $\pm 2^\circ\text{C}$. The elevated temperatures were chosen to accelerate reactions between the condensed fluid and the samples. The internal vessel pressure was approximately 16 atm at test temperatures. Previous tests with simulated borosilicate glasses have shown that the elevated temperatures accelerate glass reactions without changing the underlying glass reaction mechanism. For example, the sequence of alteration minerals produced during the reaction of test glasses at temperatures of 90 to 240°C has been shown to be similar to the pattern of glass alteration during weathering of volcanic glasses and tektites under near-surface conditions [10,11]. Pressure alone has no effect on reaction rates or reaction mechanism. Pressures up to 100 atm have also been shown to have a negligible effect on the rate at which elements leach from glass samples in a saturated environment [12].

Fig. 1. Test Vessel Reaction Apparatus for Saturated Air-Steam Tests.

The durability test matrix for the ANL slag samples is given in Table 5. Test periods of 7 and 28 days were chosen for most tests to simulate both short- and intermediate-term reaction conditions. Only a limited number of samples of slags ANL-M2 and ANL-M12 could be prepared because of fragmentation during sample preparation. Vapor test samples for these compositions were therefore limited to the 7-day runs. The 28-day test for one BWID slag (MSE 7380) leaked water, thereby invalidating the test results for this sample. All remaining tests were successfully completed.

Upon completion of the prescribed test interval, the sample vessels were removed from the oven, cooled in an ice bath, and opened. All sample disks were first examined by optical microscopy; then representative samples were chosen for detailed SEM/EDS analysis. Surfaces of the altered samples were characterized with respect to both the fate of the primary crystalline and glassy components of the waste form and the extent of alteration phase development. Both primary and alteration phases were identified on the basis of qualitative EDS chemical analysis and crystal morphology. The present results are considered tentative because the fine grained and amorphous nature of many of the crystalline phases made detailed analyses difficult. X-ray and/or electron diffraction structural analyses will need to be performed on these phases to confirm their identity.

For SEM/EDS surface examinations, samples were mounted vertically in an epoxy binder and cut normal to the reacted surfaces of the slag disks. These cross-sectioned samples were polished to a 1- μm finish and ultrasonically cleaned in methanol prior to SEM/EDS analysis. These samples allow for analysis of both the unaltered center of the sample and the altered surface.

2.2.4 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 a pH meter with an accuracy of ± 0.1 pH unit.

2.2.5 Solids Analyses

The as-melted slags were analyzed by three methods: XRD, SEM, and TEM. A Philips Powder Diffractometer (with Theta-Compensating Slit) and CuK radiation were used for the XRD analysis. 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 with a depression 16 mm in diameter and 0.2 mm deep. The sample holder holds about 0.1 g of the powdered slag with grains less than 75 μm in size.

In the SEM analysis, spectra and images for both as-melted and reacted slags were collected on a Topcon ABT 60 SEM with a Princeton Gamma-Tech or Noran EDS. The samples from the PCT tests were prepared by embedding many slag chips in a room-temperature-curing epoxy, then polishing a cross section 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.

In the TEM analysis, the reacted glassy slags were examined using a JEOL 2000FXII TEM operated at 200 kV and equipped with two EDS detectors and an electron energy loss spectrometer (EELS). One EDS detector is an ultrathin window (UTW) detector used for analyzing light elements. The other is a Be window detector that cannot detect elements below Na. The UTW detector requires the sample stage to be tilted 35°, so the area of analysis can sometimes be out of view, making analysis more difficult. Particles of slag were embedded in epoxy and sectioned by an ultramicrotome. An EELS and a technique known as second difference were used to improve the sensitivity for detecting cerium. In this technique, three spectra are obtained at increasing energy offset, which effectively removes the channel-to-channel gain variation. The structure of observed crystalline phases was determined by electron diffraction using the TEM with a double-tilt stage to obtain the zone axis pattern.

2.3 Quality Assurance

All the above activities were performed according to the guidelines in the relevant technical task plan. Technical procedures were employed for all operations in this project. The ovens and balances were calibrated according to the ANL Quality Assurance Program Plan (2/17/93). All the data were recorded in a controlled scientific notebook (#1040) and related records.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of As-Melted Slags

The unreacted glassy slags were characterized by identifying their morphology, determining element distributions among the phases, estimating the proportions of glassy and crystalline phases, and identifying these phases. This information will allow a better understanding of the corrosion behavior of glassy slag waste forms, their inability to retain hazardous/radioactive elements, and ways to optimize their formulations.

3.1.1 Morphology

As-melted slags were examined using XRD, SEM/EDS, and TEM/EDS as described in Section 2.2.5. The unaltered slag waste form was 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 coarse-grained primary crystalline phases exhibited a variety of habits, including blocky, trigonal, lath, and round crystals, as shown in Fig. 2. The distributions of glassy and crystalline phases throughout the specimens were generally nonuniform, with both glass- and crystalline-rich regions occurring in most samples, as typified by ANL-M1 and ANL-M2 (Figs. 2a and 2b). Sample ANL-M3 was especially heterogeneous, with porphyritic regions separated entirely by large glassy regions (Fig. 2c). The proportions of crystalline material and descriptions of crystalline phases identified for selected slags are given in Table 6. These proportions were estimated from microscopic observations of a single sample of each composition, so sample heterogeneity may cause some inaccuracy in these estimates.

3.1.2 Elemental Distribution

Of key interest to this study is the fate of the various hazardous components (1) during the partitioning of elements between the glassy and crystalline phases as the melt cools and (2) during the alteration processes in the leaching tests. These component elements include the hazardous metals Cr, Ni, and Pb. The fate of cerium was also of interest since it was used in this study as a surrogate for plutonium.

The elemental compositions of the glassy regions within a slag were fairly uniform, and the variations in glassy region composition among different slags were due to initial formulation differences, as shown in Table 7. The glassy regions in all samples were dominated by silicon, with smaller amounts of Al, Ca, Fe, and K, as typified by the qualitative EDS spectra shown in Fig. 3. Five elements, Si, Al, Fe, Ca, and K, were present in all samples examined. Cerium was detected as a minor constituent of the glass phase in slags ANL-M7, ANL-M8, ANL-M10, ANL-M11, and ANL-M12. In addition, the glass phase of ANL-M8 and ANL-M11 contained lead. The EDS spectral peaks for Ti, Mg, and Na were barely detectable. Figure 4 shows the presence of Ce and Pb in the glass phase of ANL-M8.

Fig. 2. Backscattered Electron Images of Polished Cross-Section Samples at 100X. (a) Sample ANL-M1, displaying well-formed network of light-colored, dendritic Fe-rich particles and dark glassy matrix; (b) sample ANL-M2, showing semi-round Fe-rich particles and dark glassy matrix; (c) sample ANL-M3, showing crystal-rich regions of Fe- and Cr-rich crystals with lesser amounts of Ni, surrounded by regions of predominantly glassy material; and (d) sample MSE 7409, showing semi-round Fe-rich crystals with lesser amounts of Cr and dark glassy matrix.

Table 6. Crystalline Phase Descriptions

Slag	Vol. %	Crystal Type	Minor Constituents
ANL-M1	80	a	
ANL-M2	80	a	
ANL-M3	20	b	Mg, Ca
ANL-M11	50	a, b	
ANL-M12	70	a	Cr, Ni
ANL-M13	70	a	Cr, Ti
MSE 7164	30	a	Cr, Ni, Mg, Ti
MSE 7165	40	a	Cr, Ti
MSE 7380	30	a	Cr, Ti, Ni
MSE 7409	40	a	Cr, Ti, Ni, Mg, Ca

^aDendritic, blocky, or trigonal Fe-dominated phase with lesser amounts of Al. These phases are probably magnetite ($\text{Fe}^{+2}\text{Fe}^{+3}\text{O}_4$)/hercynite ($\text{Fe}^{+2}\text{Al}_2\text{O}_4$).

^bRounded to blocky Fe- and Cr-dominated phase with lesser amounts of Ni and Al. These phases are probably chromite ($\text{Fe}^{+2}\text{Cr}_2\text{O}_4$) or solid solutions of magnetite with NiO.

Table 7. SEM Semiquantitative EDS Analysis of MSE Slags, Oxide wt %

Melt		Al ₂ O ₃	CaO	CeO ₂	Cr ₂ O ₃	Fe ₂ O ₃	K ₂ O	NiO	PbO	SiO ₂	SiO ₂ + Al ₂ O ₃
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-M8	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. 3. Typical EDS Spectra from Primary Glassy Regions. (a) Si-rich spectra with lesser amounts of Al, Ca, Fe, and K (sample ANL-M1); (b) spectra with minor Ce peak (sample MSE 7409); and (c) spectra with minor Ce and Pb peaks (sample ANL-M11).

Fig. 4. EDS Spectrum (a) from the Glass Phase of ANL-M8 and (b) from the Glass Phase of ANL-M8 with Vertical Axis in Log Scale to Show Minor Peaks.

Another important observation from Table 7 is that SiO_2 and Al_2O_3 were concentrated in the glass phase. With the total SiO_2 - Al_2O_3 content of the glass phases ranging from 69 to 79%, the glass phases were expected to be very durable and to release very little Ce and Pb; this was found to be the case in the leaching tests described in Section 3.2.

Elemental distributions in the crystalline phases are also tabulated in Table 7. The chromium and nickel were partitioned almost exclusively into the iron-rich crystalline phases (spinel structures) during slag solidification. Typical SEM/EDS spectra are shown in Fig. 5. Because the iron-rich crystals are relatively resistant to chemical attack, release of Cr or Ni to the environment should be minimal during corrosion of the slag waste form. Silicon was also detected in trace quantities in some crystals, probably as an inclusion impurity, since silicon is not incorporated in the spinel structure. Pockets of gas (vesicles) were also trapped in the solidified melt from which the samples were produced.

3.1.3 Crystalline Phases

The primary crystalline phases appear to be iron-rich minerals of the spinel group that contain variable amounts of Cr, and lesser amounts of Ni, Al, Ca, and Ti, as shown in Tables 6 and 7. These phases include dendritic, blocky, or trigonal Fe-dominated phases with lesser amounts of aluminum (Fig. 5a); they are probably magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$) or hercynite ($\text{Fe}^{2+}\text{Al}_2\text{O}_4$). Rounded to blocky shaped Fe-Cr-Ni-dominated phases were also found with lesser amounts of aluminum (Figs. 5b and 5c).

3.1.4 TEM Examination

Slag specimens for TEM examination were obtained from samples of ANL-M10 and ANL-M8 that had been exposed to deionized water in 7-day PCT tests. The elemental distribution between phases observed and the crystal phases identified with TEM conform to the SEM observations for the as-melted slags. The alteration of the slags as a result of corrosion was found to be negligible under this test condition.

The TEM samples were only a few micrometers square and about 100 nm thick. Therefore, we could observe very fine structure of the slags, precise EDS composition of different phases, and the diffraction patterns of crystals. The slags consisted of glass and crystalline phases. Figure 6 shows that slag ANL-M10 contained many ≈ 50 -nm crystallites rich in iron that were not observed in the SEM because of their small size. In spite of the rather harsh sectioning process, glass and crystalline phases remained attached, and sharp interfaces between glass and crystalline phases can be seen in thin section images (Fig. 7). There appears to be little diffusion between the two phases.

A typical EDS spectrum, obtained with the TEM, of the glass phase in ANL-M8 is shown in Fig. 8a. The copper peak is due to the copper grid. The major components are silica and alumina with smaller amounts of Fe, Ca, Na, Pb, and Ce oxides. The presence of cerium in the glass phase of ANL-M8 was further verified by the EELS spectrum (Fig. 8b), in which the characteristic M_4 and M_5 peaks of cerium are clearly visible.

Fig. 5. EDS Spectra from Primary Crystalline Phases. (a) Fe-rich phase with minor Al (sample ANL-M1); (b) Fe- and Cr-rich phase with minor Al, Si, and Ni (sample ANL-M3); and (c) Fe-rich phase with minor Cr, Ti, Al, and Si (sample MSE 7165).

Fig. 6.
A TEM Micrograph of ANL-M10,
Showing No Evidence of Glass Reaction
after 7-Day PCT Test. Fine iron oxide
crystals are visible in the slag matrix.

Fig. 7. A TEM Micrograph of ANL-M8, Showing that the Glass-Crystalline Interface has
Held Together during Sectioning (after 7-Day PCT Test).

Fig. 8. Spectra of Glass Phase of ANL-M8. (a) EDS spectrum, showing the presence of Ce and Pb. (b) EELS spectrum, showing the characteristic M₄ and M₅ peaks of Ce.

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 (Fig. 9). The electron diffraction of the most abundant crystals, shown in Table 8, indicated a spinel iron oxide, but it is not possible to identify it as a magnetite or maghemite phase. Figure 10 is the EDS spectrum of a Fe-Cr-Ni crystalline phase, and Fig. 11 is the selected area electron diffraction (SAED) pattern taken down the $\langle 101 \rangle$ zone axis. This pattern when indexed shows systematic absence for $\{101\}$ and $\{100\}$ reflections. This phase was identified as a spinel phase with substitution of Cr and Ni in the structure. The phase is cubic, with $a = 8.6 \pm 0.2 \text{ \AA}$, which is slightly larger than other spinel iron oxide phases. The presence of Cr and Ni (Fig. 11) in the crystals is expected to cause a change in the lattice constant compared to pure iron-spinel phases. The presence of chromium in this spinel was also verified with an EELS spectrum (Fig. 12). Another Al- and Si-rich crystal was identified as sillimanite in the form $\text{Al}_8\text{Si}_4\text{O}_{20}$. The lattice spacings and their experimental counterparts are shown in Table 9. Its composition can vary to include other oxides. It is similar in structure to a mullite, but the Al-to-Si ratio is 2:1, versus 4:1 for mullites [13].

3.1.5 XRD Examination

Powders of seven as-melted glassy slags (ANL-M1, -M2, -M3, -M4, -M6, -M7, and -M8) were analyzed by XRD. The relative amounts of amorphous materials (glass phases) in the slags can be determined by the amorphous peak counts. The order of decreasing amorphous peak counts (in parenthesis) is as following: ANL-M3 (146), ANL-M4 (118), ANL-M8 (65), ANL-M6 (62), ANL-M1 (54), ANL-M2 (54), and ANL-M7 (54). This order is consistent with the formulation data provided in Table 3. ANL-M3 has the highest INEL soil loading and the lowest metal loading, and it is therefore expected to have the highest proportion of glass phase. ANL-M2, ANL-M7, and ANL-M1 are among the slags with the highest metal loadings and are expected to have the least amount of amorphous glass phase.

The spinel phase is a face-centered cubic (fcc) structure of the MgAl_2O_3 type (lattice constant $a = 8.153 \text{ \AA}$). Many spinel-type oxides have an fcc unit cell with lattice constants in the range of 8.0-8.5 $\text{\AA}$. Solid solutions occur extensively. Magnetite (Fe_2O_3), with $a = 8.396 \text{ \AA}$ [14], can form solid solutions with Cr, Ni, Co, Mn, Ti, Al, etc. The lattice constants will increase or decrease depending on the size of the solvating atom(s).

In these glassy slags, the dominant XRD patterns observed were for spinel-type phases. The values of the major lattice constant a (in parenthesis) were, in decreasing order, ANL-M2 (8.368), ANL-M7 (8.360), ANL-M1 (8.357), ANL-M4 (8.339), ANL-M3 (8.335), ANL-M8 (8.328), and ANL-M6 (8.282). This order of lattice constants corresponds to the order of iron content in the slag; the higher the iron content, the closer the lattice constant is to the value of 8.396 $\text{\AA}$ for magnetite. Probably no magnetite was present in pure stoichiometric form (Fe_2O_3), because no lattice constants measured were close to 8.396 $\text{\AA}$. The pure iron spinel phase in these slags may include maghemite ($\gamma\text{-Fe}_2\text{O}_3$), with $a = 8.350$, because the major lattice constants measured for all the slags were around 8.35. Solid solutions of magnetite with Mg, Al, Cr, Ni, etc., are possible, and the high aluminum content

Fig. 9. (a) Microdiffraction Pattern of Iron Oxide Phase in ANL-M8 and (b) EDS Analysis of the Crystalline Phase.

Fig. 10. EDS Spectrum of a Spinel Phase of ANL-M8, Showing the Presence of Ni and Cr.

Fig. 11. Major Zone Axis $\langle 101 \rangle$ Pattern of the Cr- and Ni-Fe Spinel Phase of ANL-M8.

Fig. 12. EELS of the Cr Spinel Phase of ANL-M8, Showing an Fe-Cr Oxide.

Table 8. Major Zone Axis $\langle 101 \rangle$ Electron Diffraction Spacings ($\text{\AA}$) from Iron Oxide Phase of ANL-M8

Experimental	Magnetite ^a	Maghemite ^a
4.92 ± 0.06	4.85	4.82
4.34 ± 0.05	-	4.18
3.05 ± 0.03	2.97	2.95
2.63 ± 0.03	2.53	2.52

^aFrom [14].

Table 9. Lattice "d" Spacings in $\text{\AA}$ of a Si-Al Phase Found in ANL-M10

khl Plane	Sillimanite ^a ($\text{Al}_8\text{Si}_4\text{O}_{20}$)	Sillimanite ^a ($\text{Al}_{7.88}\text{Mn}_{0.12}\text{Fe}_{0.06}\text{Si}_{3.98}\text{O}_{20}$)	Blk 879 ($\text{Al}_8\text{Fe}_{0.04}\text{Si}_{3.7}\text{O}_x$)
120	3.41	3.42	3.45
210	3.36	3.36	3.36
220	2.68	2.68	2.67
112	2.54	2.54	-

^aSillimanite is described as a firing product of Al_2O_3 and SiO_2 . Its composition can vary to include other oxides. It is similar in structure to a mullite, but the Al-to-Si ratio is 2:1, versus 4:1 for mullites [13, p. 404].

in ANL-M3, ANL-M8, and ANL-M6 resulted in smaller a values for those slags, because the smaller Al^{3+} was present in the spinel solid solutions. Chromite ($FeCr_2O_4$), with fcc $a = 8.379 \text{ \AA}$, was probably not present in the slags, because the measured lattice constants were usually smaller than $8.379 \text{ \AA}$. This result is consistent with the above TEM results, where no pure Cr-Fe spinel phases were detected. The phase trevorite ($NiFeO_4$) is also part of the spinel group of minerals, with an fcc $a = 8.339 \text{ \AA}$. Although an XRD diffraction pattern similar in appearance to trevorite with a value of $8.339 \text{ \AA}$ was seen for ANL-M4, no pure Fe-Ni phases have been identified by SEM and TEM analyses.

3.2 Chemical Durability of Slags

3.2.1 Toxicity Characteristic Leaching Procedure Results

The results of the TCLP analyses are shown in Table 10. Most of these toxic elements were detected in the TCLP leachates in the parts per billion range (Fig. 13). These low TCLP concentrations occurred despite the fact that some slags contained high levels of hazardous elements, such as 7 wt % Cr and 2 wt % Pb, while in most other reported studies, the levels of these elements in the waste forms were only a few hundred parts per million [15]. 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, as shown in Fig. 13. There is no TCLP limit available for nickel, but all the slags pass the more restrictive land disposal limit of 0.32 ppm [16], even though the slags contain as much as 4 wt % NiO.

3.2.2 Product Consistency Test Results

The PCT results for the ANL slags are shown in Table 11 in terms of normalized mass loss and in Appendix I as elemental concentrations. The normalized elemental mass loss of a species i , $NL(i)$, is the mass of element i as measured in solution divided by the SA/V ratio used in the test and the weight fraction of element i in the slag. This normalized value allows direct comparison of the release of elements from slags with different compositions and comparison of data from tests conducted with different SA/V ratios. The $NL(i)$ values for different elements from one slag should be equal if the dissolution of the waste form is congruent. The releases of Na and K in Table 11 are much higher than those of Si and Al, indicating a selective leaching of the alkalis. Selective release of alkalis has been shown to be one of the characteristics of a durable glass [17]. Furthermore, the release of cerium was usually 100 to 400 times lower than that of silicon in these slags. The releases of hazardous elements such as Cr and Ni were usually 1000 times smaller than those of Si and alkalis.

In Figs. 14 and 15, the PCT results are compared to those obtained previously [18] from tests with simulated HLW glasses representative of those to be produced at the Defense Waste Processing Facility (DWPF) at the Savannah River Laboratory (SRL) and the West Valley Demonstration Program. SRL 131 glass is a simulated HLW DWPF glass that is very similar in composition to the reference environmental assessment (EA) glass [19]. Any glass composition produced at the DWPF that has a chemical durability better than the

Table 10. Leachate Concentrations (mg/L) Observed in EPA TCLP

Slag	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Ni
ANL-M1	1.00E-04	1.08E-01	4.00E-04	2.51E-02	6.00E-04	3.00E-04	1.43E-02	3.00E-05	8.13E-02
ANL-M2	1.00E-04	1.31E-01	6.00E-04	2.22E-02	6.00E-04	4.00E-04	1.54E-02	3.00E-05	8.75E-02
ANL-M3	4.00E-04	1.07E-01	5.00E-04	5.27E-02	2.60E-03	4.00E-04	1.64E-02	3.00E-05	1.31E-01
ANL-M4	6.00E-04	1.08E-01	3.00E-04	1.02E-01	1.70E-03	3.00E-04	2.04E-02	1.00E-05	1.81E-01
ANL-M5	3.97E-04	2.03E-01	3.71E-04	2.98E-02	1.69E-03	0.00E+00	3.69E-02	5.86E-04	1.45E-01
ANL-M6	2.00E-04	1.05E-01	4.00E-04	1.71E-02	1.00E-04	4.00E-04	2.33E-02	1.00E-04	7.74E-02
ANL-M7	4.00E-05	1.08E-01	3.00E-04	1.30E-01	3.00E-04	4.00E-04	2.32E-02	2.00E-05	2.18E-01
ANL-M8	1.00E-04	1.07E-01	2.00E-04	1.31E-01	4.09E-01	3.00E-04	2.87E-02	1.00E-05	2.24E-01
ANL-M9	6.29E-04	1.88E-01	0.00E+00	1.39E-01	8.07E-04	0.00E+00	3.66E-02	4.75E-04	2.92E-01
ANL-M10	1.44E-04	2.20E-01	0.00E+00	1.12E-01	9.64E-04	7.00E-05	3.67E-02	1.40E-04	2.57E-01
ANL-M11	1.08E-03	1.97E-01	0.00E+00	1.38E-01	3.38E-01	0.00E+00	3.60E-02	1.98E-04	3.12E-01
ANL-M12	0.00E+00	2.12E-01	0.00E+00	1.46E-01	1.38E-03	6.26E-04	4.12E-02	5.00E-05	3.18E-01
ANL-M13	0.00E+00	2.33E-01	0.00E+00	7.59E-02	9.09E-04	2.79E-04	4.42E-02	5.70E-05	1.12E-02
ANL-M14	4.40E-05	2.12E-01	0.00E+00	4.23E-02	1.74E-03	2.20E-04	4.43E-02	6.10E-05	6.96E-02
ANL-M15	0.00E+00	1.41E-01	0.00E+00	8.72E-02	3.66E-02	7.50E-05	4.95E-02	1.10E-05	1.75E-01
ANL-M16	0.00E+00	1.76E-01	0.00E+00	1.99E-02	6.44E-04	7.50E-05	7.43E-02	5.10E-05	7.07E-02
Regulatory Level	5.00E+00	1.00E+02	1.00E+00	5.00E+00	5.00E+00	2.00E-01	1.00E+00	5.00E+00	
Land Disposal Limit			6.60E-02	5.20E+00	5.10E-01			7.20E-02	3.20E-01

Fig. 13. Comparison of the TCLP Leachate Concentrations of Glassy Slags with the EPA TCLP Limits on the Hazardous Elements.

Label explanation: M = ANL-M#, e.g., M1 = ANL-M1.

Table 11. Normalized Element Losses from 7- and 28-Day PCT, g/m²

Slags	Days	Leachate pH	Al	Cr	Fe	K	Ce	Ni	Na	Si
ANL-M1	7	8.68	0.127645		0.000122	0.223297		0.007650	0.542921	0.142092
	28	7.52	0.074686		0.000000	0.271528		0.000000	0.631646	0.165934
ANL-M2	7	8.97	0.111856		0.000053	0.472017			1.210463	0.253796
	28	8.46	0.074033		0.000881	0.462618			1.009411	0.274067
ANL-M3	7	8.51	0.021981	0.000025	0.000208	0.055528		0.000068	0.137948	0.033845
	28	7.69	0.027953	0.000016	0.000000	0.072288		0.000000	0.176337	0.046253
ANL-M4	7	8.72	0.024687	0.000012	0.000413	0.082139		0.000055	0.198243	0.046657
	28	8.29	0.044748	0.000018	0.000000	0.073230		0.000000	0.195688	0.053935
ANL-M5	7	8.22	0.046074	0.003930	0.000072	0.138687	0.000436	0.020603	0.259059	0.081927
	28	7.89	0.086605	0.003794	0.000393	0.140225	0.000399	0.019820	0.309224	0.093416
ANL-M6	7	7.54	0.017052		0.000269	0.157867	0.000624		0.450290	0.090308
	28	6.33	0.006471		0.000000	0.318319	0.001516		0.658688	0.214789
ANL-M7	7	8.15	0.175504	0.000000	0.000083	0.261855	0.000422	0.000079	0.593429	0.160963
	28	7.76	0.138741	0.000064	0.000000	0.245902	0.000683	0.000088	0.627651	0.171529
ANL-M8	7	7.99	0.19452	0.000021	0.000062	0.191410	0.000769	0.000051	0.382306	0.091291
	28	7.23	0.017406	0.000008	0.000000	0.248653	0.000349	0.000000	0.417525	0.143696
ANL-M9	7	8.65	0.051963	0.000014	0.000139	0.159486	0.000565	0.000128	0.363633	0.106166
	28	8.21	0.087983	0.000000	0.000232	0.178075	0.000293	0.000125	0.472161	0.122478
ANL-M10	7	8.45	0.054157	0.000045	0.000086	0.146506	0.000354	0.000217	0.311943	0.102400
	28	7.79	0.057394	0.000060	0.000458	0.244028	0.000313	0.000352	0.502721	0.146428
ANL-M11	7	8.14	0.066101	0.000029	0.000055	0.138315	0.000302	0.000199	0.271571	0.079110
	28	7.12	0.032160	0.000048	0.000000	0.297324	0.000064	0.000077	0.488085	0.147416
ANL-M12	7	8.32	0.054399	0.000246	0.000159	0.119341	0.000475	0.001621	0.265475	0.089775
	28	7.91	0.087942	0.000068	0.000000	0.145563	0.000474	0.000021	0.351325	0.114876
ANL-M13	7	8.32	0.068134	0.000023	0.00047	0.155081	0.000315	0.000189	0.288909	0.088598
	28	7.45	0.071516	0.00087	0.00032	0.232986	0.000086	0.000109	0.483963	0.136880
ANL-M14	7	8.53	0.024213	0.000033	0.000268	0.054938	0.000217	0.000176	0.110943	0.033301
	28	8.39	0.019391	0.000054	0.000000	0.060871	0.000128	0.000037	0.153930	0.042396
ANL-M15	7	8.65	0.048992	0.000022	0.000094	0.166973	0.000278	0.000176	0.300750	0.085952
	28	6.79	0.028670	0.000238	0.000105	0.327047	0.000033	0.000615	0.552584	0.184520
ANL-M16	7	8.09	0.091510		0.000056	0.262586	0.000629		0.437340	0.144894
	28	7.00	0.054223		0.000100	0.430267	0.000411		0.728890	0.248109

TAILORED 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. 14. Comparison of 7-Day PCT Results for Glassy Slags with Those for High-Level Nuclear Waste Glasses in Terms of Release of Si, Na, and K from Waste Forms to Solutions.

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. 15. Comparison of 28-Day PCT Results for Glassy Slags with Those for High-Level Nuclear Waste Glasses in Terms of Release of Si, Na, and K from Waste Forms to Solutions.

EA glass is considered acceptable. SRL 165 glass is a more durable composition developed at the DWPF, while the SRL 202 glass represents the average glass to be made at SRL using tank wastes. The SF6 and SF10 glasses were made at Westinghouse West Valley Nuclear Services Co. and represent the glass compositions for the immobilization of the commercial HLW at the West Valley site in New York. WVCM59 and WVCM62 are the highly durable reference glass compositions developed at the Vitreous State Laboratory of the Catholic University of America for West Valley high-level wastes.

PCT test results are plotted in Figs. 14 and 15 in terms of normalized Si, Na, and K release to solution from glassy slags and HLW glasses. Most of the glassy slags are more durable than the most durable HLW glasses, such as SRL 165 and WVCM62. The figure shows that the least durable slag composition, ANL-M2, which has a metal oxide loading of about 84%, is at least four times more durable than SRL 131 and has a durability similar to the other HLW glasses. The normalized silicon release rate ($NL(Si)/\text{test duration}$) is $0.036 \text{ g/m}^2/\text{day}$ for ANL-M2, which is much lower than the rate of $0.170 \text{ g/m}^2/\text{day}$ measured for SRL 131. The normalized release rates of silicon for HLW glasses SRL 165 and WVCM62 are 0.030 and $0.022 \text{ g/m}^2/\text{day}$, respectively, while the rates for slags ANL-M3 and ANL-M14 are 0.0048 and $0.0047 \text{ g/m}^2/\text{day}$, respectively. Note also that the waste loading for HLW glasses is usually less than 30%, while the slags were made entirely from wastes (waste metals plus contaminated soil).

These results mean that the durabilities of the slags, measured in terms of major element release (e.g., Si, K, Na) are similar to or better than those of the HLW nuclear waste glasses. Furthermore, the releases of radionuclides (represented by Ce) and hazardous elements (represented by Cr and Ni) are 100 to 1000 times smaller than the releases of the major elements in the slags, as shown in Table 11.

The slag samples reacted under PCT conditions were examined with both SEM and TEM to characterize the extent of slag reaction with water. None of the samples examined showed any indication of glass dissolution or reaction product formation under SEM. Samples of ANL-M8 in the "as melted" and reacted states are compared in Fig. 16 to illustrate this conclusion. A reaction layer would result in contrast at the surface in the SEM image because of changes in density and composition. Also EDS analysis would 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 surfaces to be rich in crystalline material with void intrusions where the glass had been preferentially dissolved. This also was not observed. Even with the higher magnifications available in TEM micrographs, a slag reacted in water for seven days under PCT conditions showed only slight evidence of slag reaction with water (Fig. 17). Figure 18 is a TEM micrograph of ANL-M8 reacted for 91 days under PCT conditions; again the extent of slag reaction can barely be seen.

(a)

(b)

Fig. 16. SEM Micrographs of Glassy Slag ANL-M8 (a) "As Melted" and (b) after 7-Day PCT Test, Showing No Evidence of Slag Reaction with Water.

Fig. 17. TEM Micrographs of ANL-M8 after 7-Day PCT Test.

Fig. 18.
Micrograph of ANL-M8 after 91-Day PCT Test,
Showing an Intact Crystal-Glass Interface and
Little Evidence of Slag Reaction with Water.

3.2.3 Vapor Hydration Test Results

The surfaces of all slag samples showed similar alterations in all vapor hydration tests. A generic description will therefore be given for all slag compositions, and specific variations in alteration patterns will be noted when they occur. The altered sample surfaces are characterized by the development of patches of green-grey to rust-colored discoloration and the formation of dispersed, very fine grained white precipitates. The overall appearance of the slag samples is similar to that of reacted Savannah River Plant SRL 202 glasses reacted for similar lengths of time, with the exception that the SRL 202 glass produced a greater abundance of precipitates (Fig. 19). The greater abundance of precipitates on the SRL 202 glasses probably reflects a larger proportion of a more readily altered glass material in those samples.

SEM/EDS investigations reveal that the surface discoloration of the slags has been produced by the formation of a thin, discontinuous covering of clay minerals. The clay layer also appears to be less extensively developed in the MSE slags relative to SRL 202 glasses reacted under identical conditions (Fig. 20). Because of the very fine grained nature of this clay material, accurate EDS analyses could not be obtained because of spectral interferences from the underlying substrate material. A comparison of this clay with unaltered substrate material from a polished cross section of ANL-M3 suggests that the clays are enriched in alumina and depleted in Fe, K, and Ca relative to the unaltered glass.

Covering the clay material were a number of scattered, fine-grained white precipitates. These precipitates were composed of a variety of crystalline phases and amorphous materials of different compositions. Many of the precipitates themselves were heterogeneous, appearing to be composed of two or more separate phases. The following list describes the precipitates found on the samples examined by SEM/EDS analysis. Table 12 indicates which of the following 10 precipitate types were found on each test sample.

(a)

(b)

Fig. 19. Optical Photomicrographs of Samples Reacted for 7 Days at 200°C (Photos at 9X).
(a) Sample ANL-M1, displaying a light gray alteration coating with minor water and iron-oxide stains. (b) Savannah River Plant SRL 202 glass, showing light gray alteration film and scattered white precipitates.

(a)

(b)

Fig. 20. SEM Photomicrographs of Samples Reacted for 7 Days at 200°C (Photos at 5000X). (a) Sample ANL-M3, displaying fine-grained, platy clay crystals covering substrate of light-colored Fe- and Cr-rich crystals and dark glassy matrix. (b) Savannah River Plant SRL 202 glass, showing fine-grained, platy clay crystals.

Table 12. Alteration Phases Identified by SEM/EDS on Slags Samples Reacted for 7 and 28 Days in Vapor Hydration Tests. Alteration phases 1 through 10 are explained in Section 3.2.3.

Slag	7 Days	28 Days
ANL-M1	2, 3, 6	1, 8, 10
ANL-M2	1, 6, 8, 10	Not Sampled
ANL-M3	1, 5, 6, 7, 9	1, 8, 9
ANL-M11	1, 3	2, 4, 7, 8, 9
ANL-M12	1	Not Sampled
ANL-M13	1, 2, 3, 4, 6	1, 2, 3
MSE 7164	1, 6, 8, 9	1, 8, 10
MSE 7165	1, 3, 6, 7, 9	1, 8, 9, 10
MSE 7380	1, 6, 9	Test Failed
MSE 7409	1, 9	1, 8

- (1) The most commonly occurring alteration product was an unidentified Ca-Si dominated precipitate that exhibited crystal habits ranging from amorphous to button-shaped to botryoidal. The button-shaped deposits were the most common (Fig. 21). Spectra from this precipitate were dominated by Ca and Si and indicated the presence of variable amounts of Fe and lesser amounts of Al, K, Mg, and Na. Trace amounts of one or more of the following elements were detected in some of these precipitates: Ce, Cl, Cr, Cu, Mn, Ni, P, Pb, S, Ti, and Zn. Because of the fine-grained nature of this precipitate, it could not be ascertained whether these trace constituents were contained in the main Ca-Si phase or in secondary contaminants.
- (2) Unidentified Ca-Si needles and fibers were located on several samples, often in close proximity to the Ca-Si buttons of precipitate 1 (Fig. 22). This precipitate typically contained variable amounts of Fe; lesser amounts of Al, K, and P; and trace amounts of one or more of the following: Ce, Cl, K, Na, Pb, and S.

Fig. 21. SEM Photomicrograph and EDS Spectrum of Precipitates Present on Reacted Sample Surfaces. Sample ANL-M12 after 7-day vapor tests shows preferential development of Ca-Si precipitate type 1 on a dark, glassy substrate.

Fig. 22. SEM Photomicrograph and EDS Spectrum of Precipitates Present on ANL-M1 after 7-Day Vapor Test. Ca-Si needles (precipitate type 2) developed on dendritic Fe-rich crystal substrate.

- (3) Calcite (CaCO_3) was identified on several samples on the basis of its nearly pure calcium spectra (C and O are not detected with EDS) and rhombohedral crystal morphology (Fig. 23). Small quantities of magnesium were also detected during EDS analysis of some samples. Many of the calcite grains exhibited pitted surfaces, suggesting a period of corrosive activity.
- (4) Clear crystals identified during optical examination displayed a rhombohedral crystalline morphology and a Si-Ca-Al dominated composition. Trace amounts of one or more of the following were also detected in these precipitates: Ce, Cl, Fe, K, and Pb. On the basis of its composition and morphology, this phase may be the zeolite mineral chabazite ($\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}]\cdot 6\text{H}_2\text{O}$), although a positive identification has not been made.
- (5) Crystals with a Ca-S composition were detected on sample ANL-M3 from a 7-day hydration test (Fig. 24). This phase appeared to belong to the orthorhombic crystal system. On the basis of the crystal morphology, composition, and environment of formation, this phase appears to be the mineral anhydrite (CaSO_4), although a positive identification was not made.
- (6) During optical examinations, a number of blood-red crystal phases were identified on a number of samples. SEM/EDS examinations revealed the presence of a copper-rich material containing minor amounts of Al, Si, and Fe and one or more of the following trace constituents: Ca, Ce, Cr, K, Mg, Mn, Pb, Sn, Ti, and Zn. On the basis of its color and composition, this phase has been identified as cuprite (Cu_2O). Because copper gaskets are used to seal the test vessels, it is possible that this phase arose from degradation of the gasket material.
- (7) Near-amorphous mounds and botryoids of an unidentified Al-Si dominated material containing lesser amounts of Fe, Ca, K, Na, and Mg were detected on several samples (Fig. 25). This material may be a kaolinitic clay, but additional data would be required for positive identification.
- (8) A number of iron-rich precipitates of variable compositions were noted on the sample surfaces (Fig. 26). These alteration materials exhibited morphologies ranging from rod-shaped to flakes, and some were amorphous. The range in compositions probably reflects variable amounts of contaminants, because backscattered electron studies often revealed assemblages of precipitates with mottled colors. The iron-rich precipitates typically contained Al, Ca, Cr, K, Ti, and Si, along with trace amounts of one or more of

Fig. 23. SEM Photomicrograph and EDS Spectrum of Precipitates Present on ANL-M11 after 7-Day Vapor Test. Blocky calcite (CaCO_3 ; precipitate type 3) and fine-grained Ca-Si needles (precipitate type 2) are shown.

Fig. 24. SEM Photomicrograph and EDS Spectrum of Anhydrite Crystals (CaSO_4 ; Precipitate Type 5) Present on ANL-M3 after 7-Day Vapor Test.

Fig. 25. SEM Photomicrograph and EDS Spectrum of Si-Al Phase (Precipitate Type 7) Present on ANL-M11 after 28-Day Vapor Test.

Fig. 26. SEM Photomicrograph and EDS Spectrum of Iron-Rich Phase (Precipitate Type 8) Present on ANL-M2 after 7-Day Vapor Test.

the following elements: Ce, Cl, Mg, Mn, Na, Ni, and Pb. The iron-rich phases were probably composed of one or more oxidization products of corroded primary crystalline and glassy materials. Hematite (Fe_2O_3), limonite ($\text{FeO}\cdot\text{OH}\cdot n\text{H}_2\text{O}$), and/or goethite ($\text{FeO}\cdot\text{OH}$) may be important components of this precipitate material, given that these materials commonly occur on weathered, iron-bearing geologic and anthropogenic materials.

- (9) Several unidentified silicon-rich precipitates of variable compositions were noted on the sample surfaces. These alteration materials exhibited various morphologies, including needles, flakes, bladed forms, and amorphous shapes. The range in compositions probably reflects variable amounts of contaminants and the presence of several silicon-rich phases in these samples. The silicon-rich precipitates typically contained Al, Ca, Fe, K, and Mg, as well as trace amounts of one or more of the following elements: Ce, Cl, Na, Pb, S, and Ti.
- (10) Deposits of salts were identified by their dark backscattered electron images and large EDS spectra background response (Fig. 27). The poorly crystalline nature of these deposits suggests that they formed as evaporitic minerals deposited when thin films of saline fluids contacting the samples evaporated during the sample termination procedure. These salts contain the elements that were readily leached from the glassy component of the slag and also from the probable clay and iron-oxide contaminants. Typical EDS spectra indicated the presence of Al, Ca, Cl, K, S, and Si. Trace amounts of one or more of the following were also detected: Ce, Cr, Na, and Ti.

The overall appearance of the reacted sample surfaces and the compositions of the alteration phases suggest that the iron-rich crystalline phases are relatively immune to chemical attack compared to the glassy matrix. On most samples, slightly depressed surface regions surround the relatively unaltered crystalline material, with the depressed portions presumably resulting from preferential corrosion of the glassy matrix (Fig. 28). Crystalline materials were, however, observed to corrode in some locations on some samples. Alteration of the crystalline phases resulted in the formation of iron oxide precipitates (Fig. 26).

The altered glass zones adjacent to unaltered crystalline regions were investigated by examining cross-sectioned samples. The only evidence of greater glass alteration was the predominance of glass corrosion products in secondary phases. The overall appearance of the reacted sample surfaces and the compositions of the alteration phases suggest that the iron-rich crystalline phases were more resistant to chemical attack than the glass matrix, although both the glass and crystalline phases display very little evidence of chemical corrosion, even under the aggressive conditions of the vapor hydration test.

Fig. 27. SEM Photomicrograph and EDS Spectrum of Salt Crust (Precipitate Type 10) Present on ANL-M1 after 28-Day Vapor Test.

Fig. 28. Backscattered Electron Images from Polished Cross-Section Samples Reacted in a Saturated Air-Steam Environment at 200°C. (a) Reacted surface from sample MSE 7380 after 7 days, showing no visible evidence of a reacted layer. Note glassy material encapsulated within iron-rich crystals. (b) Formation of thin altered clay layer on surface of sample ANL-M11 after 28 days. (c) Formation of thin altered clay layer on surface of sample MSE 7164 after 28 days. Note appearance of pitted glass surface material. (d) SRL 202 glass reacted for 21 days, displaying (from left to right) unaltered glass, bright band due to electric charge buildup between glass and altered layer, ~25- μ m-thick altered layer, thin band of needle precipitates, and epoxy mounting medium.

The clay alteration layer on the slag samples was typically less than 1 μm thick after 28 days of reaction in the vapor hydration tests. By comparison, SRL 202 glasses had developed reaction layer thicknesses of 3.7 ± 0.8 , 18.7 ± 3.8 , 19.4 ± 8.6 , and 54.8 ± 10.9 μm after reaction under identical conditions for periods of 7, 14, 21, and 35 days, respectively [11]. The difference in alteration layer thickness is additional evidence that glassy slags are more resistant to corrosion under these test conditions than high-level nuclear waste glasses.

3.3 Comparison of Crucible Slags and PCF Slags

To show that the formulations developed during the crucible melting at ANL are transferable to pilot-scale production with a PCF, a total of eight formulations were recommended to MSE for test runs in a 1.5-ft Retech PCF. This assessment includes the processibility and product properties. The processibility has been successfully demonstrated by MSE, and all the melts recommended were produced in the 1.5-ft Retech PCF in August 1993. The following discussion will focus on the comparison of the properties of the slags made in the crucible melts and in the Retech PCF.

3.3.1 Comparison of Formulations

The eight formulations recommended to MSE were mainly based on the SBS modeling discussed below. The compositions of these eight slags and the corresponding ANL melts are shown in Table 13. The eight slags were made at MSE in the 1.5-ft Retech PCF using carbon steel, stainless steel, INEL soil, and other metals and metal oxides. The actual metal loadings in the product were higher than those indicated in Table 13: as-received soil was used for formulations, and ~22% of the soil weight (mostly water) was lost during melting. These formulations are designed to achieve high loadings of Fe, Ni, and Cr (representing carbon steel and stainless steel) in slags, yet still produce a durable and processible product. A slight difference in the composition of final products between crucible and PCF slags was expected because of the differences in redox states of the metals and in the contents of volatile metals of the resulting slags and because slag properties are strongly influenced by the processing environment.

3.3.2 Comparison of the As-Melted Slags

Five PCF slags, referred to as MAWS-1, MAWS-2, MAWS-4, MAWS-5, and MAWS-8, were received from MSE. They were characterized and compared to the slags produced in crucible melts at ANL. The general appearance of the slags produced in the ANL crucibles and in the 1.5-ft Retech PCF was similar. Three of the PCF slags were examined with SEM/EDS, and the results are summarized below.

3.3.2.1 MAWS-1

The sample appeared to contain glass and only one kind of crystal, on the basis of EDS analysis. The crystals near the sample surface are smaller than the particles in the sample center, but their compositions were similar (Fig. 29). The interface between the fine and coarse crystals was quite abrupt (Fig. 29a). The fine crystals are also

Table 13. Formulations Recommended to MSE, Inc., wt %

	Carbon Steel ^a	Stainless Steel ^b	Soil ^c	FeCl ₃	Lead	CeO ₂	Corresponding ANL Melt
MAWS-1	50		49			1	ANL-M5
MAWS-2	70		29			1	ANL-M16
MAWS-3		10	89			1	ANL-M14
MAWS-4		29	70			1	ANL-M4
MAWS-5	45	10	44			1	ANL-M10
MAWS-6	43	10	44		2	1	ANL-M11
MAWS-7	44	10	44	3		1	ANL-M12
MAWS-8	50	20	29			1	ANL-M7

^aCarbon steel = 99.8% Fe.

^bStainless steel = 68.4% Fe, 19% Cr, and 9.3% Ni.

^cINEL soil was used as received.

shown in Fig. 29b and the coarse crystals are shown in Fig. 29c. Figures 30 and 31 provide the EDS spectra and composition data on the glass phase of MAWS-1. The glass phase consisted mainly of Si, Al, and Fe, with lesser amounts of K and Ca, very small amounts of Ce, and negligible amounts of Cr and Ni. The crystal phase composition is shown in Fig. 32: Fe₂O₃ is the dominant oxide, at 74%; Cr₂O₃ and Al₂O₃ are present, at ~12% each; and trace amounts of NiO were detected.

3.3.2.2 MAWS-4

This sample was also similar to the crucible melt ANL-M4 in both the types of crystals present and the compositions of glass and crystalline phases (Fig. 33). There appeared to be two types of crystals in the MAWS-4 slag (Fig. 33a). The larger crystals were elongated, and the edge part of the large crystals displayed contrast in backscattered imaging. The EDS composition of the center part of the larger crystals of MAWS-4 is shown in Fig. 34a; the crystals contained mainly Fe and Al, with small amounts of Cr and Ni. The EDS composition of the edge of the crystals that displayed contrast in backscattered imaging is shown in Fig. 35; the contrast may due to the enrichment in chromium. The EDS spectrum (Fig. 34b) of crystals in the corresponding crucible melt, ANL-M4, indicates that the composition is similar to that of MAWS-4. The glass phase contained a large number of light gray fine crystals that were so small that their composition could not be determined with EDS. Figure 36 represents the EDS composition of the glass phase and the fine crystals. Two types of crystals were also observed in ANL-M4, as shown in Figs. 33b and 33c.

(b)

(c)

Fig. 29. SEM Micrographs of MAWS-1. (a) Both fine and coarse crystals. (b) Fine crystals only. (c) Coarse crystals only.

Fig. 30. EDS Spectrum of the Glass Phase of MAWS-1.

Fig. 31. EDS Spectrum of the Glass Phase of MAWS-1 with Vertical Axis in Log Scale.

Fig. 32. EDS Spectrum of the Crystalline Phase of MAWS-1.

Fig. 33. SEM Micrographs of (a) MAWS-4, (b) ANL-M4 (5 kV), and (c) ANL-M4 (15 kV).

Fig. 34. EDS Spectrum of (a) the Larger Crystals of MAWS-4 and (b) the Crystals of ANL-M4.

Fig. 35. EDS Spectrum of the Edge Part of the Large Crystals that Displayed Contrast in Backscattered Imaging.

Fig. 36. EDS Spectrum of the Glass Phase (Including the Fine Crystals) of MAWS-4.

3.3.2.3 MAWS-5

This sample showed that the metal was not fully oxidized during PCF processing. One of the examined samples contained several metallic inclusions that were probably stainless steel (Fig. 37a) because they were found to contain Fe, Ni, and Cr, with very little oxygen (Fig. 38). Also, a green band was visible in the optical microscope (Fig. 37b). This band appears bright in backscattered electron imaging and was richer in iron than the surrounding glass matrix (Fig. 39). Interestingly, the green band region did not contain crystallites, but it obviously contained more oxygen (compare Fig. 38 and Fig. 39), suggesting the iron may be mainly in a lower oxidation state; i.e., the carbon steel has not been fully oxidized to the higher oxidation state where crystallinity would be expected. However, the majority of the MAWS-5 slag (Fig. 40b) was similar to crucible melt ANL-M10 (Fig. 40a); both have similar glass and crystal phases. The glass phase of MAWS-5 exhibited contrast in backscattered imaging (Fig. 37b), suggesting the presence of very fine crystallites rich in alumina (Fig. 41), which would result in an overestimation in the amount of aluminum in the glass. Another possibility is compositional variations resulting in contrast differences; however, no compositional differences within the glass were observed. Trace amounts of cerium were detected in the glass (Fig. 42). The crystals in MAWS-5 usually contained Fe, Cr, Ni, and Al oxides (Fig. 43), as did the crystal phase of ANL-M10.

3.3.3 Comparison of Chemical Durability

A comparison of PCT test results for slags produced in the ANL crucible melts with those for the PCF slags produced by MSE at Retech provides information that can be used to evaluate how well the crucible melts replicate the durability of the PCF melts. The available results from 7- and 28-day PCT tests with the ANL slags (designated ANL-M#) and those produced in the 1.5-ft Retech PCF (designated MAWS-#) are presented in Table 14 as normalized mass losses for individual elements. In Table 14, results for slags with similar proportions of starting materials (see Table 13) are grouped together. The detailed element concentrations in analyzed leachates from these PCT tests are presented in Appendices I (for ANL-M#) and II (for MAWS-#). The average glass compositions used to calculate the NL(i) values are given in Table 2. Values for the MAWS glasses were assumed to be the same as their corresponding ANL compositions (as shown in Table 13) because they were made with similar proportions of the starting materials.

NL(Si) values are considered to be the most representative indicator of the durability of the glassy portion of the slag waste form. These values are used for three reasons: (1) silicon is a major component of the glass portion of the waste, (2) silicon concentrations are relatively high in the leachant, and (3) accurate silicon concentrations can be readily determined by ICP-MS. The use of silicon has a major drawback, in that this element can be readily incorporated in both Fe-Si colloids and many of the alteration phases that form on the altered slag surface. However, the lack of significant alteration phase development on the 7- and 28-day slag samples suggests that silicon may be used as a reliable indicator of the extent of glass reaction in the present tests. This premise may not be applicable in the longer term tests, in which more extensive alteration phases are expected to develop.

(a)

(b)

Fig. 37. SEM Micrographs of MAWS-5: (a) Metallic Inclusion and (b) Bright Band.

Fig. 38. EDS Spectrum of the Metallic Inclusion of MAWS-5.

Fig. 39. EDS Spectrum of the Bright Band of MAWS-5.

(a)

(b)

Fig. 40. SEM Micrographs of (a) ANL-M10 and (b) MAWS-5.

Fig. 41. EDS Spectrum of the Glass Phase with Fine Crystals of MAWS-5.

Fig. 42. EDS Spectrum of the Glass Phase with Fine Crystals of MAWS-5, with Vertical Axis in Log Scale.

Fig. 43. EDS Spectrum of the Crystal Phase of MAWS-5.

Table 14. Average PCT Results, Normalized Release, g/m²

Slag	Reaction Days	pH	Al	Cr	Fe	K	Ce	Ni	Na	Si
ANL-M4	7	8.72	0.0247	0.000012	0.000413	0.0821		0.000055	0.1982	0.0467
	28	8.29	0.0447	0.000018	0.000000	0.0732		0.000000	0.1957	0.0539
MAWS-4	7	7.85	0.0394	0.000131	0.000015	0.0255		0.000088	0.2001	0.0310
	28	8.73	0.0447	0.000133	0.000045	0.0443		0.000031	0.2581	0.0427
ANL-M5	7	8.22	0.0461		0.000072	0.1387	0.000436		0.2591	0.0819
	28	7.89	0.0866		0.000393	0.1402	0.000399		0.3092	0.0934
MAWS-1	7	8.07	0.1207		0.000122	0.2633	0.000060		1.8066	0.0608
	28	8.56	0.1649		0.000393	0.3433	0.000254		2.4404	0.0753
ANL-M7	7	8.15	0.1755	0.000000	0.000083	0.2619	0.000422	0.000079	0.5934	0.1610
	28	7.76	0.1387	0.000064	0.000000	0.2459	0.000683	0.000088	0.6277	0.1715
MAWS-8	7	7.33	0.0279	0.000002	0.000000	0.0187	0.000004	0.000148	0.2424	0.0561
	28	8.15	0.0570	0.000002	0.000009	0.0305	0.000173	0.000055	0.3389	0.1258
ANL-M10	7	8.45	0.0542	0.000045	0.000086	0.1465	0.000354	0.000217	0.3199	0.1024
	28	7.79	0.0574	0.000060	0.000458	0.2440	0.000313	0.000352	0.5027	0.1464
MAWS-5	7	8.13	0.1338	0.002588	0.000002	0.0332	0.000058	0.000037	0.9351	0.0624
	28	8.29	0.1365	0.002675	0.000025	0.0644	0.000229	0.000057	1.2255	0.0751
ANL-M16	7	8.09	0.0915		0.000056	0.2626	0.000629		0.4373	0.1449
	28	7.00	0.0542		0.000100	0.4303	0.000411		0.7289	0.2481
MAWS-2	7	7.39	0.2220		0.000061	0.1275	0.000043		1.7783	0.1528
	28	8.80	0.2828		0.000049	0.2352	0.000079		3.3504	0.1941

The NL(Si) values presented in Table 14 generally show good correspondence between the ANL crucible and PCF slags. Values for NL(Si) from 7- and 28-day PCT tests generally vary by less than a factor of two between the two slag products. The largest difference was found between the 7-day results for ANL-M7 and MAWS-8 samples, where the NL(Si) values varied by slightly less than a factor of three. In view of the reproducibility of the type of test employed (PCT) and the uncertainties in slag formulations, a difference of factor of two to three is not considered to be significant. Thus, the NL(Si) results indicate that the ANL crucible melts can simulate the product from the 1.5-ft Retech PCF.

Comparisons of NL(i) release patterns for the remaining elements are less consistent than these patterns for silicon. Aluminum, sodium, and potassium comprise approximately 2 to 8, 0.2 to 0.8, and 0.5 to 1.7 oxide wt %, respectively, of each of the slag compositions (Table 2). All of the Na and K and most of the Al are partitioned into the glassy portion of the slag, as determined by SEM/EDS examination. The relative concentrations of these elements in the glass phase should be substantially higher than the values listed above because Na, K, and, to a lesser extent, Al are excluded from the Fe-rich crystalline phases.

The correspondence between NL(Al), NL(Na), and NL(K) values are relatively good for the ANL-M4 and MAWS-4 samples, generally varying by less than a factor of two (Table 14). Release trends for the remaining four slag comparisons, however, show considerably more data scatter. NL(Al) values for these four sets of slags vary by a factor of two to seven, NL(Na) values by a factor of two to eight, and NL(K) values by a factor of two to fourteen. The interpretation of these results is complicated somewhat by the difficulty of analyzing for potassium with the ICP-MS and the sorption of all three elements in clays that form on the altered glass surface. Silicon thus appears to be the best indicator of the performance of the glassy portion of the slag waste form. Future results, from longer-term samples, will be used to evaluate the differences noted between the release rate of Si and that of Al, Na, and K.

Cerium served as an analogue for plutonium in these simulated slag waste forms because cerium and plutonium chemistry have been found to be similar in high-temperature glass melts [20]. SEM/EDS examinations indicated that cerium was preferentially fractionated into the glass portion of the slag. NL(Ce) values also varied between the ANL and PCF slags. The ANL slags consistently had higher NL(Ce) values than the corresponding PCF slags. The 7-day NL(Ce)s of ANL-M5, ANL-M7, ANL-M10, and ANL-M16 are higher by factors of 8, 105, 6, and 15, respectively, than the corresponding PCF slags. An examination of the 28-day NL(Ce) indicates that the differences between the crucible melts and PCF melts were greatly reduced to only a factor of 1.6, 3.9, 1.4, and 5.2, respectively. These results suggest that the differences in NL(Ce) may disappear with longer test durations. While some variation in the NL(Ce) values is expected in these tests, because of the relatively low cerium concentrations in the formulations, the consistent differences of the NL(Ce) values between the crucible and PCF products suggest that the differences may have resulted from the differences in the processing techniques that, in turn, caused differences in solution chemistry.

These differences may be reasonably explained by the difference in the redox state of the bulk slags and the leachate pH difference between the crucible and PCF slags. The examination of the PCF slags (Section 3.3.2) revealed metallic inclusions. In addition, the analysis of the BWID PCF slags (Section 2.2.2.3) showed that the Fe(II)/Fe(III) ratios in the PCF slags are at least a factor of three higher than in the ANL crucible slags. Thus, it seems likely that there was a higher proportion of Ce^{3+} in the PCF slags than in the crucible slags. The hydrolysis constant for Ce^{3+} is 1×10^{-5} [21], which is much larger than the constant for Ce^{4+} , 1.9×10^{-15} , suggesting that Ce^{3+} is more soluble in water than Ce^{4+} . Some studies [22] suggested that the contribution of Ce^{4+} to the total soluble cerium in an air-saturated water system is less than 10%. On the other hand, the total Ce^{3+} solubility and speciation are strong functions of solution pH, and the major species are carbonate complexes, produced between pH 7 and 9 [22]. Barr et al. reported that the solubility of total Ce^{3+} increased 58% for a pH change from 7 to 8 and 70% for a pH change from 7 to 9. Therefore, the total solubility of cerium in an aqueous system is a complex function of both Eh and pH. The more reducing PCF slags suggests a higher cerium release, while the lower 7-day leachate pH of PCF slags (Table 14) suggests a lower solubility of Ce^{3+} than in crucible slags. The observation that the 7-day NL(Ce) is lower in PCF slags suggests that pH is a more dominant factor in determining total cerium solubility. This may be consistent with the conclusion drawn by Baar et al. that the solubility of cerium in seawater is largely a function of pH rather than Eh [22]. Our PCT test condition is similar to a seawater system because the system is open to the oxygen and CO_2 in the atmosphere and the solution has a high salt content as a result of leaching. As the test duration increases, more and more of the Ce^{3+} on the surface of PCF slags is gradually converted to Ce^{4+} , which will reduce the cerium solubility differences between the PCF and crucible slags for the longer test times. The solution pH trend of the PCT test also increased as the test duration increased from 7 to 28 days (Table 14). This may explain why decreased differences in NL(Ce) between the crucible and PCF slags were observed for 28-day PCT tests. If this explanation holds, the NL(Ce) differences between crucible and PCF slags will be even smaller for the 91-day PCT tests that are still in progress.

Comparisons of NL(Cr), NL(Ni), and NL(Fe) values from the crucible and PCF slags indicate a considerable amount of data scatter. Most of this variation can be attributed to analytical uncertainties related to accurately detecting the relatively low concentrations of these elements in solution. These low concentrations are a result of the relatively low solubilities of these elements in the leachates. Results from longer term tests will probably not provide any improved data, because the solution concentrations of these elements will probably remain low as a result of their incorporation into clay minerals on the reacted slag surfaces. Some insight into the performance of the crystalline phases and the behavior of Cr, Ni, and Fe may be gained in solid phase examinations of the reacted slag samples that will be conducted in the future.

3.4 Testing of BWID Slags

Four slags received from MSE were part of the BWID campaign [2]. The purpose of testing these slags was to evaluate their durability under a range of conditions by measuring their corrosion resistance to water or water vapor under conditions that would accelerate their

reaction relative to storage or disposal conditions. Two types of tests were performed: (1) tests in water vapor at 200°C and (2) static leaching tests at 90°C with different SA/Vs and varying time periods. The vapor tests identified whether the glass reacts to form secondary mineral phases that may or may not contain the hazardous elements. The details of the vapor tests are discussed in Section 3.2.3, but in essence the BWID slags showed significantly less reaction than accepted high-level waste glasses.

The static tests were also done under conditions designed to accelerate reaction relative to service conditions. The test followed a modified PCT procedure that included the measurement of the elements released to solution and the examination of the reacted glass. By combining both the solution and solid analysis, an overall view of the slag corrosion behavior can be obtained.

3.4.1 Experimental

The tests were done according to the matrix shown in Table 15. Each slag was core-drilled to remove material for vapor testing, and the surrounding region of slag was crushed and sieved to yield particles in the size range between 100 and 200 mesh. The crushed grains were washed with ethanol and deionized water to remove any fines, then dried, and a representative fraction was examined using SEM to assess the effectiveness of the cleaning procedure. The tests were initiated only after SEM examination revealed no fines remaining on the grains.

The tests were conducted in 22 mL, type 304L stainless steel vessels that were sealed with Teflon gaskets. Deionized water (DIW) was used as the leachant, and the temperature was $90 \pm 1^\circ\text{C}$. Two SA/V ratios were used: 2000 m^{-1} , the standard PCT test condition, for which 1 g of glass particles was reacted with 10 mL of DIW, and $20,000\text{ m}^{-1}$, for which 5 g of glass particles was reacted with 5 mL of water. Experience in testing HLW glass has shown that the larger SA/V ratio allows leached constituents to accumulate faster than in tests done at 2000 m^{-1} , thereby allowing higher solution concentrations to be reached in a shorter time. The higher SA/V tests are designed to detect any change in the rate-controlling process that might occur at long times when leachates approach saturation. Reaction durations were chosen to yield a spread in time while still allowing data to be collected and analyzed for this report. To judge the reproducibility of the results, duplicate tests were performed for seven days with the starting time offset by six days. One set of tests at 2000 m^{-1} was allowed to continue through to 179 days because of the low reactivity of the slag.

The solutions were analyzed for pH, total and organic carbon, anions, and cations. The cations were analyzed using ICP-MS. Those cations most indicative of glass reaction and hazardous material release, including Si, K, Al, Ce, Mo, and K, were analyzed quantitatively ($\pm 15\%$), while other selected cations were analyzed semiquantitatively ($\pm 30\%$). Analyses were performed on both the test solution and the acid strip of the vessel. The acid strip was analyzed primarily for cerium because it is well established that rare earth elements

Table 15. Leach Test Matrix

BWID Number	MSE Slag Number	SA/V = 2000 m ⁻¹				SA/V = 20,000 m ⁻¹
		7 ^a Days	33 Days	89 Days	179 Days	66 Days
92-BWID-1	7164	X	X	X	X	X
92-BWID-2	7165	X	X	X	X	X
93-BWID-1	7380	X	X	X	X	X
93-BWID-3	7409	X	X	X	X	X

^aThe tests were run in duplicate, but with test periods separated by six days. The other tests were single runs.

strongly sorb to the stainless steel, and the acid strip contribution must be included to obtain total release from the slag. The solution results that summarize the contributions from leachate and acid strip solutions are provided in Tables 16 and 17 and Appendix III.

Cross sections of reacted glass specimens were analyzed using SEM and analytical electron microscopy (AEM), a combination of TEM, which provides structural information about the reaction progress, and EDS, which provides compositional information. Electron diffraction (ED) analysis is also possible if discrete crystalline phases are observed. For SEM examination, 10 to 20 particles were mounted randomly in epoxy, and the epoxy mount was polished to obtain a cross section of a reacted slag particle. For AEM examination, a few individual particles were hand selected on the basis of their appearance in an optical microscope, and each particle was mounted in an epoxy block. The grains were then cut into cross sections 500 to 1000 Å thick by using a diamond knife, and 10 to 30 sections were placed on a copper grid for AEM examination.

3.4.2 Solution Results

The results of the solution analyses (Table 16) show that the slag leachates contained essentially no anionic (other than OH⁻) nor carbon component, which is important because these components are known to be complexing agents for metals and could increase the solubility of hazardous elements in solution. Only slag 7165 at 20,000 m⁻¹ (sample MSE-24) showed an increase in organic carbon.

The cation analyses are presented in Table 17 in terms of normalized release. The complete set of raw release values is presented in Appendix III. The average glass compositions that were provided by MSE and used to calculate the NL(i) values are given in Table 18.

Table 16. Anion and Carbon Analysis of the Leachates of BWID Slags

Sample ID	Slag Type	Time, days	SA/V, m ⁻¹	pH	Anions, mg/L						Carbon, mg/L	
					F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ²⁻	SO ₄ ²⁻	Total	Organic
MSE-1	7164	7	2000	8.75	NA ^a	NA	NA	NA	NA	NA	5.5	2.6
MSE-2	7409	7	2000	8.79	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	5.1	3.2
MSE-3	7380	7	2000	9.04	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	5.4	3.4
MSE-4	7165	7	2000	8.43	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	6.4	4.1
MSE-9	7164	7	2000	9.02	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	4.3	2.4
MSE-10	7409	7	2000	8.75	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	4.3	2.9
MSE-11	7380	7	2000	9.09	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	4.2	2.9
MSE-12	7165	7	2000	8.82	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	5.2	2.9
MSE-17	7164	33	2000	8.53	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	2.3	1.5
MSE-18	7409	33	2000	8.67	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	2.1	1.3
MSE-19	7380	33	2000	8.87	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	9.9	1.1
MSE-20	7165	33	2000	8.36	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	4.7	2.7
MSE-5	7164	89	2000	9.23	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	6.5	2.6
MSE-6	7409	89	2000	9.07	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	5.4	3.5
MSE-7	7380	89	2000	9.33	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	5.3	2.1
MSE-8	7165	89	2000	8.65	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	7.4	4.1
MSE-13	7164	179	2000	9.18	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	2.8	2.0
MSE-14	7409	179	2000	8.92	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	3.4	2.3
MSE-15	7380	179	2000	9.45	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	3.8	1.2
MSE-16	7165	179	2000	8.35	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	6.7	3.6
MSE-21	7164	66	20,000	9.97	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	11.1	5.8
MSE-22	7409	66	20,000	9.74	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	10.3	5.6
MSE-23	7380	66	20,000	10.20	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	11.6	6.6
MSE-24	7165	66	20,000	8.65	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	37.6	24.4
DIW				5.81	<1.0	<1.0	<1.0	<2.0	<2.0	<2.0	0.3	0.2

^aNA = Not available.

Table 17. Normalized Elemental Mass Losses from BWID Slags

Sample	NL(i), g/m ²					
	NL(Si)	NL(Al)	NL(Na)	NL(K)	NL(Mo)	NL(Ce)
MSE-1	0.06	0.03	0.20	0.11	0.10	0.006
MSE-2	0.04	0.02	0.19	0.08	0.07	0.004
MSE-3	0.04	0.02	0.25	0.07	0.06	0.002
MSE-4	0.04	0.02	0.13	0.06	0.02	0.005
MSE-5	0.06	0.02	0.34	0.08	0.50	0.004
MSE-6	0.06	0.02	0.31	0.08	0.07	0.004
MSE-7	0.07	0.02	0.44	0.10	0.22	0.004
MSE-8	0.06	0.02	0.22	0.06	0.07	0.004
MSE-9	0.06	0.04	0.22	0.08	0.06	0.004
MSE-10	0.06	0.03	0.27	0.12	0.16	0.004
MSE-11	0.04	0.03	0.29	0.09	0.08	0.004
MSE-12	0.04	0.04	0.15	0.07	0.01	0.004
MSE-13	0.06	0.02	0.46	0.11	0.11	0.003
MSE-14	0.07	0.02	0.41	0.13	0.13	0.002
MSE-15	0.07	0.02	0.58	0.13	0.14	0.000
MSE-16	0.05	0.02	0.31	0.09	0.02	0.008
MSE-17	0.05	0.02	0.26	0.09	0.08	0.006
MSE-18	0.05	0.03	0.27	0.09	0.07	0.004
MSE-19	0.05	0.02	0.36	0.10	0.07	0.002
MSE-20	0.04	0.03	0.17	0.06	0.02	0.004
MSE-21	0.01	0.002	0.23	0.02	0.03	0.004
MSE-22	0.01	0.002	0.19	0.02	0.03	0.004
MSE-23	0.01	0.003	0.31	0.02	0.03	0.004
MSE-24	0.01	0.001	0.18	0.02	0.02	0.004

Table 18. Average Glass Compositions Used to Calculate Normalized Losses for BWID Glasses

BWID Number	MSE Slag Number	Concentration, mg/kg					
		Si	Al	Na	K	Mo	Ce
92-BWID-1	7164	227,697	52,978	6620	13,347	47.4	607.4
92-BWID-2	7165	227,128	46,044	7905	14,967	133.5	6314
93-BWID-1	7380	231,214	61,010	6181	13,324	81.4	9445
93-BWID-2	7409	205,167	53,607	5608	11,948	128	8038

While the slag is a multicomponent system and selected elements may come solely from one particular phase, the normalized release approach is used to provide a comparison with other waste glasses that, while considered homogeneous and glassy, also contain some devitrified components. If the glass reacts via a congruent dissolution process in which the matrix dissolves at the same rate, then all NL(i) values will be equal. Nonequal NL(i) values indicate selective leaching from a single phase, different leach rates from separate phases, or reprecipitation of secondary phases onto the glass surface. Sodium, potassium, and molybdenum were chosen as elements representative of leaching from HLW glasses, because they are among the elements released fastest from the glass. In the slag, the sodium and potassium are known to be concentrated in the glass phase, so the analogy with HLW glass should be valid. However, the slag contains very little molybdenum, and its concentrations are within detection limits. Silicon and aluminum were then chosen as major constituents of the glass phase to provide information about glass matrix dissolution.

3.4.3 Results of Solids Examinations

SEM examinations of the corroded slags from both the 2000 and 20,000 m⁻¹ tests showed that the edges of the particles were sharp and the crystalline phases were intact, showing little evidence of reaction. Optical micrographs in transmitted and reflected light, which highlight the crystalline inclusions, are shown in Fig. 44; SEM micrographs of slags reacted for 66 days at 20,000 m⁻¹ are shown in Fig. 45.

TEM micrographs of the reacted slags from tests 13 through 24 are shown in Fig. 46. In Fig. 46, slag 7164, reacted for 33 days at 2000 m⁻¹ (sample MSE-17), is shown to have formed a small amount of a clay layer. The white region at the surface is the epoxy binder. The outer surface of the slag shows evidence of very slight reaction with water, as shown by the faint fringes that appear horizontal to the glass surface. These fringes, in HLW glass, transform into layer clays, which would eventually cover the surface of the glass in increasing thickness. For this slag, the fringes are just beginning to form and have not reached the stage at which they can be unambiguously identified, but their appearance

Fig. 44. Optical Micrographs in (a) Transmitted (250X) and (b) Reflected (20X) Light of BWID Slag 7164 Reacted for 7 Days at 2000 m^{-1} .

Fig. 45. SEM Micrographs of Each BWID Slag in Cross Section after Reaction for 66 Days at $20,000 \text{ m}^{-1}$: (a) Slag 7164, (b) Slag 7165, (c) Slag 7380, and (d) Slag 7409.

Fig. 46. Sample MSE-17 (Block 898) of Slag 7164, Showing Evidence of a Small Amount of Clay Layer.

suggests a combination restructuring of the glass surface and reprecipitation from solution. Figure 47 shows that the interface between the glass and crystalline phase was intact even after sectioning. In Fig. 48, sample MSE-23 (slag 7380), reacted for 66 days at $20,000 \text{ m}^{-1}$, also shows good bonding between the glass and the crystalline phase and very little evidence for glass-water reaction.

The samples run for 179 days at 2000 m^{-1} were also examined with SEM and AEM. A thin layer of wispy clay filaments was visible on the surfaces of most of the samples. The filaments were often bundled together and extended about 100 nm from the slag surface (see Fig. 49). The layer was not continuous but was scattered over the surface. Clay material was also observed on top of the crystalline phase, suggesting that perhaps these small bundles of clay have precipitated from solution onto the surface (see Fig. 50). Figure 51 shows three low-magnification micrographs of the reacted layer. The layer sometimes had the appearance of a gel, and at other times it contained wispy clay filaments.

The bond between crystal and glass phases appears to be quite strong, because the glass-crystal interface in some regions has remained intact despite the sectioning process, as can be seen in Figs. 52 and 53. This has been found to be true for all the slag samples examined, yet there does not seem to be a visible diffusion zone. The boundary between the two phases is extremely sharp. Higher magnifications were used to explore the nature of this interface, which appears to be less than a few nanometers thick.

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Fig. 47. Sample MSE-17 (Block 901), Showing Intact Glass-Crystal Interface.

Fig. 48. Sample MSE-23 (Block 892), Showing Crystals within Glass Matrix; No Reaction of Glass Is Visible.

Fig. 49.
Reacted Layer from Sample MSE-15,
Reacted 179 Days at 2000 m^{-1} .

Fig. 50.
Reacted Layer on Crystals in
Sample MSE-13.

(a)

(b)

(c)

Fig. 51. Reacted Layer from Samples (a) MSE-14, (b) MSE-13, and (c) MSE-17.

Fig. 52. Reacted Layer Showing Intact Boundary between Crystals and Glass of MSE-10.

(a)

(b)

(c)

Fig. 53. Intact Crystal-Glass Interfaces in Samples (a) MSE-13, (b) MSE-16, and (c) MSE-17.

Electron diffraction patterns obtained from the crystalline part of the glass are typical of a cubic material and can be easily indexed as such, indicating that these crystals are all spinel phases. Figure 54 is a SAED pattern taken along the $\langle 101 \rangle$ zone axis. EDS and EELS were used to determine the glass and crystalline phase compositions. Spectra from some of the samples are shown in Fig. 55, and selected compositions are given in Table 19. EELS was used to determine the cerium content in the glass samples because EDS detection sensitivity for this element is not as good as that of EELS. EELS also eliminates overlap, because the energy scale is much finer. EELS spectra are shown in Fig. 56, which highlights the presence of cerium in the glass but not the crystalline phases.

3.4.4 Discussion of BWID Slags

Both solution and surface analyses showed very little evidence for reaction under accelerated leaching conditions. For the 2000 m^{-1} test there was evidence that the glass was initially reacting by means of an ion-exchange process, whereby alkali elements are released more rapidly from the glass matrix than Si or Al. For example, NL(Na) reached $\sim 0.3\text{ g/m}^2$ after 89 days, while NL(Si) and NL(Al) remained at ~ 0.05 and 0.02 g/m^2 , respectively, throughout the entire reaction period. The NL(Ce) is a factor of 10 less than NL(Si). Over 90% of the cerium released was associated with the acid strip solution rather than being in true solution.

Fig. 54. SAED Pattern of the $\langle 101 \rangle$ Zone Axis of BWID 7409.

Fig. 55. EDS Spectra of the Glassy Phase of BWID Slags (a) 7164, (b) 7409, (c) 7380, and (d) 7165.

Table 19. Compositions for Selected BWID Slags, oxide wt %

	SiO ₂	MgO	Al ₂ O ₃	K ₂ O	CaO	Fe ₂ O ₃	CrO ₃	NiO
MSE-17 (block 898) ^a	63.1	0.9	12.7	3.1	8.4	11.1	0.0	0.2
MSE-17 (block 898, surface)	62.4	0.7	12.2	2.8	7.9	13.0	0.2	0.3
MSE-18	64.4	0.5	13.0	3.45	8.3	8.35	0.2	0.2
MSE-19	64.65	0.2	13.3	3.0	6.7	10.5	0.2	0.1
MSE-20	65.9	0.6	13.15	3.0	8.1	8.0	0.2	0.2
MSE-21 (block 885)	57.1	1.2	12.05	2.5	9.95	16.6	0.1	0.15
MSE-21 (block 886)	56.7	0.7	12.1	3.2	9.0	17.1	0.3	0.5
MSE-22 (block 887)	66.0	0.3	12.7	3.5	7.8	8.1	0.1	0.15
MSE-22 (block 888)	65.6	0.6	13.5	3.2	7.8	7.8	0.2	0.15
MSE-23 (block 890)	57.6	0.8	12.2	2.7	7.3	18.0	0.1	0.14
MSE-24 (block 891)	63.3	0.9	14.2	2.9	8.2	9.2	0.2	0.18
MSE-24 (block 892)	66.0	0.9	14.6	3.2	8.7	4.8	0.4	0.4

^aInternal sample tracking number.

Fig. 56. EELS Spectra (Obtained with Second Difference Technique), Showing Cerium in Glass Phase of BWID Slags (a) 7409 and (b) 7380 and (c) Crystalline Phase of Slag 7380.

Examinations by optical microscopy and SEM showed no detectable reaction. They also showed the crystalline phase to be firmly bonded into the glass matrix. The AEM results showed that for some slags the "clay" layer was just beginning to form on the glass and crystalline surfaces after the 28-day test, which would decrease the release of Si, Al, and Ce. Although the release of other hazardous metals, e.g., Cr and Ni, were not given in terms of NL(i) in Table 17 because the acid strip component could include metals etched from the stainless steel vessels, the actual amounts of these elements in the leachate solutions are in the low parts per billion range (including the material on the vessel walls), and thus their release is very low.

Under the extreme conditions used in the vapor hydration tests discussed in Section 3.2.3 (200°C and 100% relative humidity), the slag was more stable than HLW glasses. This better stability is attributed to the higher Si and Al content and lower alkali content of the glass phase in the slag, which inhibits the development of the secondary phases that form under vapor conditions and that accelerate the glass reaction. The metal-rich phases in the slags are also quite stable under the accelerated conditions. The overall performance of these slags is superior to that of the best HLW glasses being considered in the United States, and since the anticipated service conditions for storage of mixed or low-level wastes do not include temperatures above ambient, slags have good potential to be durable over the long term.

3.5 Modeling with the Structural Bond Strength Model

The SBS model [3-5] is based on structural thermodynamic considerations and has been used to describe the chemical durability and the melt viscosity of nuclear waste glasses [4,5,23,24]. This model was applied to a set of 300 glasses for which there were MCC-1 test data [23]. The SBS model was also tested using MCC-3 leach data from about 100 glasses, including nuclear waste glasses, commercial aluminosilicate and soda-lime glasses, and natural glasses (such as Hanford basalt glass, obsidians, and tektites) [3]. A fair correlation was reported between glass composition and durability (as measured by the glass constituent releases in MCC-1 and MCC-3 tests). More recently, Toven et al. [24] used this model to correlate the initial corrosion rates of waste glasses, determined under Soxhlet conditions, with their compositions; the model provided a satisfactory approximation of the initial rates.

This model has been successfully applied to the correlation of glass composition with (1) modified MCC-3 leach test results on nuclear waste glasses measured at various laboratories and (2) the viscosities of numerous glasses over a temperature range of 850°C to 1600°C. It has also been demonstrated that this model can identify some glass compositions that have high durabilities but low processing temperatures. This capability is the result of the major features of this model, viz., the recognition that the structural role of a given constituent (e.g., B_2O_3) may vary depending on the temperature range involved. This feature accounts for differences between the effects of glass composition on viscosity (measured around 1000°C) and on chemical durability (measured below 100°C), and it permits systematic identification of compositional variations that increase leach resistance without causing a commensurate increase in viscosity. Moreover, geometric factors such as cation size may have different effects on the two phenomena.

3.5.1 Basic Assumptions

A model based upon structural thermodynamic considerations has been developed for both chemical durability and viscosity of nuclear waste glasses. This model assumes the bond strength between atoms in the glass to be the predominant factor in controlling the composition dependence of physical properties, such as viscosity, and chemical properties, such as reaction with water. These characteristic bond strengths in the glass are obtained from the known heats of formation of the constituent oxides, combined with a few simple structural rules deduced by distinguishing the structural roles of the various oxides. These rules separate those components that are clearly "network formers" (e.g., SiO_2 , Al_2O_3 , and ZrO_2) from those that are clearly "network breakers" (e.g., alkali oxides).

Pure silica glass is a completely polymerized, three-dimensional, randomly interconnected network of Si-O bonds without periodic order and with energy content comparable to that of the corresponding crystalline material, as pointed out by Zachariasen [25]. This glass, characterized by the large bond strength of Si-O, has very high chemical durability.

Upon addition of other oxides to the glass structure, the presence of X-O bonds other than Si-O changes the durability. Although the values of X-O bond energies in this structure are somewhat different from the corresponding values in pure oxides, they can be expected to be closely related.

As a first approximation, it may be assumed that durability can be correlated to the composition of the glass through its total enthalpy of formation. This simple approach is far from satisfactory [3]. An improvement can be obtained by distinguishing the structural roles of the various oxides, i.e., separating those components that are clearly "network formers" (e.g., SiO_2 , Al_2O_3 , and ZrO_2) from those that are clearly "network breakers" (e.g., alkali oxides). Several authors [26-28] have classified glass formers, intermediates, and glass modifiers on the basis of single bond strengths. For instance, Sun [27] calculated various single bond strengths from the heat of dissociation of the simple oxide for the various oxide components of a complex oxide according to Pauling's scheme [29]. The conclusion was that all the glass formers have bond energies above 80 kcal per bond, those of the intermediates are between 60 and 80 kcal/bond, and those of the modifiers are below 60 kcal/bond.

There are other ways of differentiating glass formers from other oxides. Zachariasen classified glass formers according to the coordination number and structural role of an oxide [25]. According to this theory, the coordination number of an atom determines its role in a glass structure, and the following four rules should be fulfilled for an oxide to form glass:

1. Each oxygen atom must be linked to no more than two cations;
2. The number of oxygen atoms around any one cation must be small, i.e., three or four;

3. The oxygen polyhedra must share corners, not edges or faces, to form a three-dimensional network; and
4. At least three corners must be shared.

For one-component glasses, each polyhedron shares corners with at least three other polyhedra in such a way that the network is continuous in three dimensions. In multicomponent glasses, additional cations are distributed holes in the network.

Subsequently, Stanworth distinguished the role of different oxides in glass formation by size, charge, and electronegativity [30]. For example, (1) cation valence should be three or greater, (2) glass formation should increase with decreasing cation size, and (3) the Pauling electronegativity should be between 1.5 and 2.1.

In the SBS model, both bond strength and structural role are used to classify oxides. In the class of glasses under consideration, SiO_2 , Al_2O_3 , ZrO_2 , and B_2O_3 are the most important glass formers. B_2O_3 has special effects on glass structure and properties that will be discussed later. The total bond energies corresponding to each of the glass formers, according to Sun [27], are given in Table 20. These bond strength energies in each case represent the product of the single bond strength and the number of bonds per molecule of oxide in the glass. The corresponding heats of formation in the pure oxides, according to Dean [21], are given in the left column. It can be seen from Table 20 that in the case of major glass formers, $2 \cdot \Delta H_i^\circ$ represents, to a good approximation, the contribution of 1 mole of any of these glass formers to the strength of the network.

Table 20. Heat of Formation and Total Bond Energy, kcal/mole

Glass Former	Heat of Formation, $-\Delta H_i^\circ$ ^a	Sun's Total Bond Energy ^b	$2(-\Delta H_i^\circ)$
SiO_2	215.9	424	431.8
Al_2O_3	400.4	808	800.8
ZrO_2	262.3	486	524.6

^aFrom Dean [21].

^bFrom Sun [27].

According to Sun [27], the fundamental condition for oxide glass formation is the existence of strong, extensive networks formed by joining atoms together through two or more strong chemical bonds in the structure of the glass. In the case of the nuclear waste glasses under consideration here, these multiple strong chemical bonds may include Si-O, Al-O, and Zr-O bonds. Thus, the skeleton of the glass structure can be represented as:

where X is either Al or Si. In the case of Zr, the configuration is octahedral instead of tetrahedral. Those three oxides are designated here as network formers. When alkali oxides, M_2O , are introduced into the system, the resulting structure will be:

One of the network bonds is broken for each added molecule of alkali oxide and the glass network is interrupted. Thus, the alkali oxides are considered network breakers [25]. When oxides other than these network breakers and network formers, such as divalent ions, are added to the glass, the network will contain weaker bonds such as:

where M^{2+} is a divalent cation.

Note that alkaline earths are considered intermediates in this model, unlike in most of the other models [26-28], where alkaline earth oxides are generally considered network breakers. Because an alkaline earth ion carries twice as much positive charge as alkali oxide and is usually smaller, the alkaline earth in the oxide has higher charge density and exerts a much stronger attraction to the negative, nonbridging oxygen in the matrix. More importantly, the alkaline earth ion, M^{2+} , maintains a weak bond between two oxygens, while alkali ion terminates the glass network. Numerous glass composition studies have

demonstrated that the addition of alkaline earth oxides to glasses is much less harmful than the addition of alkali oxides [18]. In the case of durable glasses, it has almost no negative effect on the durability of the resulting glass. This is why alkaline earth oxides, like other divalent metal oxides, are treated as intermediates in this model. Of course alkaline earth oxides are still basic oxides which can serve as the counter oxides for acidic oxides in determining the acidity of the glass, in addition to the alkali oxides.

Iron oxide is one of the major constituents of the nuclear waste glasses considered in this study. The structural role of Fe_2O_3 in the glass has been a matter of controversy. Composition studies of nuclear waste glasses showed that the structural role of iron oxide depends on its local environment (nearest neighbors) [18]. As Fe_2O_3 , iron oxide serves partially as a network former in the "less durable glasses," such as WV205, which are deficient in network formers. In the "more durable glasses," most of the Fe_2O_3 functions as an intermediate. Since FeO has a value of heat of formation very different from that of Fe_2O_3 , the current model does distinguish FeO and Fe_2O_3 in terms of bond strength, and FeO is always treated as an intermediate. The "more durable glasses" are defined as the glasses that are not very sensitive to changes in glass composition, while the "less durable glasses" are very sensitive to such changes [18].

3.5.2 Calculation of Structural Bond Strength

The foregoing discussion provides the basic assumptions of this model. These assumptions are realized in the following four rules established for the calculation of the structural bond strength.

3.5.2.1 Rule 1: Network Formers

The bonds of network formers represent the main framework of the glass, and the SBS values for SiO_2 , Al_2O_3 , ZrO_2 , and Fe_2O_3 are obtained as:

$$\Delta V_i = 2\Delta H_i^\circ \quad (4)$$

where ΔH_i° is the standard heat of formation of the pure oxide i and ΔV_i is the SBS value of oxide i in the glass. The standard heat of formation of the various pure oxides corresponds to their most stable state, except in the case of SiO_2 , where the value for the amorphous or vitreous state has been used. (For the factor of two, see Table 20 and Section 3.5.1.) Therefore, using the standard heat of formation values from Dean [21], the SBS values for network-forming Al_2O_3 , ZrO_2 , SiO_2 , and Fe_2O_3 are -800.8, -524.6, -431.8, and -394 kcal/mole, respectively. These values are very close to Sun's total bond energies [27]. It is also interesting to note that the value of the ratio of $\Delta V_{\text{Al}_2\text{O}_3}/\Delta V_{\text{SiO}_2}$, 1.53, is very close to the empirical value of silica equivalence for alumina when the silica melts had a mole fraction of alumina to alkali and alkali earth ratio of less than 1.0 in Turkdogan and Bill's model [31]. For instance, in a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, they observed that addition of one mole of alumina had an effect on the melt viscosity equivalent to adding 1.5 to 1.6 moles of

silica, i.e., alumina has a silica equivalence value of 1.5 to 1.6 [31]. It is important to recognize that only those Al_2O_3 , ZrO_2 , and Fe_2O_3 that are charge balanced by alkalis will have SBS values calculated according to the above formula; this point is discussed in more detail below.

The Al-O bonds with a tetrahedral coordination of Al have a fairly high degree of covalence and a large formation energy; therefore, when Al_2O_3 acts as a network former, after forming $[\text{AlO}_{4/2}]^+$ groups in the network of the glass, it increases the rigidity of the framework of the glass and improves its strength. Moreover, aluminum in this role aids in the homogenization of the glass [32], as illustrated by the lowering of the thermal expansion coefficient and the steady increases in the softening temperature and strength of the glasses [32] as the alumina content is increased. The increase in the degree of ordering of the glass structure resulting from the addition of Al_2O_3 appears as a reduction in the size and number of the liquid-phase areas and a reduction in nonuniformities of microscale of the original glasses. According to Bobkova et al. [32], when Al_2O_3 was added to the melt, the IR spectra of the melt suggested that a high degree of polymerization of the network was retained. However, it should be noted that the structural role of Al_2O_3 is dependent on the mole ratio of alumina to the total alkalis and alkaline earth oxides. Many experiments and structural studies [32-34] indicate that alumina has a tetrahedral configuration only when the mole ratio of alumina to the total alkalis and alkaline earth oxides is less than or equal to one. The tetrahedral configuration can form a glass network like silica. When this ratio is greater than one, some of the alumina adopts a six-coordinated structure that cannot serve as a network former. Therefore, this dual role of alumina is also built into the present model: i.e., when the mole ratio of alumina to total alkali oxides is less than or equal to one, all of the Al_2O_3 units are considered network formers; otherwise, only those Al_2O_3 units that are in a tetrahedral configuration count as network formers, and the rest, which exist in a six-coordinated configuration, are taken to be intermediates.

Bobkova et al. [32] also demonstrated that Al_2O_3 has an active influence on the structural position of the Zr^{4+} ion in glass. The weakly bonded oxygen ions from alkalis and alkaline earth oxides go first to transform Al^{3+} into quaternary coordination. The remainder can be used by the Zr^{4+} ions to form $[\text{ZrO}_{6/2}]^{2-}$ groups in the anionic network of the glass. Therefore, the ZrO_2 is considered a network former in this model only when the alkali oxide content is sufficiently high to change the coordination state of ZrO_2 from eight to six.

Only the Fe^{3+} was in Fe_2O_3 that are charge balanced by alkalis and that are in four-coordination state are treated as network formers, and the Fe_2O_3 that is not charged balanced by alkalis is considered to be intermediate, as discussed later. The order for the oxides to receive alkalis is Al_2O_3 first, ZrO_2 second, and Fe_2O_3 last. The evidence for this order is discussed later.

3.5.2.2 Rule 2: Network Breakers

From the above discussion, it is concluded that each molecule of network breaker breaks one network bond. Therefore, the SBS values for these network breakers are adjusted according to

$$\Delta V_i = \Delta H_i^\circ - E_{\text{net}} , \quad (5)$$

where ΔV_i and ΔH_i° follow the definition above, and E_{net} is the average bond strength of the network formers. E_{net} can be calculated from the following equation:

$$E_{\text{net}} = \frac{\sum_i m_i \cdot \Delta V_i}{\sum_i a_i \cdot m_i} = \frac{m_{\text{Al}_2\text{O}_3} \cdot \Delta V_{\text{Al}_2\text{O}_3} + m_{\text{SiO}_2} \cdot \Delta V_{\text{SiO}_2} + m_{\text{ZrO}_2} \cdot \Delta V_{\text{ZrO}_2} + m_{\text{ZrO}_2} \cdot \Delta V_{\text{Fe}_2\text{O}_3}}{8 \cdot m_{\text{Al}_2\text{O}_3} + 4 \cdot m_{\text{SiO}_2} + 6 \cdot m_{\text{ZrO}} + 8 \cdot m_{\text{Fe}_2\text{O}_3}} , \quad (6)$$

where m_i is the mole fraction of the network former i in the glass and a_i is the number of bonds formed from each mole of network former i .

3.5.2.3 Rule 3: Intermediates

Oxides other than network formers or network breakers are classified as intermediates. The SBS values of these oxides are taken to be their standard heats of formation, i.e.:

$$\Delta V_i = \Delta H_i^\circ . \quad (7)$$

3.5.2.4 Rule 4: Special Rule for B_2O_3

Boron oxide is considered to be an excellent glass former. According to Sun's single bond energy [27], the bond in this case is even stronger than the bonds in SiO_2 or in Al_2O_3 . Accordingly, B_2O_3 forms a single-component glass. However, addition of B_2O_3 to a silica melt decreases both the viscosity and the durability of the resulting glass. The viscosity of pure boron oxide glass at a temperature of 1260°C is smaller than that of silica glass by a factor of 3.98×10^{11} [35]. This anomalous behavior of B_2O_3 [36-39], characterized by low viscosity, has been interpreted in terms of a mechanically induced coordination change of boron, according to Krogh-Moe [36]. Krogh-Moe's model involves a transition from an sp^2 planar triangular coordination to an sp^3 tetrahedral configuration in the presence of alkali ions. The transition proceeds most rapidly at the high temperature of the melt. Accordingly, flow can proceed through a continuous coordination change that has a low activation energy and does not require complete cleavage of the strong

B-O bonds. Thus, in terms of effects on viscosity, the boron atom behaves like an alkali atom that breaks one network bond, presenting no resistance to viscosity flow. Boron oxide is accordingly treated as a network breaker in modeling viscosity. The SBS value of B_2O_3 for viscosity modeling [5] is obtained according to the following equation:

$$\Delta V_{B_2O_3} = \Delta H^\circ_{B_2O_3} - 2E_{net} \quad (8)$$

where the constant of 2 is due to the presence of two boron atoms in every mole of B_2O_3 .

In considering the effects of B_2O_3 on durability, it is necessary to take into account the fact that boron cannot readily change its coordination at the low temperatures characterizing its interaction with water. For durability issues, B_2O_3 should be treated as an intermediate.

However, the structural role of boron also depends on the mole ratio of acidic oxides to basic oxides. An excellent study on the structural role of boron in aluminosilicate glasses was carried out by Bobkova et al. [32]. By using electron microscopy and IR, Raman, and electron spin resonance (ESR) spectroscopy, they found that when the R_2O/B_2O_3 ($R = Na, Li, K$) ratio is much greater than one, the aluminum added to the glass is incorporated into the borosilicate network of the glass in a fourfold coordinated state. When the amount of Al_2O_3 increases beyond the ratio of $Al_2O_3/R_2O = 1$, further formation of $[AlO_4]$ tetrahedra is only possible by reducing the number of $[BO_4]$ tetrahedra. In this case, the boron atoms change to ternary coordination to release additional R_2O , which the Al_2O_3 needs. If the initial ratio R_2O/B_2O_3 is less than or equal to one, then the process of destroying the $[BO_4]$ tetrahedra begins straight away with the first addition of Al_2O_3 to the glass.

On the other hand, Bobkova's research [32] has also shown that boron has a slight inertia in relation to the use of the polarized oxygen of alkali oxides. This can be explained by assuming that the trigonal rather than the tetragonal coordination is the stable one for boron, while for zirconium the most stable state is sixfold coordination. Therefore, among Al_2O_3 , ZrO_2 , and B_2O_3 , Al_2O_3 will satisfy its coordination requirements in the glass framework first, and B_2O_3 probably will do so last. Fe_2O_3 is assumed to have a preference for alkalis over B_2O_3 , but ZrO_2 has a greater preference for alkalis than Fe_2O_3 .

As a result, in the durability modeling of this study, B_2O_3 is only treated as an intermediate when there are enough alkalis left as "free oxides" (not bonded to Al_2O_3 , ZrO_2 , or Fe_2O_3) in the glass to maintain B_2O_3 in its tetrahedral configuration. If there are not enough basic oxides to do so, only some of the B_2O_3 units are taken to be intermediates, and the rest of them are treated as network breakers. The latter case was observed by Feng et al. [18]. When B_2O_3 was added to a glass that already had a ratio of acidic oxides to basic oxides that was greater than one, the addition of B_2O_3 was even more harmful to durability than the addition of Na_2O to the glass. Note that when

deciding whether there are enough basic oxides to transform B_2O_3 into tetrahedral configuration, SiO_2 is not considered to take up alkali oxides, implying that B_2O_3 will bind to those basic oxides prior to SiO_2 .

It should be emphasized that B_2O_3 is always treated as a network breaker in viscosity modeling regardless of the ratio of acidic oxides to basic acids because of the easy coordination change of B_2O_3 under high temperature conditions [5].

The redox state of oxides are considered in the SBS model because oxides with different oxidation states have different ΔH° . For example, $\Delta H^\circ_{Fe_2O_3} = -197$ kcal/mole, while $2 \cdot \Delta H^\circ_{FeO} = 2 \times (-65) = -130$ kcal/mole. That means that FeO will contribute less to the waste form durability than Fe_2O_3 , even though both are treated as intermediates. Network-forming Fe_2O_3 will contribute $2 \times (-197)$ kcal/mole to the waste form durability, which is substantially more than the contribution of iron oxides serving as intermediates.

With these four rules, the total SBS value for the glass can be calculated as:

$$\Delta V = \sum_i X_i \Delta V_i \quad (9)$$

where X_i is the molar fraction of oxide i and ΔV_i is the SBS value of oxide i .

3.5.3 Application of the Structural Bond Strength Model to Glassy Slags

The SBS model has been applied to the correlation of glass chemical durability in terms of MCC-1 [23], MCC-3 [4], and forward glass reaction rates [24], and glass compositions. This model has been used in this project to correlate slag formulations with their chemical durability.

3.5.3.1 Guidance for Slag Formulation

In a purely Edisonian waste form development project, work would be guided solely by the durability test results; i.e., the next formulation campaign would be based on the durability test results of the previous formulations. The art of achieving the optimized compositions would depend on experience and on the accumulation of a large and complete durability data base on the same waste form. The waiting period between each formulation campaign would be the total time required for the completion of the durability tests (such as 7- or 28-day PCT-type tests), the analysis of the leachates from the durability tests, and the compilation and interpretation of the leach data. This would be usually a time-consuming process.

At the initiation of this project to develop glassy slags for the remediation of low-level and mixed waste, there was no empirical data base on the chemical durabilities of glassy slags, and there was no time to amass such a data base. Because ANL was requested to recommend formulations to MSE within three months, the SBS model was used to provide guidance on slag formulations, although the model had not previously been applied to glass-crystalline systems with high metal oxide contents.

The approach used was to select, on the basis of past experience, an initial formulation with the highest possible waste loading (ANL-M2). This formulation was found to pass TCLP limits on RCRA metals and to have an acceptably low leachability as measured by the PCT. The SBS value calculated for this formulation was -197 kcal/mole. This formulation, ANL-M2, served as the starting point of the formulation campaign, and any subsequent slag formulations were required to have an SBS energy less than -197 kcal/mole, which means they should have a chemical durability better than ANL-M2. With this guideline, the rest of the slag compositions were selected such that the limits on loadings of metals such as Ni, Cr, and Fe could be explored with little or no purchased additives as long as the formulations met the requirement for the SBS value. The next section will show that the other fifteen ANL-M formulations all had more negative SBS energies than that of ANL-M2, and the test results confirmed that ANL-M2 had the poorest chemical durability.

The SBS modeling results indicated that (1) the SBS model is sensitive to minor variations in slag composition as shown in Table 21; (2) durable slags can be made with carbon steel loading up to 80%, stainless steel loading up to 30%, and total waste loading (metal plus soil) up to 100%; and (3) slag durability is sensitive to the redox states of the oxides in the slags, especially for iron, since it is the major component that is present in more than one oxidation state under slag melting conditions. The durability order predicted by the model also matches that measured by the element release in PCT tests, as shown in the next section. This demonstrated that the SBS model is a useful tool for waste form optimization. It reduces the need to perform crucible melts to find the optimized formulations and shortens the development time in the optimization of waste form composition.

This model focuses on understanding the dependence of durability on glass composition, as reflected in thermodynamic and structural considerations, rather than on understanding the detailed kinetics of the corrosion process. Thus, this model can be used at present only to compare the durabilities of various glasses and to predict the final elemental concentrations at certain times in certain tests, but not to elucidate the mechanism of the glass dissolution. The main advantages of the present model lie in its simplicity, multiple applicability, correlation between observed properties and basic structural and thermodynamic parameters, and convenience. It does not require selecting specific reactants and products for the hydration process and, therefore, avoids the difficulty of obtaining accurate values for the hydration products and applicable to both homogeneous glasses and multiple-phase glassy slags.

Table 21. SBS Values for ANL Slags, kcal/mole

ANL Slag	SBS Value for Bond Energy, $-\Delta V_i^\circ$
ANL-M1	-226
ANL-M2	-197
ANL-M3	-349
ANL-M4	-325
ANL-M5	-256
ANL-M6	-271
ANL-M7	-210
ANL-M8	-239
ANL-M9	-246
ANL-M10	-244
ANL-M11	-244
ANL-M12	-244
ANL-M13	-243
ANL-M14	-355
ANL-M15	-229
ANL-M16	-207

3.5.3.2 Correlation of Structural Bond Strength Model with PCT Results

The results show a satisfactory correlation between SBS energies and the extent of slag corrosion measured in PCT tests on the 16 slags produced in this phase of the work. The SBS energy, ΔV (kcal/mole), is plotted against the normalized K, Na, and Si releases in Figs. 57 to 59. The best-fit equations for these correlations are as follows.

- For 7-day results:

$$\log NL(K) = -0.047022\Delta V + 0.380359, \quad R = 0.93$$

$$\log NL(Na) = -0.004399\Delta V + 0.636510, \quad R = 0.85$$

$$\log NL(Si) = -0.004439\Delta V + 0.089199, \quad R = 0.94$$

Fig. 57. The Correlation between SBS Energy and the Normalized Potassium Release from (a) 7-Day and (b) 28-Day PCT Tests.

Fig. 58. The Correlation between SBS Energy and the Normalized Sodium Release from (a) 7-Day and (b) 28-Day PCT Tests.

Fig. 59. The Correlation between SBS Energy and the Normalized Silicon Release from (a) 7-Day and (b) 28-Day PCT Tests.

- For 28-day results:

$$\log \text{NL(K)} = -0.0051089\Delta V + 0.606437, \quad R = 0.90$$

$$\log \text{NL(Na)} = -0.0044215\Delta V + 0.763658, \quad R = 0.92$$

$$\log \text{NL(Si)} = -0.0047008\Delta V + 0.303475, \quad R = 0.92$$

In these equations, NL(K), NL(Na), and NL(Si) are the normalized releases (g/m^2) to the PCT leachates, and ΔV is the total SBS energy of the slag (kcal/mole).

4.0 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; (4) their less stringent requirements on processing parameters, such as viscosities, compared to glass waste forms; and (5) their low requirements for 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 contain 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 this approach is chosen, 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 a Retech pilot-scale PCF at Ukiah, California, with up to 100% waste loadings. These successful campaigns demonstrated the processibility of glassy slag.

The SBS model provided a useful correlation between slag composition and chemical durability. This model assumes that the strength of the bonds between atoms in the waste form is the predominant factor controlling in the composition dependence of the chemical durability of the slag. Use of this model greatly reduced the number of crucible melts and durability tests required to determine acceptable composition ranges and reduced the time and cost needed to identify a useful slag compositional envelope. This model was useful as a guide for optimizing formulations in the absence of a durability data base for the glassy slags.

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

5.0 FUTURE STUDIES

The slags produced in this project at ANL represent a novel waste form that contains significant amounts of both crystalline and glass phases. Continued development of glassy slag waste forms is in progress at ANL. The objective of the extension of this program is to use glassy slag waste forms to expand the range of waste streams that can be treated by using the MAWS approach. The work is aimed at those waste streams not amenable to producing glass waste forms and will complement efforts to develop a composition envelope for glass waste forms. The applicability of the MAWS approach to any DOE waste stream could then be assessed, including whether a glass or a glassy slag waste form is suitable and what additives are required. These composition envelopes will serve as guides for remediation of a wider variety of waste streams and reduction of overall disposal costs.

Glassy slags will be produced in the laboratory by using actual waste streams from DOE sites. The acceptable composition range for glassy slag waste forms will be determined through a crucible melt study that will involve plutonium-doped simulated wastes and actual soils from DOE sites. The plutonium-doped work is especially important because it will be used to validate a large data base of studies of cerium-doped wastes that has been accumulated by the waste management community. The list of metals considered will be expanded to include Al, Cu, Pb, Ti, Fe, Cd, Cr, Ni, P, and Zr. Slags will be characterized to determine the limits on blending these metals into slags. The SBS model will be further tested and improved to relate the overall composition (including the waste loading) of the slag to its durability. That information can then be used to reduce the number of crucible melts and slag tests that must be performed in future studies.

More effort will be needed to develop slag formulations that will result in durable and stable crystalline phases within the slag that will sequester a wide range of radionuclides and hazardous elements. If this work is successful, the durability of the glass phase in the slags will be of less concern, and slags can be used to treat high-sodium wastes. These slags will be fully characterized to determine how composition and heat treatment affect phase development, and they will be examined in a variety of corrosion tests to see how radionuclide release is improved by crystalline phase formation.

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APPENDIX I

**DILUTION-CORRECTED PCT LEACHATE CONCENTRATIONS
OF ANL GLASSY SLAGS (mg/L)**

TEST	ANALY ID	DURATION (days)	pH	AL	B	BA	CA	CE	Co	CR	CS	CU	FE
M1-7-1		7	8.59	4128	0	0.00	3541	0.06	0.00	0.00	0.00	0.00	128
M1-7-2		7	8.76	4114	0	6.80	3929	0.05	0.00	0.00	0.00	1.15	132
M1-28-1		28	7.04	1413	0	8.13	7164	0.14	0.00	1.03	0.00	0.12	0
M1-28-2		28	8.00	3409	0	3.05	4017	0.15	0.00	1.02	0.00	0.51	0
M1-91-1		91	8.54	3037	505	1.69	4533	0.05	0.03	2.54	0.00	1.65	48
M1-91-2		91	8.48	2652	498	1.43	4188	0.05	0.03	2.51	0.00	2.34	54
M2-7-1		7	8.97	2264	0	34.13	6776	0.03	0.00	0.51	0.00	0.52	65
M2-7-2		7	8.96	2449	0	31.35	6264	0.04	0.00	0.52	0.00	0.63	60
M2-28-1		28	8.44	1548	0	8.01	6088	0.00	0.00	4.79	0.00	0.00	2081
M2-28-2		28	8.47	1571	0	9.03	5911	0.00	0.00	0.21	0.00	0.10	0
M2-91-1		91	8.76	1050	2725	6.47	11446	0.04	0.03	2.84	0.00	1.31	33
M2-91-2		91	8.85	912	3141	7.41	11334	0.01	0.02	3.22	0.00	1.14	40
M3-7-1		7	8.51	2270	0	4.09	2204	0.07	0.00	1.47	0.00	3.15	71
M3-7-2		7	8.50	2332	0	3.88	2241	0.07	0.00	1.15	0.00	0.84	30
M3-28-1		28	8.25	4248	0	3.01	3816	0.01	0.00	0.00	0.00	6.23	0
M3-28-2		28	7.12	1604	0	10.20	5927	0.05	0.00	1.66	0.00	4.16	0
M3-91-1		91	8.47	3600	100	3.14	4002	0.02	0.01	2.91	0.00	1.34	28
M3-91-2		91	8.40	3273	92	3.73	4182	0.02	0.01	2.37	0.00	0.88	33
M4-7-1		7	8.71	2080	0	4.92	2635	0.10	0.00	1.47	0.00	2.93	70
M4-7-2		7	8.73	2012	0	4.51	2551	0.09	0.00	0.94	0.00	1.68	260
M4-28-1		28	8.16	3689	0	3.85	4000	0.14	0.00	1.25	0.00	145.65	0
M4-28-2		28	8.41	3728	0	3.13	3868	0.01	0.00	2.40	0.00	0.00	0
M4-91-1		91	8.55	3323	97	3.63	4610	0.02	0.02	2.37	0.00	0.70	36
M4-91-2		91	7.69	3785	102	3.20	4422	0.04	0.05	4.22	0.00	1.01	42
M5-7-1		7	8.01	1908	0	6.17	2712	7.91	0.00	0.53	0.00	4.71	72
M5-7-2		7	8.43	2247	0	5.73	2998	7.69	0.00	0.54	0.00	4.48	60
M5-28-1		28	7.95	4006	0	3.74	3743	7.16	0.00	1.04	0.00	1.04	722
M5-28-2		28	7.83	3666	0	3.45	3932	6.87	0.00	0.00	0.00	0.00	0
M5-91-1		91	8.29	4179	78	2.58	3716	5.33	0.05	1.85	0.00	0.93	41
M5-91-2		91	8.35	4197	0	3.57	3850	6.39	0.00	2.02	0.00	1.35	48
M5-7-1		7	7.55	1390	0	2.20	1540	9.43	0.00	0.02	0.00	1.07	323
M6-7-2		7	7.52	1949	0	2.02	1537	7.22	0.00	0.00	0.00	0.68	155
M6-28-1		28	6.37	631	0	22.85	5008	20.36	0.00	0.00	0.00	0.00	0
M6-28-2		28	6.28	636	0	24.89	4872	20.12	0.00	0.00	0.00	5.70	0
M6-91-1		91	7.39	1676	0	2.12	4737	9.97	0.00	2.28	0.00	1.21	103
M6-91-2		91	7.26	1784	0	1.72	1492	13.13	0.00	1.97	0.00	2.32	155
M7-7-1		7	8.59	4305	0	5.23	2944	7.34	0.00	1.82	0.00	1.15	96
M7-7-2		7	8.76	4315	0	8.36	3099	7.21	0.00	2.11	0.00	0.94	76
M7-28-1		28	7.58	3337	0	8.21	3731	12.06	0.00	7.69	0.00	0.00	0
M7-28-2		28	7.94	3477	0	4.15	3551	11.53	0.00	0.00	0.00	0.00	0
M7-91-1		91	8.25	2341	0	2.25	2431	12.49	0.00	1.81	0.00	1.22	74
M7-91-2		91	8.29	2172	0	2.71	3245	12.52	0.00	2.09	0.00	1.10	82
M8-7-1		7	8.00	2074	0	6.38	1737	11.11	0.00	1.88	0.00	1.99	65
M8-7-2		7	7.98	2081	0	6.40	1871	13.18	0.00	0.42	0.00	2.10	42
M8-28-1		28	6.79	731	0	36.40	6182	2.85	0.00	0.90	0.00	17.68	0
M8-28-2		28	7.66	2987	0	4.97	3322	8.16	0.00	0.00	0.00	0.00	0
M8-91-1		91	7.90	3004	0	4.42	2739	11.61	0.00	2.56	0.00	1.85	122
M8-91-2		91	7.94	3194	0	4.13	3067	6.07	0.00	3.36	0.00	3.49	69

TEST	ANALY ID	DURATION (days)	Gd	K	LA	LI	MG	MN	Mo	NA	Nd	NI	P
M1-7-1		7	0	2345	0	0	0	0.00	2.09	2315	0.00	0.00	0.00
M1-7-2		7	0	2401	0	0	321	5.33	3.66	2519	0.00	2.40	0.00
M1-28-1		28	0	3649	0	0	353	21.45	6.43	3321	0.00	0.00	0.00
M1-28-2		28	0	2121	0	0	161	0.41	1.52	2302	0.00	0.00	0.00
M1-91-1		91	0	2963	0	76	34	0.60	1.81	3100	0.00	1.02	0.00
M1-91-2		91	0	2871	0	85	35	0.50	1.64	3147	0.00	0.97	0.00
M2-7-1		7	0	3381	0	0	138	0.88	13.93	3560	0.00	1.24	0.00
M2-7-2		7	0	3202	0	0	137	1.46	11.08	3265	0.00	1.67	0.00
M2-28-1		28	0	3207	0	0	51	23.93	10.41	2845	0.00	19.77	0.00
M2-28-2		28	0	3245	0	0	56	0.00	11.42	2846	0.00	0.00	0.00
M2-91-1		91	0	4097	0	113	3	0.41	11.19	3366	0.00	1.50	0.00
M2-91-2		91	0	4912	0	126	19	0.41	11.90	3932	0.00	0.97	0.00
M3-7-1		7	0	1912	0	0	356	5.45	0.50	1927	0.00	2.10	0.00
M3-7-2		7	0	1923	0	0	366	4.71	0.50	2044	0.00	1.36	0.00
M3-28-1		28	0	2060	0	0	617	0.00	0.19	2253	0.00	0.00	0.00
M3-28-2		28	0	2933	0	0	740	46.82	2.19	2823	0.00	0.00	0.00
M3-91-1		91	0	2255	0	22	531	1.55	0.41	2733	0.00	1.12	0.00
M3-91-2		91	0	2124	0	23	517	1.99	0.28	2597	0.00	1.28	0.00
M4-7-1		7	0	2265	0	0	257	3.46	0.38	2273	0.00	1.78	0.00
M4-7-2		7	0	2235	0	0	248	7.65	0.40	2257	0.00	3.56	0.00
M4-28-1		28	0	1965	0	0	417	0.00	0.52	2234	0.00	0.00	0.00
M4-28-2		28	0	2047	0	0	365	0.00	1.04	2238	0.00	0.00	0.00
M4-91-1		91	0	1853	0	23	301	1.03	0.27	2447	0.00	1.26	0.00
M4-91-2		91	0	1344	0	22	295	1.28	0.22	1910	0.00	1.73	0.00
M5-7-1		7	0	2165	0	0	148	8.97	0.76	1645	0.00	3.77	0.00
M5-7-2		7	0	1980	0	0	149	6.04	0.77	1584	0.00	2.71	0.00
M5-28-1		28	0	2011	0	0	175	13.50	1.04	1900	0.00	6.23	0.00
M5-28-2		28	0	2100	0	0	193	0.00	1.05	1883	0.00	0.00	0.00
M5-91-1		91	0	2139	0	0	120	0.52	0.80	2097	0.00	1.29	0.00
M5-91-2		91	0	1802	0	0	121	1.03	0.77	1817	0.00	1.12	0.00
M6-7-1		7	0	879	0	0	133	33.37	0.70	1023	0.00	2.07	0.00
M6-7-2		7	0	798	0	0	137	28.04	0.59	981	0.00	0.60	0.00
M6-28-1		28	0	1742	0	0	324	312.63	1.35	1459	0.00	0.00	0.00
M6-28-2		28	0	1641	0	0	312	297.64	1.56	1473	0.00	0.00	0.00
M6-91-1		91	0	1014	0	0	88	8.19	0.80	1087	0.00	1.34	0.00
M6-91-2		91	0	1328	0	0	87	8.93	0.73	1301	0.00	0.86	0.00
M7-7-1		7	0	2104	0	0	189	2.10	0.84	2002	0.00	1.68	0.00
M7-7-2		7	0	2157	0	0	131	2.61	1.25	2048	0.00	2.82	0.00
M7-28-1		28	0	1981	0	0	135	0.00	0.79	2177	0.00	4.99	0.00
M7-28-2		28	0	2020	0	0	96	0.00	1.04	2106	0.00	0.00	0.00
M7-91-1		91	0	2292	0	0	27	0.63	1.21	2247	0.00	1.27	0.00
M7-91-2		91	0	2140	0	0	32	0.83	1.11	2063	0.00	1.08	0.00
M8-7-1		7	0	1802	0	0	92	5.02	0.56	1569	0.00	1.78	0.00
M8-7-2		7	0	1884	0	0	96	5.46	0.54	1494	0.00	1.47	0.00
M8-28-1		28	0	2918	0	0	216	119.61	3.64	1955	0.00	0.00	0.00
M8-28-2		28	0	1870	0	0	121	6.73	0.98	1390	0.00	0.00	0.00
M8-91-1		91	0	1707	0	0	95	2.06	0.40	1364	0.00	1.58	0.00
M8-91-2		91	0	1717	0	0	115	2.02	0.64	1327	0.00	1.54	0.00

TEST	ANALY ID	DURATION (days)	PB	S	SI	SR	Th	TI	U	ZN	ZR
M1-7-1		7	0.00	0.00	22512	0	0.00	0	0.00	0.00	0.00
M1-7-2		7	0.01	0.00	22122	19	0.00	17	0.00	7.32	0.10
M1-28-1		28	0.00	0.00	30989	27	0.00	30	2.90	20.37	0.54
M1-28-2		28	0.00	0.00	21133	11	0.00	11	2.44	20.31	0.41
M1-91-1		91	0.40	0.00	23247	9	0.01	12	4.34	5.49	0.09
M1-91-2		91	0.44	0.00	24765	8	0.01	11	5.17	6.09	0.09
M2-7-1		7	0.00	0.00	26372	30	0.00	29	0.00	8.69	0.04
M2-7-2		7	0.00	0.00	25590	30	0.00	28	0.00	8.47	0.04
M2-28-1		28	0.00	0.00	28064	21	0.00	24	1.87	17.69	0.42
M2-28-2		28	0.00	0.00	28047	21	0.00	24	1.25	11.42	0.21
M2-91-1		91	0.25	0.00	33559	18	0.00	20	0.69	6.73	0.28
M2-91-2		91	0.29	0.00	36695	19	0.00	21	0.69	7.97	0.10
M3-7-1		7	0.63	0.00	17393	12	0.00	10	0.00	5.03	0.03
M3-7-2		7	0.42	0.00	17032	12	0.00	12	0.00	2.51	0.03
M3-28-1		28	0.00	0.00	20617	14	0.00	16	0.00	9.56	0.10
M3-28-2		28	0.00	0.00	26429	28	0.00	26	0.10	41.62	0.31
M3-91-1		91	0.18	0.00	20884	11	0.00	11	0.11	5.78	0.04
M3-91-2		91	0.18	0.00	21101	11	0.00	12	0.11	6.94	0.02
M4-7-1		7	0.71	0.00	19055	15	0.00	13	0.00	6.91	0.07
M4-7-2		7	0.44	0.00	18535	14	0.00	13	0.00	7.54	0.08
M4-28-1		28	0.00	0.00	21483	16	0.00	17	0.21	117.56	0.21
M4-28-2		28	0.00	0.00	21971	15	0.00	15	0.21	11.46	0.21
M4-91-1		91	0.19	0.00	22592	12	0.00	12	0.17	6.01	0.05
M4-91-2		91	0.44	0.00	21775	13	0.00	13	0.13	23.06	0.11
M5-7-1		7	0.61	0.00	18935	16	0.01	14	0.47	14.86	0.21
M5-7-2		7	0.55	0.00	16970	15	0.01	13	0.85	14.48	0.10
M5-28-1		28	0.00	0.00	19873	11	0.00	12	0.21	41.53	0.31
M5-28-2		28	0.00	0.00	20299	14	0.00	14	0.26	9.93	0.13
M5-91-1		91	0.17	0.00	21765	9	0.00	10	ERR	6.19	0.12
M5-91-2		91	0.18	0.00	21296	9	0.01	10	ERR	6.72	0.05
M6-7-1		7	0.00	0.00	19882	6	0.00	6	0.15	6.51	0.07
M6-7-2		7	0.00	0.00	21386	5	0.00	6	0.09	9.37	0.07
M6-28-1		28	0.00	0.00	50021	28	0.00	16	0.23	31.16	0.10
M6-28-2		28	0.00	0.00	48130	27	0.00	19	0.25	47.70	0.11
M6-91-1		91	0.69	0.00	30629	5	0.00	5	0.38	5.27	ERR
M6-91-2		91	0.41	0.00	31151	5	0.01	5	0.06	5.14	ERR
M7-7-1		7	0.00	0.00	18953	21	0.00	13	0.00	6.61	0.05
M7-7-2		7	0.00	0.00	19509	20	0.00	14	0.00	5.85	0.04
M7-28-1		28	0.00	0.00	20235	15	0.00	12	0.53	46.79	0.36
M7-28-2		28	0.00	0.00	20752	11	0.00	10	0.80	8.31	0.15
M7-91-1		91	0.33	0.00	20057	7	0.02	9	0.69	5.62	0.11
M7-91-2		91	0.31	0.00	19448	8	0.02	9	0.35	4.76	0.09
M8-7-1		7	30.78	0.00	12636	12	0.00	8	0.00	15.80	0.01
M8-7-2		7	42.70	0.00	13155	13	0.00	9	0.00	2.52	0.02
M8-28-1		28	0.00	0.00	24016	32	0.00	25	0.11	26.02	0.25
M8-28-2		28	0.00	0.00	16581	13	0.00	7	0.06	13.46	0.12
M8-91-1		91	39.19	0.00	14785	10	0.01	10	0.05	6.58	0.09
M8-91-2		91	17.65	0.00	15235	12	0.01	10	0.09	13.66	0.08

TEST	ANALY ID	DURATION (days)	pH	AL	B	BA	CA	CE	Co	CR	CS	CU	FE
M3-7-1		7	8.58	2076.81	0.00	4.93	2892.29	9.32	0.00	0.56	0.00	4.48	97.00
M3-7-2		7	8.72	2048.37	0.00	5.12	2958.64	10.56	0.00	0.84	0.00	6.38	152.58
M3-28-1		28	8.26	3604.21	0.00	4.42	3800.35	5.25	0.00	0.00	0.00	7.16	0.00
M3-28-2		28	8.15	3380.53	0.00	4.15	3729.28	5.07	0.00	0.01	0.00	0.00	417.25
M3-91-1		91	8.55	2370.79	0.00	2.40	3805.64	3.29	0.00	2.02	0.00	1.94	47.42
M3-91-2		91	8.44	2450.45	0.00	3.14	3982.90	4.37	0.00	2.60	0.00	1.15	53.52
M10-7-1		7	8.46	2100.32	0.00	4.86	2750.59	5.54	0.00	0.52	0.00	4.60	51.44
M10-7-2		7	8.45	2130.28	0.00	5.00	2977.37	4.71	0.00	2.51	0.00	10.98	108.76
M10-28-1		28	8.31	3407.76	0.00	4.05	3228.02	4.55	0.00	2.70	0.00	0.00	856.10
M10-28-2		28	7.27	1075.70	0.00	4.78	6307.79	4.51	0.00	1.35	0.00	0.00	0.00
M10-91-1		91	8.59	2444.17	0.00	2.90	4011.66	2.35	0.00	1.92	0.00	0.74	52.77
M10-91-2		91	9.61	2272.41	0.00	2.97	4397.55	1.95	0.00	2.21	0.00	0.60	43.35
M11-7-1		7	8.11	2723.25	0.00	6.81	2901.24	4.41	0.00	1.36	0.00	6.39	61.75
M11-7-2		7	8.16	2454.40	0.00	7.32	2534.95	4.33	0.00	0.60	0.00	6.90	37.35
M11-28-1		28	7.12	1244.31	0.00	9.68	6348.56	0.94	0.00	1.77	0.00	0.00	0.00
M11-28-2		28	7.11	1274.74	0.00	6.98	6646.56	0.91	0.00	1.46	0.00	0.00	0.00
M11-91-1		91	8.20	3433.60	0.00	4.14	2177.02	2.69	0.00	2.10	0.00	0.81	21.72
M11-91-2		91	8.28	3456.16	0.00	3.45	2299.96	3.77	0.00	2.07	0.00	0.47	15.75
M12-7-1		7	8.29	2049.51	0.00	7.62	2714.25	5.76	0.00	0.82	0.00	14.30	29.95
M12-7-2		7	8.34	2199.99	0.00	7.43	2576.95	8.00	0.00	15.81	0.00	50.99	267.01
M12-28-1		28	7.90	3196.89	0.00	6.09	3372.11	7.76	0.00	2.73	0.00	0.80	0.00
M12-28-2		28	7.91	3672.93	0.00	4.85	3167.39	5.98	0.00	1.86	0.00	0.00	0.00
M12-91-1		91	8.27	2567.53	0.00	3.31	2076.31	7.52	0.00	2.08	0.00	0.39	49.56
M12-91-2		91	8.23	2558.24	0.00	2.88	2229.81	7.23	0.00	2.10	0.00	0.44	43.27
M13-7-1		7	8.29	2626.98	0.00	5.34	2704.43	4.33	0.00	0.61	0.00	6.61	39.35
M13-7-2		7	8.35	2652.19	0.00	5.65	2732.72	4.69	0.00	0.66	0.00	4.09	50.09
M13-28-1		28	7.85	4272.90	0.00	4.57	5341.38	2.33	0.00	2.70	0.00	0.00	61.34
M13-28-2		28	7.05	1259.07	0.00	11.45	7422.25	0.14	0.00	1.98	0.00	0.00	0.00
M13-91-1		91	8.09	3292.01	0.00	3.12	2071.18	3.81	0.00	1.95	0.00	0.74	35.09
M13-91-2		91	8.09	3175.86	0.00	3.34	2241.72	4.06	0.00	1.96	0.00	0.55	37.86
M14-7-1		7	8.70	2579.64	0.00	5.09	2841.59	4.32	0.00	1.96	0.00	5.86	47.56
M14-7-2		7	8.35	2541.19	0.00	5.66	2845.08	4.08	0.00	1.02	0.00	5.97	72.93
M14-28-1		28	8.24	4096.03	0.00	4.03	3584.93	2.52	0.00	2.79	0.00	0.00	0.00
M14-28-2		28	8.53	3201.65	0.00	3.93	3579.22	2.45	0.00	2.07	0.00	0.00	0.00
M14-91-1		91	8.41	2902.65	0.00	3.35	2504.11	1.54	0.00	2.47	0.00	0.37	29.88
M14-91-2		91	8.60	ERF	0.00	3.70	2705.05	1.13	0.00	2.89	0.00	2.55	35.63
M15-7-1		7	8.58	1545.34	0.00	12.63	2602.02	3.93	0.00	0.68	0.00	3.76	56.80
M15-7-2		7	8.72	1649.15	0.00	14.74	2805.01	3.87	0.00	0.75	0.00	3.76	126.35
M15-28-1		28	6.68	889.93	0.00	47.06	6893.59	0.55	0.00	12.55	0.00	61.70	47.06
M15-28-2		28	6.89	979.47	0.00	27.93	6525.31	0.38	0.00	3.00	0.00	0.00	158.25
M15-91-1		91	8.52	3096.23	0.00	4.35	2313.39	4.13	0.00	2.15	0.00	1.26	23.82
M15-91-2		91	8.42	3064.75	0.00	4.30	2067.72	7.23	0.00	2.34	0.00	1.63	52.08
M16-7-1		7	8.19	2107.42	0.00	6.08	2816.88	8.74	0.00	0.78	0.00	3.98	78.07
M16-7-2		7	7.95	2367.25	0.00	7.33	3181.13	7.86	0.00	0.62	0.00	5.55	45.34
M16-28-1		28	7.02	1146.05	0.00	8.45	5373.78	5.68	0.00	2.29	0.00	0.00	237.34
M16-28-2		28	6.92	1505.56	0.00	10.38	6545.10	5.15	0.00	1.76	0.00	0.00	0.00
M16-91-1		91	8.47	2553.19	0.00	1.98	2232.75	5.95	0.00	2.04	0.00	0.50	26.22
M16-91-2		91	6.48	2377.52	0.00	1.96	2330.05	7.19	0.00	2.07	0.00	0.47	56.14

TEST	ANALY ID	DURATION (days)	Gd	K	LA	LI	MG	MN	Mo	NA	Nd	NI	P
M9-7-1		7	0.00	2044.44	0.00	0.00	130.52	5.24	0.50	2020.43	0.00	2.91	0.00
M9-7-2		7	0.00	2139.29	0.00	0.00	128.55	6.69	0.38	1972.08	0.00	3.45	0.00
M9-28-1		28	0.00	2309.06	0.00	0.00	153.59	3.01	1.04	2561.24	0.00	1.04	0.00
M9-28-2		28	0.00	2362.33	0.00	0.00	159.84	8.30	0.73	2622.85	0.00	5.19	0.00
M9-91-1		91	0.00	2026.51	0.00	0.00	ERR	0.38	1.12	2600.66	0.00	1.52	0.00
M9-91-2		91	0.00	1882.96	0.00	0.00	ERR	1.19	0.95	2554.77	0.00	0.93	0.00
M10-7-1		7	0.00	1834.77	0.00	0.00	118.14	4.39	0.83	1651.82	0.00	2.40	0.00
M10-7-2		7	0.00	1959.81	0.00	0.00	106.67	6.18	0.64	1680.59	0.00	4.81	0.00
M10-28-1		28	0.00	2065.44	0.00	0.00	53.51	13.51	0.62	2118.42	0.00	0.92	0.00
M10-28-2		28	0.00	4255.03	0.00	0.00	62.20	9.03	5.81	3252.02	0.00	1.08	0.00
M10-91-1		91	0.00	1947.49	0.00	0.00	56.90	0.59	0.70	2187.05	0.00	0.94	0.00
M10-91-2		91	0.00	1890.74	0.00	0.00	58.39	0.44	0.64	2148.99	0.00	1.01	0.00
M11-7-1		7	0.00	1701.38	0.00	0.00	154.96	8.69	0.32	1373.67	0.00	3.87	0.00
M11-7-2		7	0.00	1881.08	0.00	0.00	99.70	7.53	0.45	1527.46	0.00	2.82	0.00
M11-28-1		28	0.00	3661.07	0.00	0.00	267.60	37.49	5.73	2537.55	0.00	1.35	0.00
M11-28-2		28	0.00	4039.80	0.00	0.00	248.91	31.24	7.71	2676.54	0.00	1.25	0.00
M11-91-1		91	0.00	1648.54	0.00	0.00	132.38	1.41	0.44	1658.81	0.00	1.04	0.00
M11-91-2		91	0.00	1758.12	0.00	0.00	134.88	1.43	0.46	1771.59	0.00	1.13	0.00
M12-7-1		7	0.00	1546.53	0.00	0.00	120.01	6.16	0.97	1405.64	0.00	5.11	0.00
M12-7-2		7	0.00	1544.49	0.00	0.00	121.47	74.55	1.16	1430.36	0.00	48.90	0.00
M12-28-1		28	0.00	1936.81	0.00	0.00	135.35	3.57	0.69	1903.24	0.00	0.55	0.00
M12-28-2		28	0.00	1833.37	0.00	0.00	126.90	1.24	0.95	1849.88	0.00	0.15	0.00
M12-91-1		91	0.00	1373.54	0.00	0.00	91.43	0.97	0.52	1505.63	0.00	2.94	0.00
M12-91-2		91	0.00	1425.26	0.00	0.00	86.14	0.70	0.54	1525.44	0.00	1.21	0.00
M13-7-1		7	0.00	2038.79	0.00	0.00	136.06	6.93	0.78	1569.91	0.00	3.15	0.00
M13-7-2		7	0.00	1926.39	0.00	0.00	137.00	3.76	0.73	1516.43	0.00	1.90	0.00
M13-28-1		28	0.00	2138.53	0.00	0.00	218.32	4.37	0.73	2504.48	0.00	1.87	0.00
M13-28-2		28	0.00	3790.73	0.00	0.00	391.25	62.43	7.28	2646.12	0.00	1.04	0.00
M13-91-1		91	0.00	1535.58	0.00	0.00	175.47	1.33	0.78	1512.88	0.00	1.10	0.00
M13-91-2		91	0.00	1466.90	0.00	0.00	176.90	1.51	0.79	1500.00	0.00	0.85	0.00
M14-7-1		7	0.00	1898.58	0.00	0.00	487.22	3.95	0.30	1602.06	0.00	3.08	0.00
M14-7-2		7	0.00	1932.35	0.00	0.00	483.09	4.61	0.23	1624.26	0.00	4.82	0.00
M14-28-1		28	0.00	2058.88	0.00	0.00	604.21	4.97	0.85	2167.51	0.00	0.83	0.00
M14-28-2		28	0.00	2185.81	0.00	0.00	553.44	1.97	0.53	2308.91	0.00	0.83	0.00
M14-91-1		91	0.00	1593.15	0.00	0.00	599.37	1.58	0.21	2003.08	0.00	0.91	0.00
M14-91-2		91	0.00	1632.80	0.00	0.00	434.01	1.18	0.47	1975.79	0.00	0.94	0.00
M15-7-1		7	0.00	1810.55	0.00	0.00	140.96	12.22	0.53	1330.25	0.00	2.19	0.00
M15-7-2		7	0.00	1793.37	0.00	0.00	128.55	15.26	0.39	1347.12	0.00	3.45	0.00
M15-28-1		28	0.00	3483.40	0.00	0.00	286.54	140.13	5.86	2471.11	0.00	15.73	0.00
M15-28-2		28	0.00	3575.53	0.00	0.00	273.05	98.26	6.00	2448.15	0.00	3.00	0.00
M15-91-1		91	0.00	1846.58	0.00	0.00	109.47	0.42	0.41	1694.77	0.00	1.18	0.00
M15-91-2		91	0.00	2177.70	0.00	0.00	115.16	0.81	0.62	1676.59	0.00	2.05	0.00
M16-7-1		7	0.00	2095.89	0.00	0.00	139.32	2.20	0.87	1457.69	0.00	2.09	0.00
M16-7-2		7	0.00	2176.62	0.00	0.00	139.31	1.89	1.13	1527.19	0.00	2.09	0.00
M16-28-1		28	0.00	3124.37	0.00	0.00	203.35	25.03	4.80	2366.23	0.00	2.40	0.00
M16-28-2		28	0.00	3876.47	0.00	0.00	245.02	46.65	6.74	2602.53	0.00	0.05	0.00
M16-91-1		91	0.00	1832.71	0.00	0.00	58.51	0.45	1.12	1575.46	0.00	0.83	0.00
M16-91-2		91	0.00	1941.02	0.00	0.00	42.00	0.67	1.17	1616.03	0.00	0.90	0.00

TEST	ANALY ID	DURATION (days)	PB	S	SI	SR	Th	TI	U	ZN	ZR
M9-7-1		7	0.43	1.58	29352.54	14.41	0.01	12.22	0.28	15.07	0.15
M9-7-2		7	0.71	0.00	20598.67	15.36	0.01	12.85	0.20	14.00	0.15
M9-28-1		28	0.00	0.00	23858.55	13.49	0.00	13.49	0.28	11.42	0.18
M9-28-2		28	0.00	0.00	23384.53	13.49	0.00	11.42	0.37	9.34	0.19
M9-91-1		91	1.21	0.00	18729.26	9.67	0.00	10.72	0.44	5.31	0.19
M9-91-2		91	0.23	0.00	18954.75	10.64	0.01	11.37	0.31	5.46	0.07
M10-7-1		7	1.96	0.00	18981.27	14.32	0.01	11.71	0.45	12.65	0.09
M10-7-2		7	1.24	0.00	19904.54	15.48	0.01	12.65	0.28	17.99	0.08
M10-28-1		28	0.00	0.00	21953.04	13.51	0.00	13.51	0.24	12.47	0.22
M10-28-2		28	0.00	0.00	33651.95	19.73	0.00	27.00	0.12	10.38	0.11
M10-91-1		91	0.20	0.00	19763.99	10.84	0.00	11.57	0.22	5.70	0.05
M10-91-2		91	0.18	0.00	19291.13	11.72	0.00	12.13	0.17	4.94	0.03
M11-7-1		7	23.97	0.00	14964.81	16.61	0.01	12.34	0.12	15.72	0.06
M11-7-2		7	20.03	0.00	15106.15	14.86	0.01	10.78	0.12	15.59	0.06
M11-28-1		28	0.00	0.00	27458.03	28.11	0.00	29.16	0.07	12.50	0.08
M11-28-2		28	0.00	0.00	28577.51	26.04	0.00	30.20	0.08	9.06	0.19
M11-91-1		91	5.81	0.00	14861.68	11.38	0.00	10.96	0.12	5.39	0.08
M11-91-2		91	7.07	0.00	15654.24	10.67	0.00	11.09	0.05	5.02	0.05
M12-7-1		7	0.65	0.00	16970.04	17.01	0.01	11.44	0.79	22.44	0.06
M12-7-2		7	7.19	0.00	17121.35	15.39	0.02	10.99	0.55	136.12	0.15
M12-28-1		28	0.00	0.00	21823.21	15.11	0.00	16.79	0.28	11.54	0.13
M12-28-2		28	0.00	0.00	21800.31	14.44	0.00	13.41	0.32	9.60	0.11
M12-91-1		91	0.18	0.00	17068.68	11.25	0.01	10.84	0.06	6.25	0.11
M12-91-2		91	0.41	0.00	17216.73	10.64	0.01	10.53	0.23	6.15	0.07
M13-7-1		7	0.61	0.00	16698.62	14.02	0.02	11.72	0.46	16.85	0.09
M13-7-2		7	0.61	0.00	16697.51	14.12	0.01	11.82	0.56	8.60	0.08
M13-28-1		28	0.00	0.00	19992.16	13.52	0.00	15.52	0.31	10.40	0.34
M13-28-2		28	0.00	0.00	31372.61	34.34	0.00	32.26	0.41	9.36	0.06
M13-91-1		91	0.18	0.00	14736.66	10.09	0.01	11.04	0.28	6.20	0.06
M13-91-2		91	0.17	0.00	15175.86	10.33	0.00	10.97	0.29	4.99	0.04
M14-7-1		7	0.74	0.00	17194.13	15.09	0.01	12.78	0.34	8.91	0.20
M14-7-2		7	0.46	0.00	17032.77	15.30	0.02	12.68	0.37	9.85	0.10
M14-28-1		28	0.00	0.00	20981.94	13.45	0.00	15.52	0.21	19.66	0.10
M14-28-2		28	0.00	0.00	22592.56	12.41	0.00	15.52	0.19	7.24	0.10
M14-91-1		91	0.17	0.00	16148.85	12.22	0.00	12.11	0.06	3.99	0.04
M14-91-2		91	0.07	0.00	16805.29	12.54	0.00	12.99	0.13	3.98	0.04
M15-7-1		7	25.54	0.00	13771.28	18.27	0.02	11.07	0.14	11.07	0.10
M15-7-2		7	33.13	0.00	13436.69	19.75	0.01	11.81	0.07	10.45	0.09
M15-28-1		28	0.00	0.00	29521.57	45.92	0.00	30.33	0.07	59.61	0.15
M15-28-2		28	0.00	0.00	28887.60	40.34	0.00	28.96	0.04	11.38	0.07
M15-91-1		91	13.01	0.00	16668.83	12.70	0.01	11.05	0.05	5.51	0.05
M15-91-2		91	21.89	0.00	16309.37	12.14	0.01	11.00	0.06	12.66	0.07
M16-7-1		7	0.39	0.00	17083.60	15.72	0.01	11.84	0.88	7.75	0.10
M16-7-2		7	0.82	0.00	17268.35	17.70	0.01	13.51	1.17	10.47	0.15
M16-28-1		28	0.00	0.00	27005.70	25.03	0.00	25.99	0.21	10.22	0.15
M16-28-2		28	0.00	0.00	31812.80	31.13	0.00	30.09	0.26	12.45	0.10
M16-91-1		91	0.20	0.00	17345.13	9.03	0.01	10.85	0.28	4.99	0.05
M16-91-2		91	0.22	0.00	17624.99	8.72	0.01	11.14	0.27	4.72	0.07

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APPENDIX II

**DILUTION-CORRECTED PCT LEACHATE CONCENTRATIONS OF
PCF GLASSY SLAGS (mg/L)**

Test Number	Al	B	Ba	Ca	Ce	Cr	Cu	Fe	K	Li	Mg	Mn	Mo
PF1-7-1	5.48	0.682	0.0023	0.727	0.0012	0.0005	0.013	0.094	3.77	0.032	0.252	0.0023	0.036
PF1-7-2	5.43	0.824	0.0027	0.874	0.0012	0.0006	0.014	0.078	4.13	0.030	0.314	0.0019	0.036
PF1-28-1	7.60	0.894	0.0027	0.812	0.0054	0.0006	0.039	0.285	5.19	0.047	0.215	0.0038	0.046
PF1-28-2	7.31	0.905	0.0024	0.616	0.0046	0.0004	0.036	0.271	5.11	0.040	0.217	0.0042	0.038
PF2-7-1	5.28	0.051	0.0032	0.894	0.0005	0.0020	0.0032	0.052	0.83	0.022	0.536	0.012	0.006
PF2-7-2	5.55	0.107	0.0029	0.874	0.0007	0.0017	0.0051	0.054	1.26	0.032	0.536	0.010	0.013
PF2-28-1	7.09	0.058	0.0019	0.879	0.0011	0.0016	0.0051	0.040	2.07	0.031	0.391	0.004	0.008
PF2-28-2	6.72	0.066	0.0017	0.764	0.0011	0.0019	0.0056	0.046	1.79	0.031	0.340	0.003	0.008
PF4-7-1	3.25	0.0729	0.0056	0.646	0.0002	0.0123	0.0016	0.008	0.74	0.083	0.265	0.047	0.049
PF4-7-2	3.28	0.0178	0.0051	0.521	0.0003	0.0135	0.0027	0.001	0.66	0.080	0.218	0.047	0.046
PF4-28-1	3.68	0.0402	0.0035	0.666	0.0005	0.0127	0.0022	0.013	1.02	0.095	0.237	0.032	0.066
PF4-28-2	3.74	0.0345	0.0033	0.625	0.0008	0.0135	0.0033	0.014	1.40	0.103	0.254	0.032	0.065
PF5-7-1	5.16	0.196	0.0029	0.820	0.0010	0.0943	0.0015	0.003	0.39	0.016	0.150	0.017	0.038
PF5-7-2	5.28	0.182	0.0027	0.775	0.0009	0.0807	0.0013	bd	0.48	0.015	0.154	0.016	0.037
PF5-28-1	5.38	0.296	0.0019	0.790	0.0035	0.0869	0.0027	0.016	0.90	0.019	0.153	0.012	0.042
PF5-28-2	5.26	0.252	0.0021	0.834	0.0039	0.0939	0.0063	0.019	0.77	0.019	0.169	0.013	0.049
PF8-7-1	0.73	0.0092	0.010	0.358	0.0001	0.0001	0.0031	bd	0.109	0.0042	0.048	0.100	0.018
PF8-7-2	0.64	0.010	0.012	0.373	0.0000	0.0001	0.0066	bd	0.198	0.0047	0.050	0.102	0.023
PF8-28-1	1.39	0.020	0.0071	0.635	0.0032	0.0002	0.0020	bd	0.318	0.0079	0.066	0.074	0.046
PF8-28-2	1.41	0.017	0.0062	0.481	0.0033	bd	0.0013	0.014	0.182	0.0080	0.055	0.063	0.040

Test Number	Na	Ni	Pb	Sb	Si	Sn	Sr	Th	Ti	Tl	U	V	Zn	Zr
PF1-7-1	10.63	0.0027	0.0005	0.0035	13.46	bd	0.0051	3E-06	0.0040	0.0002	0.0001	0.032	0.0024	0.0001
PF1-7-2	11.77	0.0050	0.0004	0.0037	13.19	bd	0.0057	2E-06	0.0047	0.0001	9E-05	0.033	0.0026	0.0002
PF1-28-1	15.17	0.0032	0.0011	0.0054	16.80	0.0002	0.0037	2E-05	0.0042	0.0001	0.0003	0.045	0.0049	0.0003
PF1-28-2	15.10	0.0032	0.0010	0.0048	16.19	0.0002	0.0036	2E-05	0.0037	9E-05	0.0003	0.043	0.0044	0.0003
PF2-7-1	5.00	0.0007	0.0001	0.0001	17.17	0.0004	0.0077	3E-06	0.0043	1E-05	5E-05	0.0055	0.029	7E-05
PF2-7-2	7.10	0.0007	0.0001	0.0002	19.09	bd	0.0070	3E-06	0.0042	5E-05	8E-05	0.0069	0.0027	9E-05
PF2-28-1	11.95	0.0013	0.0000	0.0002	24.20	bd	0.0057	9E-06	0.0039	4E-06	9E-05	0.0072	0.0025	0.0002
PF2-28-2	10.83	0.0014	0.0001	0.0002	21.84	bd	0.0047	1E-05	0.0036	bd	0.0001	0.0071	0.0020	0.0002
PF4-7-1	2.39	0.0016	0.0003	6E-05	12.32	bd	0.0084	bd	0.0031	1E-05	4E-05	0.022	0.0030	9E-06
PF4-7-2	2.17	0.0020	0.0000	5E-05	12.66	bd	0.0072	1E-06	0.0025	7E-06	1E-05	0.020	0.0027	4E-06
PF4-28-1	2.62	0.0010	0.0002	9E-05	16.44	bd	0.0073	1E-06	0.0028	bd	3E-05	0.025	0.0032	2E-05
PF4-28-2	3.27	0.0019	0.0000	8E-05	17.97	0.019	0.0069	2E-06	0.0027	bd	2E-05	0.025	0.0043	2E-05
PF5-7-1	5.10	0.0006	bd	0.0003	11.80	bd	0.0061	2E-06	0.0043	5E-06	1E-05	0.033	0.0017	5E-05
PF5-7-2	5.37	0.0007	bd	0.0003	11.90	bd	0.0057	2E-06	0.0041	1E-05	1E-05	0.030	0.0019	4E-05
PF5-28-1	7.06	0.0008	0.0001	0.0004	14.50	bd	0.0052	1E-05	0.0041	bd	1E-05	0.034	0.0018	0.0002
PF5-28-2	6.67	0.0011	0.0006	0.0004	14.05	bd	0.0049	1E-05	0.0043	7E-05	9E-05	0.036	0.0060	0.0002
PF8-7-1	0.78	0.0036	bd	0.0002	7.07	0.0008	0.0062	2E-06	0.0019	bd	5E-06	0.008	0.0028	bd
PF8-7-2	0.87	0.0048	bd	0.0003	6.35	bd	0.0062	1E-06	0.0018	3E-06	2E-06	0.008	0.0039	4E-05
PF8-28-1	1.27	0.0017	0.0002	0.0005	15.14	0.0002	0.0082	4E-06	0.0029	bd	7E-06	0.019	0.0033	3E-05
PF8-28-2	1.03	0.0014	0.0002	0.0005	14.94	0.0004	0.0070	1E-06	0.0027	bd	5E-06	0.019	0.0068	2E-05

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APPENDIX III

**RAW ICP-MS CONCENTRATIONS OF ELEMENTS IN THE TEST SOLUTIONS
AND ACID STRIPS FROM TESTING OF BWID SLAGS**
(concentrations in parts per trillion [ppt])

Sample	Si	Al	Na	K	Mo	Ce	Mg	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu
MSE 1	17636	2050.7	1891.8	2026.1	6.6199	0.80049	401.37	1962.7	10.919	4.1783	1.3869	8.4759	33.227	0.7298	65.825
MSE 2	17999	2036.9	2118.4	1771.8	17.454	2.6824	294.59	2189.9	10.232	3.2908	1.8892	19.424	842.38	9.4531	9.7340
MSE 3	17106	2107.1	2984.6	1946.4	10.080	0.83016	337.12	1916.3	8.8559	1.3592	2.9051	7.7906	63.849	2.8425	12.857
MSE 4	16460	1988.2	1925.8	1706.3	6.2661	5.6220	405.49	2390.2	11.317	2.0006	3.5724	22.326	291.39	8.1763	20.32
MSE 5	25544	2426.6	4416.8	2238.5	46.693	0.28053	20.167	2889.6	12.999	8.0931	17.04	1.0174	74.572	3.9303	4.4057
MSE 6	25421	2450.3	3458.7	1898.7	18.825	2.1601	38.789	2624.6	11.586	4.6746	20.275	25.133	752.13	19.508	6.2676
MSE 7	30389	2249.2	5418.6	2645.2	34.902	1.0888	10.928	2334.5	10.193	0	67.202	31.53	2029.2	26.181	17.883
MSE 8	25891	2123.7	3499.9	1953.1	19.196	0.48850	186.77	3087.4	14.296	3.4969	19.405	2.2738	98.425	0.9205	3.3215
MSE 9	26259	4200.1	2865.6	2241.5	5.2113	0.22348	616.79	3608.4	15.581	5.6018	3.3403	5.3797	109.58	1.6296	6.1099
MSE 10	20031	2803.2	2423.5	2330.8	33.059	3.3364	490.94	3594.8	15.406	7.0924	8.4703	28.258	63.178	8.949	24.778
MSE 11	19096	3238.3	3587.5	2347.9	13.098	1.7033	581.4	3139.3	13.214	2.5051	3.8791	57.657	122.05	12.205	39.598
MSE 12	18978	3389.6	2398.7	2045.7	3.6134	1.1522	751.47	3719.3	15.825	2.1304	3.6377	11.489	52.202	0.4943	6.8367
MSE 13	29950	2419	6484	3275	11	0.119	9.25	2813	9.09	14.3	26.8	145	0	27.4	17.9
MSE 14	27100	2317	4582	3126	32.9	0.716	18.6	2827	9.19	12.1	29.5	0.142	0	0.325	1.85
MSE 15	30430	2415	7055	3480	22.7	1.72	2.59	2322	7.21	10.6	29.2	0	0	0.235	1.45
MSE 16	25230	2116	5012	2733	5.63	0.19	43.3	3541	11.7	5.13	13	119	0	7.65	6.87
MSE 17	22452	2437.7	3458.7	2328.2	7.6854	0.11286	60.514	2514.6	12.764	8.2323	10.581	2.6538	15.87	2.4771	5.9142
MSE 18	21007	2798.8	3040.1	2216.4	17.402	2.8035	143.07	2537.3	12.563	3.8283	4.0546	11.984	20.143	4.8814	5.0225
MSE 19	22074	2722.4	4587.6	2705.9	11.603	0.86367	42.18	2391	9.9191	2.0573	4.7395	2.596	2.9037	1.6493	6.0057
MSE 20	16734	2762	2698.4	1803.1	6.5536	0.91564	463.99	2675.4	13.476	2.0994	9.2827	9.1259	157.91	4.5059	19.437
MSE 21	55827	2199.1	29616	5088.9	30.369	1.4213	12.126	1641.6	6.1199	22.152	9.309	4.5018	234.03	3.926	27.856
MSE 22	51985	1788.4	20533	4171.5	76.006	15.291	8.6823	1515.0	6.1431	14.609	51.193	18.346	911.27	15.456	22.412
MSE 23	60992	3280.6	36706	5357.3	45.783	56.892	18.535	1427.6	6.3279	10.437	9.8831	5.5724	197.95	1.3918	27.903
MSE 24	42480	1205.8	27059	5435.2	59.564	6.6754	64.318	3468.1	16.536	0	99.458	35.639	511.87	10.870	21.550
MSE 1 AS		92.415	131.94	30.523			33.333	152.05	4.4931	0.2308	158.6	503.73	784.8	71.842	321.03
MSE 2 AS		94.505	61.823	7.6425			26.644	99.4	2.6388	0.5942	262.42	602.76	1419.5	115.11	237.54
MSE 3 AS		92.655	130.86	12.35			33.293	117.93	2.053	0.3475	139.52	86.948	951.42	77.099	3011.1
MSE 4 AS		112.31	155.08	3.1623			30.177	122.79	1.6132	0.2392	131.28	89.216	1047.6	60.44	143.65
MSE 5 AS							90.661	253.39	12.135	0	184.95	77.907	1139.2	56.668	74.539
MSE 6 AS							91.551	251.29	5.2201	0	201.66	231.47	1753.0	116.98	360.1
MSE 7 AS							88.109	425.4	4.6919	0	563.16	452.65	2896.1	196.68	2095.0
MSE 8 AS							85.225	351.2	4.8413	0	490.9	136.79	3053.8	127.99	206.25
MSE 9 AS							114.88	441.92	9.4089	0.2959	187.67	103.07	1117.9	71.798	221.21
MSE 10 AS							133.87	759.18	5.6443	7.3062	1618.5	232.49	7979.5	153.72	208.81
MSE 11 AS							71.173	304.23	3.6428	1.2038	445.26	231.49	2146.7	92.499	263.36
MSE 12 AS							48.332	284.57	2.6577	0.3575	249.89	309.48	1024.5	95.456	192.29
MSE 13 AS		628	54.6		0.714	3.76	109	625	12.5	94.3	324	134	2007	127	291
MSE 14 AS		1265	154		4.2	32.1	175	995	9.85	135	464	464	2717	327	812

MSE 15 AS	31.2	5.56		0.312	0.183	95.4	520	1.21	0.133	0.54	18.7	0	25.8	15.7	
MSE 16 AS	634	37.2		0.792	103	129	512	8.94	119	409	483	2408	155	591	
MSE 17 AS	375.26	139.88	29.77			184.74	353.86	14.654	0.6909	108.2	67.777	1226.1	46.579	77.891	
MSE 18 AS	197.45	0	36.525			99.76	386.42	5.612	1.4297	387.4	195.85	2020.6	118.69	62.415	
MSE 19 AS	301.9	0	21.145			133.57	326.98	4.9457	0.578	153.2	61.284	3333.8	65.506	74.311	
MSE 20 AS	236.88	35.626	79.942			146.65	290.85	4.6235	0.8536	240	55.418	1401.1	60.531	55.987	
MSE 21 AS						64.167	341.06	9.9669	0	200.00	57.923	1108.9	76.941	92.791	
MSE 22 AS						31.188	101.19	2.4457	0	145.7	37.104	1647.7	60.033	47.669	
MSE 23 AS						43.558	238.17	3.5042	0	216.62	71.904	1159.4	99.545	104.23	
MSE 24 AS						41.230	174.86	3.0879	0	310.12	128.74	1536.1	115.41	107.54	
M3-7-1	16590	2165.2	1837.8	1824	0.47771	0.06489	339.55	2102.1	10.295	6.6635	1.4369	5.181	67.655	1.9966	3.322
M3-7-2	16356	2225.7	1950.8	1835.3	0.48400	0	349.25	2139.4	10.608	6.7389	1.0848	4.474	28.891	1.3056	0.8355
M4-7-1	18192	1985.6	2170.2	2162.3	0.37626	0.09087	244.81	2515.9	12.38	7.7296	1.3648	3.3226	66.542	1.6633	2.8261
M4-7-2	17688	1919.8	2153.4	2133.3	0.38286	0.08407	237.3	2434.1	12.088	7.6126	0.8502	7.2681	248.06	3.4313	1.6146
M8-7-1	12079	1982.5	1500.2	1722.7	0.53586	10.623	87.834	1660.2	7.9979	5.6034	1.8414	4.7771	61.694	1.7628	1.8497
M8-7-2	12538	1982.5	1423.6	1795.9	0.51247	12.565	91.911	1783.1	8.6569	6.4853	0.4255	5.2179	40.5	1.4158	2.0199
M6-7-1	18949	1324.7	974.96	838.4	0.66838	8.9934	127.23	1468.2	5.8721	12.653	0.0172	31.781	308.02	1.9699	1.02
M6-7-2	20442	1863.4	938.46	762.63	0.56642	6.9039	131.31	1469.1	5.8025	10.433	0	26.819	147.71	0.5669	0.6481
DIWG	0	0	0	13.689	-	0	0	0	0.0651	0.9308	0.692	29.492	1.0772	0.8808	

Zn	Sr	Zr	Mo	Sn	Sb	Ba	Ce	Tl	Pb
70.664	14.851	0.0	7.5276	0.08850	0.20104	6.2708	0.2593	0.0139	5.1824
8.2985	17.159	0.0	22.718	0.07907	0.23512	5.6444	2.7125	0.0091	2.0508
8.6564	16.394	0.07409	13.302	0.08360	0.22252	4.1742	0.9185	0.0104	0.5503
10.308	20.537	0.12537	8.3531	0.07563	0.20610	7.4869	5.9823	0.0154	5.0013
3.563	10.417	0.0	19.328	0.04857	0.28765		0.17014		1.3656
4.3366	10.24	0.06399	28.185	0.10976	0.18885		2.3131		1
18.401	8.4315	0.0	23.733	0.13251	0.29315		1.0844		1.9941
4.0574	13.181	0.0		0.17900	0.21831				1.0882
12.962	18.838	0.0	8.1524	0.13976	0.17304	4.3732	0.2359	0.0111	1.3521
14.736	18.925	0.0	51.723	0.02626	0.14512	4.6148	3.5688	0.01	0.1195
44.455	15.017	0.0	20.493	0.02693	0.13337	3.7572	1.8203	0.0089	1.6982
16.196	19.019	17.38	5.6523	0.03453	0.14471	4.7719	1.2303	0.0137	0.351
10.5	7.75	0.01300	12.1		0.20400		0.053		0.872
3.48	8.62	0.02900	37.7		0.20900		0.732		0.383
2.1	6.49	0.03800	23.9		0.26100		1.48		0.493
4	9.96	0.00400	6.76		0.14700		0.179		0.325
13.057	14.341	0.0	11.378	0.05211		3.6279	0.1188	0.0175	0.5492
8.0257	15.686	0.0	25.835	0.26560		3.8354	3.1115	0.0131	1.6106
8.2805	12.625	0.0	17.182	0.05161		2.1542	0.9432	0.0207	0.7114
24.555	17.747	0.0	9.8061	0.06944		3.2692	1.0163	0.0175	1.8343
26.289	2.6354	0.11226		0.58719	0.81226				5.4489
40.274	3.0865	0.15783		0.34458	0.77985				3.782
16.530	2.0378	0.75756		0.49505	0.86856				9.1882
11.594	13.650	0.0		0.32033	0.64809				2.3203
150.45	1.454	0.13249	0.2132	0.22469	0.29326	5.1637	1.7892	0.0067	59.418
58.066	1.3485	0.08494	1.4861	0.24323	0.12422	4.6282	28.125	0.001	57.874
156.65	1.4168	0.14165	0.624	0.48960	0.15628	4.5751	17.936	0.0035	62.348
95.228	1.6545	0.01470	0.2381	0.07001	0.07354	6.3868	25.503	0.0041	57.834
52.8	2.3941	0.97432		0.80629	0.11486				58.851
194.19	2.2614	1.31810		1.39050	0.09428				92.264
255.12	3.6399	0.87350		1.32500	0.05054				92.705
106.46	3.3894	1.06510		1.23710	0.04773				61.972
73.672	2.8516	0.10068	0.1618	0.11848	0.02885	7.2761	1.3497	0.0026	43.336
53.927	4.437	0.51251	29.019	1.77320	0.23094	13.37	22.211	0.0038	43.652
57.733	2.248	0.0	1.2329	0.17597	0.04804	6.6492	14.921	0.0007	43.476
81.96	1.9564	0.10300	0.435	0.11382	0.20335	6.9832	19.402	0.0015	42.168
206	3.85	1.26000	0.714		0.05800		3.76		64.7
921	6.74	34	4.2		0.08400		32.1		362

11	3.26	0.06700	0.312		0.00200		0.183		1.27
68.3	3.56	1.74000	0.792		0.03200		103		52.3
70.408	3.5041	0.29718	0.5064	0.42689		18.114	3.2588	0.009	23.057
39.24	2.4071	0.23772	3.392	0.60881		15.494	27.03	0.014	37.802
44.171	2.8325	0.00000	1.0348	0.44627		10.459	22.769	0.0188	36.627
2860.9	2.5467	0.18221	0.8263	0.41482		10.457	27.653	0.009	30.12
129.93	1.9596	1.00780		0.47081	0.00594				30.286
39.261	1.0854	0.33767		0.64715	0.00541				28.65
109.06	1.666	0.76583		0.55906	0.17382				43.359
117.03	2.0591	0.59274		0.47076	0.01799				39.163
4.8267	11.476	0.02500	0.5327	0.03905	0.11869	3.8746	0.096	0.0236	0.5968
2.3908	11.409	0.02896	0.5928	0.05898	0.18172	3.7162	0.0721	0.0209	0.3732
6.6236	13.548	0.07450	0.4732	0.06393	0.50374	4.7235	0.0829	0.0244	0.676
7.1766	13.095	0.08221	0.3506	0.04683	0.81423	4.3172	0.0674	0.0194	0.4191
15.086	10.68	0.01004	0.8998	0.05621	0.46756	6.0547	11.702	0.0054	29.378
2.4249	11.507	0.02083	0.6435	0.03769	0.36530	6.0955	13.428	0.0041	40.722
6.1985	5.2658	0.00000	1.0445	0.01512	0.04902	2.1187	9.6258	0.0032	0
8.9603	4.9084	0.00000	0.8849	0.52601	0.07183	1.9345	7.3886	0.0025	9.7648
1.9352	0.0126	0.00000	0.1409	0.03146	0.15275	0.0436	0.0544	0.0008	0.2871

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