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Chemical and Mechanical Performance Properties for Various Final Waste Forms—

PSPI Scoping Study

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LOCKHEED MARTIN

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ABSTRACT

The U.S. Department of Energy is obtaining data on the performance properties of the various final waste forms that may be chosen as primary treatment products for the alpha-contaminated low-level and transuranic waste at the Idaho National Engineering Laboratory's Transuranic Storage Area. This report collects and compares selected properties that are key indicators of mechanical and chemical durability for Portland cement concrete, concrete formed under elevated temperature and pressure (FUETAP), sulfur polymer cement, borosilicate glass, and various forms of alumino-silicate glass, including *in situ* vitrification glass and various compositions of iron-enriched basalt and iron-enriched basalt IV. Compressive strength and impact resistance properties were used as performance indicators in comparative evaluation of the mechanical durability of each waste form, while various leachability data were used in comparative evaluation of each waste form's chemical durability. The vitrified waste forms were generally more durable than the non-vitrified waste forms, with the iron-enriched alumino-silicate glasses and glass/ceramics exhibiting the most favorable chemical and mechanical durabilities. It appears that the addition of zirconia and titania to iron-enriched basalt (forming iron-enriched basalt IV) increases the leach resistance of the lanthanides. The large compositional ranges for iron-enriched basalt and iron-enriched basalt IV more easily accommodate the compositions of the waste stored at the Idaho National Engineering Laboratory than does the composition of borosilicate glass. It appears, however, that the large potential variation in iron-enriched basalt and iron-enriched basalt IV compositions resulting from differing waste feed compositions can impact waste form durability. Further work is needed to determine the range of waste stream feed compositions (waste loading and waste type) and rates of waste form cooling that will result in acceptable and optimized iron-enriched basalt or iron-enriched basalt IV waste form performance.

SUMMARY

Efforts are underway to provide for potential treatment of alpha-contaminated mixed low-level and transuranic wastes stored at the Idaho National Engineering Laboratory (INEL) in accordance with Environmental Protection Agency (EPA) Land Disposal Restrictions and U.S. Department of Energy requirements. As part of this effort, the Department of Energy has been investigating the possibility of having private industry treat the waste stored at the INEL's Transuranic Storage Area. The stored waste is largely heterogeneous solid mixed wastes from the Rocky Flats Plant that contain transuranic radionuclides; some of these wastes are classified as alpha-low-level waste (<100 nCi/g), others as TRU waste (>100 nCi/g). Essentially all are contaminated with various EPA hazardous constituents (toxic organics and metals) and are, therefore, "mixed" wastes.

Materials properties data are needed for the final waste forms that may be selected as primary treatment products for the alpha-contaminated waste. These data are essential for performance comparison and for risk assessment for these waste forms. This report provides 1) a compilation of selected mechanical and chemical durability properties data available for eight candidate final waste form materials that represent the most likely primary treatment products for alpha-contaminated waste, and 2) a scoping-level comparative evaluation of these waste forms.

The waste form materials selected for evaluation were Portland cement concrete (PCC), concrete formed under elevated temperature and pressure (FUETAP), sulfur polymer cement (SPC), borosilicate glass (BSG), and various forms of alumino-silicate glass (ASG), including *in situ* vitrification glass and different compositions of iron-enriched basalt (IEB) and iron-enriched basalt-IV (IEB4). Key performance indicator properties that were investigated for each waste form included compressive strength, generation of fines upon impact, and leachability. Leachability was evaluated via either the Materials Characterization Center procedures for static leach testing (MCC-1) and Product Consistency Testing (PCT), or the American Nuclear Society test standard for leach testing (ANS 16.1), as appropriate. The potential effects of different cooling rates, as well as the effect of compositional changes, on the chemical and mechanical durability of IEB and IEB4 were also briefly investigated.

A literature search was conducted to collect readily available data on each of the selected key indicator properties for mechanical and chemical durability. When the necessary information was unavailable, a limited set of tests were performed to obtain values for compressive strength, impact resistance, and leachability (PCT and MCC-1 leach testing).

The property-based comparison found that the compressive strengths of the vitrified waste forms were always greater than those of the cementitious waste forms (6 to 26 times greater). In all but one case, the alumino-silicate glasses were stronger than borosilicate glass. For the vitrified materials, waste composition appeared to affect compressive strength, as evidenced by lower values for the IEB produced from the 743 sludge composition. For the range of cooling rates tested, the effect of cooling rate on the compressive strength of vitrified materials appeared to be small. There was no significant difference found in compressive strength between IEB and IEB4 for comparable compositions (average compositions).

The impact resistance data indicated that the IEB/IEB4 waste forms are the most resistant to impact, followed by BSG, SPC, PCC, and FUETAP. For the IEB/IEB4 waste forms, no particulate less than 15.5 μm in diameter was created during the nine impact tests. To indicate the extent of fracture, the amount of

fines less than 96 μm in diameter was also determined for IEB and IEB4. There were no <96-μm fines created from the IEB:Average composition and IEB4:741/742 sludge composition samples, and minimal <96-μm fines creation from the other IEB and IEB4 waste form compositions.

The results of the 28-day MCC-1 tests (generally more indicative of initial high leach rates in unsaturated solutions) on SPC and the various vitrified waste forms (nonporous materials) showed that SPC is significantly more leachable than the vitrified waste forms. This was expected and is attributed primarily to the encapsulating nature of SPC. Similar results would be expected for the other encapsulating media, FUETAP and PCC, based on ANS 16.1 results showing similar cesium leachabilities for the three cementitious waste forms (PCC, FUETAP, and SPC).

PCT leach rates for IEB and IEB4 are approximately one to two orders of magnitude smaller than the MCC-1 values for the IEB/IEB4 waste forms. This is consistent with previously reported data for both BSG and *in situ* vitrification glass. The reason for the lower leach rates is that the PCT test uses a high surface area particulate sample while the MCC-1 test uses a monolithic sample with much smaller surface area. Because of the higher surface area to volume ratio, the leachant becomes saturated much sooner in a PCT test than in an MCC-1 test. This slows the dissolution process, resulting in a lower calculated dissolution rate for the PCT data relative to the MCC-1 data. PCT data are considered to be more representative of long-term disposal conditions where the fluid is relatively stagnant and becomes saturated. The MCC-1 data are more representative of short-term disposal where the fluid is not yet saturated.

Based on MCC-1 tests, sodium leachabilities for each of the tested IEB and IEB4 waste forms were significantly greater than values previously reported for IEB in other work. In fact, sodium leachabilities for the various IEB/IEB4 waste form materials tested and reported herein are closer to the reference literature alumino-silicate glass values, with the IEB:743 composition providing a sodium leachability even greater than alumino-silicate glass or borosilicate glass. The higher than expected sodium leachabilities are likely due to the presence of sodium-free augite crystals in the IEB MCC-1 samples tested, which increases the concentrations of alkaline elements (e.g. sodium) in the remaining non-crystalline more leachable, glassy portion of the multiphase waste form. Recent studies have indicated that heavily crystallized glasses (greater than 10 wt%) are less homogeneous on a microstructure level than less-crystalline glasses as would be expected in a multiphase crystalline solid. Fabrication of the various IEB/IEB4 MCC-1 samples may also have resulted in higher concentrations of the alkaline-rich and leachable glass phase on the surface of the samples. Further analysis would be needed to confirm this, however.

The PCT data indicate that the various IEB/IEB4 waste forms will have greater long-term sodium leachabilities than BSG and *in situ* vitrification glass, and smaller silicon leachabilities than BSG. The lower bulk silicon leachability in general indicates a more durable overall glass/ceramic waste form, since the bulk of the material is an assemblage of silicon-based crystals and residual glass phases. The higher sodium leachability is attributed to the sodium enrichment in the less durable (more easily dissolved) phases or residual glass. The results also show that heat treating the IEB/IEB4 samples reduces their PCT sodium leachability significantly. However, the effect of heat treatment on PCT leachability was reversed for some other elements (calcium, cesium) within some of the IEB/IEB4 waste forms. This is also attributed to partitioning of these elements into phases of varying durability. The bulk silicon leachability remains very low, however, indicating the overall glass/ceramic remains highly durable.

A comparison of PCT data for the IEB and IEB4 average compositions found that the zirconia and titania additions to the IEB4 waste forms caused a net reduction in the leachability of the TRU surrogates (samarium and cerium). Similar results were observed for the MCC-1 leachability of cerium. This is attributed to the zirconolite crystals in IEB4, which are expected to incorporate both transuranic and simulated transuranic components in the more durable crystal phase structure, thereby reducing the overall leachability of TRU-contaminated elements. The net reduction in cerium and samarium leachability achieved by IEB4 relative to IEB was, however, less than expected (only 40-50%, and 9-22%, respectively). The small reduction in lanthanide (TRU surrogate) leachabilities was attributed to minor growth of zirconolite crystals in the IEB4. Additional reductions in cerium and samarium leachability would be expected if longer heat treatments were used to promote zirconolite crystal growth. Further evaluation is needed, however, to determine whether the estimated achievable net reduction in actinide leachability (9-60%) is worth the small additions (<5 wt%) of zirconia and titania needed to produce IEB4. The addition of zirconia and titania to the melt may also cause a small increase in the leachability of other elemental components that become enriched in other, less desirable, crystal or residual glass phases in the IEB4, as evidenced by the slight increase in calcium leachability for the IEB4 average composition.

Although some scoping-level indications of the relative mechanical and chemical durability of the most likely final waste form materials have been obtained, it is clear that quantitative prediction of final waste form performance at any reasonable confidence level will require considerable additional, well-planned and controlled, testing and analysis of data.

It is also clear that final waste form chemical durability is a complex function of a large number of variables. These include the nature of the product material—its chemical composition, material structure, and phases—which is dependent upon the waste composition and treatment process conditions. Chemical durability is primarily assessed using leachability data obtained through a particular test method. The type of test and the location in the waste form that is sampled significantly affect the leachability data. For these multi-material (in the case of encapsulated waste material forms like PCC) and multiphase/microstructure materials (in the case of glass/ceramics), additional testing and simple correlations, although necessary, will be insufficient to develop the quantitative performance prediction capability needed to support process optimization, licensing, and public acceptance. It is recommended that a set of simple, predictive analytical models be developed to aid in planning future testing and in properly interpreting the results from leach testing of multiphase materials. Once validated, the models can be used to predict future in-service waste form performance.

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ACRONYMS

α-LLW	Alpha-contaminated low-level waste
ASG	Alumino-silicate glass ceramic
BSG	Borosilicate glass
DOE	U.S. Department of Energy
EDXS	Energy dispersive x-ray spectroscopy
FC	Fast cooling
FUETAP	Hydraulic cement formed under elevated temperature and pressure
FWF	Final waste form
HT	Heat treated
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP/MS	ICP-mass spectroscopy
IEB	Iron-enriched basalt
IEB4	Iron-enriched basalt with Group IV additives
INEL	Idaho National Engineering Laboratory
ISV	*In situ* vitrification
NRC	Nuclear Regulatory Commission
PCC	Portland cement concrete
PNL	Pacific Northwest Laboratory
PSPI	Private Sector Participation Initiative
RFP	Rocky Flats Plant
RWMC	Radioactive Waste Management Complex
S/V	Surface area to volume ratio
SC	Slow cooling
SEM	Scanning electron microscopy
SPC	Sulfur polymer cement
TRU	Transuranic
TSA	Transuranic Storage Area
XRD	X-ray powder diffraction

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1. INTRODUCTION

Transuranically-contaminated wastes stored at the Idaho National Engineering Laboratory (INEL) are planned to be treated and disposed of in accordance with Environmental Protection Agency Land Disposal Restrictions and U.S. Department of Energy (DOE) requirements (e.g., Order 5820.2A). These wastes primarily consist of waste materials from operations at the Rocky Flats Plant (RFP) and contain <100 nCi/g of transuranic (TRU) radionuclides. Most of them are stored at the INEL Transuranic Storage Area (TSA), located in the INEL's Radioactive Waste Management Complex (RWMC). These "mixed" wastes are stored in either drums or large boxes, and include various metals, wood and paper products, cements, and inorganic and organic sludges contaminated with EPA hazardous organics, toxic metals, and transuranic radionuclides. Treatment of the varied wastes will likely result in the production of several different final waste forms (FWFs).

DOE has been pursuing the possibility of having private industry treat these wastes [Advanced Mixed Waste Treatment Project, private sector participation initiative (PSPI)]. As part of this effort, it was deemed necessary to obtain scoping-level preliminary data on selected key properties indicative of the mechanical and chemical durabilities of the various FWFs that may be selected as primary treatment products in order to support independent evaluations of the various treatment and FWF options. This report documents results from initial studies conducted to compile these properties data.

The most likely candidate FWFs were first identified and key performance indicator properties were selected. A literature search was conducted to identify existing data on each waste form and determine where the data were incomplete. Tests were conducted as necessary to obtain minimal scoping-level performance indicator properties data. The waste forms were then comparatively evaluated using the performance indicator properties data. For iron-enriched basalt (IEB) and iron-enriched basalt-IV (IEB4), two of the waste forms under consideration, the evaluation also included examining some limited data on how cooling rate and compositional variations might affect mechanical and chemical durability. The microstructures, mineralogies, and chemical durabilities of IEB and IEB4 were also briefly evaluated to better quantify the property comparisons for these two material types.

Selection of the key performance indicators for mechanical and chemical durability of the FWFs is discussed in Section 2. Section 3 provides some information on the various potential waste compositions and loadings for the FWFs. Section 4 gives an overview of the existing mechanical and chemical durability indicator properties data for each FWF as compiled from the literature, identifying where the data were incomplete. Section 5 provides information on sample preparation and characterization procedures for the properties testing conducted to fill gaps in the data, including the microstructural, mineralogical, and redox ratio analyses of the IEB and IEB4 waste forms examined. Section 6 describes the chemical and mechanical durability tests that were performed, while Section 7 presents the results of the properties tests. A summary of the complete compilation of indicator properties data collected for each FWF is given in Section 8. Conclusions are summarized in Section 9.

2. IDENTIFICATION OF CANDIDATE FWFs AND THEIR SELECTED PERFORMANCE INDICATORS

2.1 Representative Final Waste Forms

In light of previous treatment systems scoping studies,[1,2,3] the waste forms identified as representative of those expected to be proposed were Portland cement concrete (PCC), hydraulic cement formed under elevated temperature and pressure (FUETAP), sulfur polymer cement (SPC), borosilicate glass (BSG), and various forms of alumino-silicate glass ceramics (ASGs), including *in situ* vitrification (ISV) glass, iron-enriched basalt (IEB), and iron-enriched basalt with Group IV additives that are thought to increase the leach resistance of transuranic materials (IEB4).

Of the waste forms selected, three (PCC, FUETAP, and SPC) involve physical encapsulation of the waste materials with little or no change in the waste compounds, while the others (BSG and the ASGs) are glassy ceramics in which the waste has been completely broken down chemically by thermal energy and the resulting elements are incorporated into the microstructure of the amorphous/crystalline product. Use of the cementitious waste forms generally results in significantly increased waste volumes, while the vitrified waste forms generally reduce the waste volume, due to the destruction (gasification) of any combustible materials in the waste and densification of remaining solids. The reasons for selecting the seven waste forms in this study are given below.

Portland Cement Concrete - Although PCC is generally considered to be less durable than the other six waste forms identified, it may be suitable for certain low-level wastes. Because PCC is the best demonstrated available technology for low-level waste according to the Nuclear Regulatory Commission's (NRC) Technical Position on Low-Level Waste Forms,[4] it must be included in any discussion of low-level waste forms, at least for comparison purposes. A disadvantage of PCC is the large increase in waste volume it entails, typically a factor of 2.5 to 5. This is due to its maximum waste loading of 20-40% and the limited amount of densification experienced.

FUETAP - Because FUETAP is formed under elevated temperature and pressure, it contains less water than standard hydraulic cements, such as Portland cement. As a result, FUETAP is generally considered to be the most durable of the hydraulic cements investigated, and there were significant efforts in the 1980s to demonstrate its applicability to high-level nuclear waste containment.[5] FUETAP was selected for this work as a representative of the best form of hydraulic cement for waste applications. However, its cementitious nature necessitates a large increase in waste volume. In addition, there are no companies within the United States that are currently producing FUETAP.

Sulfur Polymer Cement - SPC, which consists of 95 wt% sulfur, 2.5 wt% dicyclopentadiene, and 2.5 wt% cyclopentadiene oligomers, is a thermoplastic ceramic that melts at 120 to 135°C.[6] SPC has been proposed for microencapsulation of various low-level wastes; it is not recommended for transuranic wastes because its expected lifetime is only 300 years.[6,7] The cold strength of SPC, with normal construction aggregate, is 4000 to 12,000 psi.[6] SPC was selected for this work because of its potential suitability for the nontransuranic portion of the TSA waste. In addition, SPC might be appropriate for certain waste components, such as sulfur or mercury, that are not readily encapsulated in Portland cement or glassy ceramics. As with cement, its use involves an increase in waste volume, typically by a factor of two to three.

Borosilicate Glass - BSG is a high alkali (sodium and potassium) alumino-silicate glass that is fluxed with boron. As with other glassy-ceramic waste forms, it chemically incorporates the waste material within the crystalline/glass matrix, in contrast to cement waste forms which generally encapsulate the waste.[8] The lower alumina content, coupled with the addition of boron, enables processing at temperatures below 1150°C.[8] This is much lower than other high-temperature waste form materials, and allows BSG to be prepared using a joule-heated ceramic melter.[9] Lower melting temperatures are desirable because they are generally less corrosive to the processing equipment and cause less volatilization of hazardous species. BSG has been studied and extensively developed for vitrification of a well-characterized high-level liquid waste stream; it has been selected for remediating high-level wastes within the DOE complex.[10] A critical limitation of BSG with regard to the highly heterogeneous INEL wastes is its relatively strict compositional requirements, due largely to electrical conductivity and processing temperature limitations. The required composition does not match the range of high metal, high silica content materials of the TRU waste, so considerable separation and preliminary homogenization or additions of flux material to the BSG waste stream would be necessary to produce BSG, with attendant volume increases.[1,11]

Alumino-Silicate Glass Ceramics - ASGs have excellent chemical and thermal stability as well as mechanical durability due to their high silica and alumina contents.[12] ASGs generally require processing at temperatures well over 1350°C, similar to the temperatures achieved in plasma arc/torch processing and proposed higher temperature joule melters.[12] A potential disadvantage of ASGs, as with all high melting point glassy ceramics, is that the high melting temperatures may result in greater volatilization of some hazardous metal species (e.g. cesium, lead) than with the borosilicate glasses.[13] However, ASGs have been found to have superior leach resistance to BSG.[12,14] In addition, ASG waste forms generally involve less restrictive waste feed compositional homogeneity requirements than BSG (a major factor in heterogenous buried waste processing).[1,12] For transuranic mixed wastes at the INEL, three types of ASG are applicable: ISV glass and various compositions of IEB and IEB4. These are summarized below.

ISV Glass - ISV glass is an iron-enriched alumino-silicate glass ceramic produced by *in situ* vitrification of buried waste and soils typical of those found at the INEL. In this process, graphite electrodes are placed into a buried waste site and used to melt the waste and surrounding soil into a relatively homogenous waste form.[15] Upon hardening, the ISV glass is a form of IEB and resembles natural basalt or obsidian. During processing, the organics in the waste are completely removed and destroyed, while the inorganic wastes and radionuclides are incorporated into the glassy-ceramic melt matrix. Because of the large volumes of soil processed by ISV along with the wastes,[1,15] the potential compositional variations are expected to be of less concern than with potential variations in stored wastes processed *ex situ* to produce IEB or IEB4. The graphite electrodes used in the ISV process result in an extremely reduced form of iron-enriched basalt.[16]

Iron-Enriched Basalt - IEB, which has a geologic analog in natural basalts, is a class of iron-enriched alumino-silicate glass ceramics that can immobilize heavy metal oxides within the iron alumino-silicate matrix.[12,17,18] The resultant waste form is highly resistant to chemical or physical decomposition. Any thermal process that converts INEL soil and exhumed RWMC waste into a stable waste form can produce a glass-ceramic resembling natural basalt.[19] The vitrified waste compositions considered in this study are based upon the IEB waste form. The IEB process also involves fewer compositional concerns than BSG.[1,12]

Iron-Enriched Basalt–IV - IEB4 is a tailored IEB that has additions of titanium oxide, zirconium oxide, and possibly calcium oxide.[12,19,20] The resulting waste form generally has the same structural and volume reduction capabilities as IEB. The reason for adding titanium and zirconium oxides is to enable formation of zirconolite crystals, which can preferentially incorporate transuranic elements and are highly leach resistant. IEB4 was selected for this study because of its potentially improved performance, with respect to IEB, in immobilizing transuranic elements.

Other waste forms that were briefly considered but not included further in this study are bitumen, other organic binders, and Synroc. Bitumen was rejected because of its potential flammability. The organic binders were rejected because their application is restricted to certain specialized waste types and they would be unsuitable for the long-lived transuranic radionuclides. In addition, if included in a treatment option for evaluation, sufficient data on bitumen and the other organic binders is available.[21] Synroc is a high titania material that is an extremely good waste form, but it is intended to be produced from a well-characterized waste stream that emanates from a well-defined process with the proper compositions for Synroc. Highly controlled, low production rate, hot isostatic pressing conditions (via use of a hot isostatic press) are also necessary to produce it.[12,22] These conditions probably cannot be met for the wastes at the INEL. Synroc is primarily an assemblage of titinate ceramic phases while INEL wastes are largely silica with little or no titania. Synroc performance is also felt to be unnecessary for the low concentrations of TRUs that are typically encountered in INEL wastes; however, this performance may be approached by IEB4, which can be produced in a high temperature melter.[19,23,24]

2.2 Key Performance Indicator Properties of Final Waste Forms

To select key indicator properties for evaluating final waste forms, a number of potential mechanical and chemical properties were briefly considered for their relative importance in waste form performance. Mechanical durability properties considered included compressive strength, fines generation upon impact, radiation stability, resistance to thermal cycling, and void fraction. Chemical durability properties considered included aging, biodegradation, compositional flexibility, corrosivity, flammability, reactivity, criticality, free liquids, gas generation, immersion stability, and leach resistance. Table 1 provides a summary list of each property, the performance of concern, and the reason for its selection or lack of further consideration in this scoping study. Based on the results of the investigation, the following mechanical and chemical durability properties were selected as key indicators for evaluating and comparing final waste form performance at a scoping level.

- **Mechanical Durability:** "Compressive strength" and "generation-of-fines-upon-impact"

- **Chemical Durability:** Leach resistance (all waste forms) and compositional flexibility for incorporating the waste materials (for the IEB and IEB4 waste forms only).

A detailed description of the properties selected is included in Section 6. Information on waste form density was also collected to assist in evaluating the potential for waste volume reduction/expansion during treatment.

Table 1. Evaluation of prospective mechanical and chemical durability properties.

Property	Functionality of Concern	Resolution
	Mechanical Durability Properties	
Compressive Strength	The waste form must be able to withstand significant weight loadings without failure	Property is considered critical in evaluating waste form mechanical durability
Fines Generation Upon Impact	The amount of respirable fines generated upon impact is needed to determine how waste form integrity is affected by accidents that may occur during transportation and handling	Property is considered critical in evaluating waste form mechanical durability
Radiation Stability	Physical effect of radiation exposure equivalent to that expected during the projected lifetime of the waste form (300 years for LLW, 10,000 years for TRU wastes[25])	Not considered further; each waste form has already been evaluated for radiation resistance, at least up to its projected lifetime[6,7,12,21]
Resistance to Thermal Cycling	Waste form must undergo extreme variations in temperatures (including freeze/thaw cycles) without losing its integrity	Not considered further because it is another measure of the strength of the product and generally involves only those waste forms containing water (PCC or FUETAP); potential water intrusion into other waste forms is almost negligible
Void Fraction	May impact a waste form's volume reduction potential and compressive strength	Not considered further. All of the selected waste forms have negligible void volumes
	Chemical Durability Properties	
Aging concerns	Effect of environmental aging factors such as ultra-violet (UV) degradation	Not considered further. Most effects associated with aging can be approximated by leach testing and comparing the results with natural analogs. UV degradation has already been extensively evaluated on all prospective waste forms.[6,12]
Biodegradation	Waste forms need to be resistant to any organisms that may be present in the final storage environment	Not considered further, primarily due to the inability to specify what microbial environment may exist during final storage. In addition, all biodegradation tests performed to date indicate that there is no concern with any of the waste forms[6,7,12]

Table 1. (continued).

Property	Functionality of Concern	Resolution
Compositional Flexibility	Ability to stabilize the wide variety of waste compositions expected without effects on product quality	Property is critical for waste forms chemically incorporating a wide range of compositions (IEB/IEB4). Also need to consider the effect of cooling rates and redox on waste form quality
Corrosivity, Flammability, Reactivity (RCRA compliance issues)	The corrosivity, flammability, and reactivity of the waste form need to be known to ensure that it is in compliance with land disposal restrictions	Not considered critical for evaluation as RCRA compliance was used to select all the prospective waste forms
Criticality	The degree of moderation and densification accompanying each waste form dictate whether or not a critical condition could result	Not considered further because of the relatively low levels of TRU contamination in the waste, and the limited potential for high density compaction of critical materials
Free Liquid Concerns	NRC guidelines limit the amount of free liquids in the waste form to less than 0.5 wt%[25]	Not considered further. The waste forms pass the criterion of <0.5 wt% free liquid, provided they have been prepared properly
Gas Generation Concerns	Waste form must be resistant to gasses generated by the decay of either radioactive material or organic material in the waste form	Not considered further. Porous nature of cementitious waste forms eliminates concerns regarding degradation due to gas generation. Organic materials are assumed to be eliminated prior to production of the vitrified waste forms. Extensive testing of radionuclide gas generation has already been performed for the various glassy-ceramic waste forms[12]
Immersion Stability	Waste form must not be degraded by immersion in a solution that may be found in a final storage environment	Not considered further because the monolithic leach resistance tests are expected to provide enough information to quantitatively determine if there is any swelling or loss of durability as a result of leaching

Table 1. (continued).

Property	Functionality of Concern	Resolution
Leach Resistance (MCC-1, PCT, ANS 16.1, TCLP)	Both RCRA compliance (meeting TCLP) and the relative potential leachability of the waste forms and natural analogs (Materials Characterization Center tests)	TCLP not considered further. All prospective waste forms will be designed to meet TCLP criteria. In addition, this test is not good for waste form comparisons. Other leach tests (MCC-1, PCT, or ANS 16.1) are considered critical to evaluate waste form chemical durability. Leach testing should also be used to evaluate the compositional flexibility of IEB and IEB4

3. TSA WASTE COMPOSITION AND WASTE FORM LOADING

The composition of the waste stream being treated affects the properties of the vitrified final waste forms because the elements in the waste become integral parts of the glass/ceramic. Therefore, to evaluate prospective final waste forms, it is necessary to know the compositions of the prospective waste streams. Based on previous waste segregation studies, six primary waste streams have been designated for the TRU-contaminated mixed waste that is stored at the TSA. These waste streams are as follows:[11]

- Rocky Flats Plant (RFP) Series 741 inorganic sludge (designated as H1)
- RFP Series 742 inorganic sludge (designated as H2)
- RFP Series 743 organic sludge (designated as S)
- RFP Series 744 organic sludge (designated as P)
- RFP Series 745 nitrate salt cake (designated as N)
- Combined metal and ceramic waste materials (designated as M).

In addition to these six waste streams, a seventh waste stream, designated A, has been proposed. This seventh waste stream represents the "average" stored waste, based on the estimated compositions and amounts of the above six waste streams, after it has undergone high temperature oxidation. The average, or A, waste stream composition was used in all properties testing for the non-IEB/IEB4 waste forms in this study. Literature values on non-INEL waste streams are reported where available.

For simplicity, each FWF was to be evaluated at its reported maximum waste loading. This resulted in evaluations of IEB and IEB4 at nominal waste loadings of 60 wt%, and of the other five FWFs at nominal waste loadings of 40 wt%. However, due to the limited effect of waste composition variations on the non-IEB/IEB4 waste forms, literature values at other waste loadings were also used in the comparative evaluations of the non-IEB/IEB4 FWFs.

4. EXISTING PROPERTY DATA

A literature search was performed to identify readily available data for the selected indicator properties for all of the FWFs chosen. Data on compressive strength, fines generation upon impact, and the various leach tests were obtained; results of the literature search are summarized in Tables 2 and 3. Evaluation of the collected data indicated that, for the purposes of this scoping study, the information was incomplete in the following areas:

- **Portland Cement Concrete** - Fines generation upon impact and ANS 16.1 leaching data for nonradioactive materials were not available.
- **FUETAP** - ANS 16.1 leaching data was not available (although International Atomic Energy Agency [IAEA] data, a precursor to ANS 16.1, is available for Cs, Sr, and Pu).
- **Sulfur Polymer Cement** - Fines generation upon impact and MCC-1 leaching data were not available.
- **Borosilicate Glass** - All data available.
- **Iron-Enriched Basalt** - Compressive strength, fines generation upon impact, and PCT and MCC-1 leaching data for the various expected IEB compositions were not available.
- **Iron-Enriched Basalt-IV** - Compressive strength, fines generation upon impact, and PCT and MCC-1 data on Na, Ca, and bulk leachability data were not available.

The data collected from literature were evaluated and qualitatively ranked to identify the minimal additional data that must be obtained. A summary of the results of the evaluation process is shown in Table 4. Because IEB and IEB4 have very similar compositions, it was not deemed necessary to perform a full evaluation of all properties for both waste forms at this level of scoping study.

With regard to compressive strength, only a few of the different compositions of IEB (A and S) and IEB4 (A and H1) were selected for the property evaluation, since the compressive strengths of the other IEB and IEB4 waste forms are expected to be similar.

Additional “fines-generation-upon-impact” data was only deemed critical for PCC, SPC, and a few of the different compositions of IEB (A and S) and IEB4 (A and H1). The other IEB and IEB4 waste compositions are expected to exhibit similar mechanical durability to the IEB and IEB4 compositions evaluated.

Of the three types of leach tests (MCC-1, PCT, and ANS 16.1), ANS 16.1 measures the leachability of specific components from porous substrates. Therefore, it is primarily applicable to the cementitious waste forms. The MCC-1 and PCT tests are primarily applicable to nonporous vitrified waste forms with slower, more unified rates of dissolution. Interpretation of leach rate data from MCC-1 tests provides a measure of the waste form's short-term durability, while interpretation of the PCT leach rate data provides a measure of the vitrified waste form's long-term durability. Additional details on each of the leach tests are given in Section 6.2.

Table 2. Existing data on mechanical durability for the final waste forms selected.

Final waste form	Compressive strength[27] (MPa)	Density (g/cm^3)	Fines generation upon impact[28] (wt% < 10 μm)
Portland Cement Concrete	1.6-14.1 (ion-x[a])[29] 20.6-55.2 (conc[b])[30] 3.5-40[3]	~ 1.5[21]	No Data Available
FUETAP	20[12]	~ 2[12]	0.43[12,28]
Sulfur Polymer Cement	12.6-44.4[7] 41.4-69 (with aggregate)[3]	1.4-2.1[7]	No Data Available
Borosilicate Glass	281-314[30]	2.6[12]	0.17[12,28]
Alumino-silicate Glass	Data not available but not needed	2.7-3.0[12]	Data not available but not needed
Iron Enriched Basalt	409 (red. IEB only)[30]	2.9-3.0[31]	No Data Available
Iron Enriched Basalt-IV	No data available, all compositions	3.0-3.1[31]	No data available, all compositions

a. ion-x - Portland cement, mixed with ion-exchange resins.
b. conc - Portland cement, mixed with concentrated waste solutions.

Table 3. Existing data on chemical durability for the seven final waste forms.

	Test procedure		
Final waste form	MCC-1 (28 day) (g/m^2)	PCT (7 day) (g/m^2)	ANS 16.1 leach index
Portland Cement Concrete	Data not applicable	Data not applicable	Cs-137, 6-10.6; Sr-90, 7-10.7; Co-60, 9.7-13; C-14, 12.9-14.2; H-3, 7.4-9[3]
FUETAP	Data not applicable	Data not applicable	IAEA Data: Cs, 12.2; Sr, 8.2; Pu, 16.2[5,a]
Sulfur Polymer Cement	No Data Available	Data not applicable	Co-60, 10.7-14.6; Cs-137, 9.7-11.2[7,b]
Borosilicate Glass	Na, 14-37; Si, 11-28; Cs, 29-49; B, 15-39; Fe, 0-.2; blk, 12; Sr, 1.0-2.1; Ce, <.1; Ca, 1.9-7.2; Mo, 39; U, 1.3-1.5[8,9,12,14,c]	Na, .40; Si, .21; Cs, .13; B, .44; Al, .12; Cr, .0086; Li, .49; Ca, .041; Mg, .25; Zr, .027; Ni, .12; La, .029; Nd, .027; Mo, .43; Mn, .20; Ce, .026[9,c]	Data not applicable
Alumino-silicate Glass (Generic)	U, 1.5; Cs, .8; & Ce, .39[14] Na, 21; Si, 5.8; Ca, 6.4; Mo, 6.1; Sr, 4.7; Ba, 1.8[12]	No Data Available	Data not applicable
ISV Glass	Na, 3.2; Si, 3.0; Al, 2.8; B, 2.8; Ca, 8.7; Fe, .56; K, 3.7[30]	Al, .01; B, .09; Ca, .29; Fe, .00; K, .06; Na, .08; Si, .04; V, .25[30]	Data not applicable
Iron Enriched Basalt (IEB)	Na, 1.4-7.8; Si, 1.6-6.2; Al, .35-6.4; Fe, .03-.8; Ca, .8-5.3; Mg, 1.6-5.9; K, 3.4-7.3; blk, 2.2-4.0; U, .02-.25; La, .02; Cs, 1.7; Sr, 1.6[12,17,18] No data for different compositions	No Data Available	Data not applicable
Iron Enriched Basalt-IV	Pu, .006; Np, 6.2; Cs, 21; Am, .008; Cm, .006[12] No data for different compositions	No data available	Data not applicable

a. After converting to leach indices
b. For 20-40 wt% sodium sulfate/incinerator ash
c. Ref. 9, 2000/m MCC-3 data for PCT

Table 4. Ranking of missing critical property data.

Waste form	Compressive strength	Fines on impact	MCC-1	PCT	ANS 16.1
PCC	Have	Need	N/A	N/A	OK
FUETAP	Have	Have	N/A	N/A	OK
SPC	Have	Need	Need	N/A	N/A
BSG	Have	Have	Have	Have	N/A
ASG					
· ISV Glass	Have	Prefer	OK	OK	N/A
• IEB					
- A comp	Need	Need	Need	Desire	N/A
- H1 comp	Prefer	Prefer	Prefer	Prefer	N/A
- S comp	Desire	Desire	Need	Desire	N/A
- N comp	Prefer	Prefer	Prefer	Prefer	N/A
- M comp	Prefer	Prefer	Prefer	Prefer	N/A
· IEB4					
- A comp	Need	Need	Need	Desire	N/A
- H1 comp	Desire	Desire	Need	Desire	N/A
- S comp	Prefer	Prefer	Prefer	Prefer	N/A
- N comp	Prefer	Prefer	Prefer	Prefer	N/A
- M comp	Prefer	Prefer	Prefer	Prefer	N/A

LEGEND

Need - Data critical for waste form evaluation but unavailable

Desire - Data worth obtaining but not critical

Prefer - Data of only mild interest

Have - Data already available for particular waste form

OK - Data not complete, but probably adequate for waste form evaluation

N/A - Property not applicable for particular waste form

For the purpose of obtaining a minimal set of properties data for comparative evaluations, the only additional leach tests needed were the MCC-1 tests for SPC and selected compositions of IEB (A and S) and IEB4 (A and H1). However, it was also considered desirable to evaluate IEB vs. IEB4 performance at a fixed waste composition/concentration to quantify the small differences expected in leachability. This comparison was performed using the average TSA waste composition and a 60 wt% waste loading. PCT data were also deemed to be desirable to provide additional information on the leach resistance of the glassy ceramic waste forms. PCT data provide a better indication of the potential long-term leach resistance than MCC-1 data because the PCT samples are crushed and have a larger surface area. In addition, crushing allows the potential effects of different rates of cooling on leachability to be evaluated more accurately because it more homogeneously exposes the crystalline phases in the sample.

Based on the literature review, the following tests were identified as necessary to generate the minimum additional properties data required to comparatively evaluate waste form performance for the purposes of this scoping study:

- **Compressive Strength** (per ASTM C39) - IEB/A, IEB4/A, IEB/S, and IEB4/H1 (all 60 wt% waste loadings).
- **Fines Generation Upon Impact** - PCC (40 wt% waste loading, average composition); SPC (40 wt% waste loading, average composition); IEB/A, IEB4/A, IEB/S, and IEB4/H1 (all 60 wt% waste loadings).
- **MCC-1** - SPC (40 wt% waste loading, average composition); IEB/A, IEB4/A, IEB/S, and IEB4/H1 (all 60 wt% waste loadings).
- **PCT** - Different rates of cooling for IEB/A, IEB4/A, IEB/S, and IEB4/H1 (all 60 wt% waste loadings).

The remainder of this report describes the generation of this additional properties data and utilizes these data, along with the previously existing data, in a simple comparative evaluation of the various FWFs.

5. SAMPLE PREPARATION AND CHARACTERIZATION

5.1 PCC and SPC

5.1.1 Preparation of Simulated Waste Material

The simulated waste materials used for these final waste form properties experiments represented the "average" composition of waste materials stored at the TSA, after they had undergone complete oxidation during incineration.[11] The "average" oxide composition of thermally oxidized wastes at the TSA (including containers) is as follows:

SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O
38.0	7.4	34.5	8.3	4.6	4.8	2.4

The chemicals used to prepare this simulated waste for SPC and PCC (including trace metals) are listed in Table 5. The chemicals include both tracer additives and carbonate forms of sodium and potassium.

The tracer additives used in the study included simulated TRU compounds (CeO_2, Sm_2O_3), LLW nuclide tracers (Cs_2O), and high vapor pressure metals (CdO, PbO_2, Cr_2O_3, ZnO). These compounds were added to the waste at a nominal concentration of 2.5 wt%, which gave a concentration of approximately 1 wt% in the waste form.

The carbonate forms of sodium and potassium were used since their oxide forms are unstable in ambient air at room temperature. As a result, the simulated PCC and SPC waste material had to be pre-heated to eliminate the carbonates before it was added to the PCC or SPC mix. The assumption of oxidized waste materials in PCC or SPC is consistent with the pre-conceptual treatment option to incinerate the stored waste prior to its stabilization in PCC or SPC.

Approximately 500 g of the simulated waste material was prepared initially for the PCC and SPC waste forms. This mixture was distributed among six 100 mL crucibles and heat treated at 1000°C in air for 4 h to decompose the carbonates. The resultant oxide material was crushed to a fine particle size (<250 μm) using a mortar and pestle, yielding 476 g of simulated oxidized waste.

Table 5. Chemicals used to simulate "average" waste composition, after thermal treatment, for PCC and SPC.

	wt%		wt%		wt%
SiO_2	30.24	MgO	3.66	CdO	2.27
Al_2O_3	5.89	Na_2CO_3	6.53[a]	PbO_2	2.3
FeO	22.88	K_2CO_3	2.8[a]	Cr_2O_3	2.91
Fe_2O_3	4.58	CeO_2	2.44	ZnO	2.48
CaO	6.61	Cs_2O	2.11	Sm_2O_3	2.31

a. The waste was pre-heated to drive off the carbonates, prior to mixing with the PCC or SPC.

5.1.2 Preparation of Portland Cement Concrete FWF Specimens

The formula chosen for the PCC final waste form specimens was 40 wt% simulated waste, 35 wt% water, and 25 wt% Type I Portland cement. This mixture was believed to be a typical formulation for waste treatment.[21] The PCC specimens were prepared according to ASTM C 192,[32] with 200 g of simulated oxidized waste material, 125 g of Portland cement, and 175 g of deionized water. The mix was then poured into Teflon molds and rodded, per ASTM C192 specifications, to ensure proper consolidation. Upon mixing, it was immediately obvious that the PCC mixture contained excessive amounts of water. The most probable explanation is that the simulated waste form did not absorb the 35 wt% water. In future samples, it may be better to either mix the dry materials first and add water in small increments until the desired consistency is achieved, or reduce the water content to 30 wt%, with 30 wt% Portland cement.

Two mold sizes were used: 25.4 mm high by 25.4 mm diameter for impact specimens and 25.4 mm diameter by 50.8 mm high for compressive strength specimens. (The compressive strength samples were prepared in anticipation of future compressive strength tests, not for this study.) The filled molds were placed in a sealed container for 24 h to cure. After curing, the hardened concrete samples were removed from the molds. Considerable standing water was observed on the top of the samples, and the water exhibited a yellow color. The concrete samples shrank approximately 22% in weight, although the sample diameters did not shrink. Because of the shrinkage, the impact specimens, at 18.7 mm in height, were too small and irregular to be used for impact tests. As a result, the specimens that were planned for possible future compressive strength tests had to be cut down for use in the impact tests. After cutting, the concrete samples were stored in a saturated lime solution until impact testing could begin.

5.1.3 Preparation of Sulfur Polymer Cement Specimens

The SPC composition chosen was 95 wt% sulfur 2.5 wt% dicyclopentadiene, and 2.5 wt% cyclopentadiene oligomers. To prepare the samples, 350 g of SPC was heated to the melting temperature of 140°C and held for 40 min. The hot SPC was combined with 233.3 g of the simulated oxidized waste to give a 40 wt% waste loading. The resultant mixture was poured into cylindrical Teflon molds. The decision to use Teflon molds was based on concerns over the ability of SPC to maintain its integrity during coring.

Three sizes of molds were used: 25.4 mm diameter by 25.4 mm high for drop weight impact test samples, 9.53 mm diameter by 9.53 mm high for MCC-1 leach testing samples, and 25.4 diameter by 50.8 mm inches high for possible future compressive strength testing samples. Six samples of each size were created.

The MCC-1 leach testing samples were poured first. The material was then returned to the oven for approximately 15 min to reheat before the remaining samples were poured. In an attempt to maintain a homogeneous SPC mixture, the molten SPC was stirred after each pour. Nevertheless, a large amount of waste settling was observed immediately after stirring ended. Although settling is a concern with SPC, it can be avoided via numerous design options, such as the addition of fly ash. Because no modifications were made to the samples of SPC, it is expected that the first samples poured may be relatively high in sulfur and low in waste, while the last samples may be relatively low in sulfur and high in waste. It was decided to verify this later as part of the MCC-1 tests.

Considerable waste form subsidence was also observed upon solidification, creating a large cavity in the top surface of each specimen. This made it necessary to periodically pour additional SPC into the molds. A possible method of avoiding this problem would be to make the molds higher than necessary, then cut the samples to size after removal from the mold.

After cooling for 18 hours, the MCC-1 leach testing and impact testing samples were removed from the molds and examined (the compressive strength samples remained in the molds until needed for later tests). The 25.4 mm diameter by 25.4 mm high impact test samples were removed from the molds with little trouble. However, the 9.53 mm diameter by 9.53 mm high MCC-1 leach testing samples were more difficult to remove, as evidenced by the destruction of one as it was removed from the mold. The top and bottom of each sample were then ground flat, using 240 grit paper (with water cooling). The impact samples had very little subsidence, but the leach samples had significant subsidence and considerable material was removed to get a smooth surface (the smallest MCC-1 sample was ground to less than 6.10 mm in height). All the samples exhibited some chipping and cracking around the edges from handling. Experience indicates that this is an unavoidable part of processing. After preparation, four leach specimens and five impact specimens were judged to be suitable for testing.

5.2 IEB and IEB4

5.2.1 Arc Melter Equipment Description

A DC arc melter was used to make the IEB and IEB4 melts. A brief description of the equipment is given here, for more details see Kong et al.[23] and Eddy et al.[24] The capacity of the melter is approximately 20 kg, with a maximum power of about 40 kW. The melter uses two graphite electrodes with sustained submerged arcs near the melt surface as shown in Figure 1. In the usual operating mode, the electrodes are close to or just within the melt with short arcs occurring between the electrodes and the melt. The current passing through the relatively high resistance melt results in a Joule-heating mode with small arc radiation losses to the chamber. The arc gap above the melt can be continuously adjusted by a stepper motor to maintain a stable arc operation.

The water-cooled crucible assembly has a removable stainless steel crucible insert that can be lined with a castable mortar or a refractory liner. An example of waste forms produced in the melter with the refractory liner is shown in Figure 2.

5.2.2 Preparation of IEB and IEB4 Final Waste Forms

The IEB and IEB4 samples were prepared from a mix of 40 wt% RWMC soil with 60 wt% simulated waste. In addition, 1 wt% each of the oxides of Pb, Zn, Cd, Cr, Cs, Ce, and Sm was added to the mixture to determine the behavior of trace metals during processing and in the final waste form. Specific waste form compositions are shown in Table 6; details in the preparation of each IEB or IEB4 waste form are discussed below.

The initial plan was to melt 9 kg batches of each specified composition and produce waste forms thick enough that monolithic compression, fines generation upon impact, and MCC-1 leach testing samples could be removed using a diamond coring tool. However, it was found that the glass monolith was too stressed for intact slag samples to be obtained via coring. As a result, only PCT samples could be taken from the original slag melts.

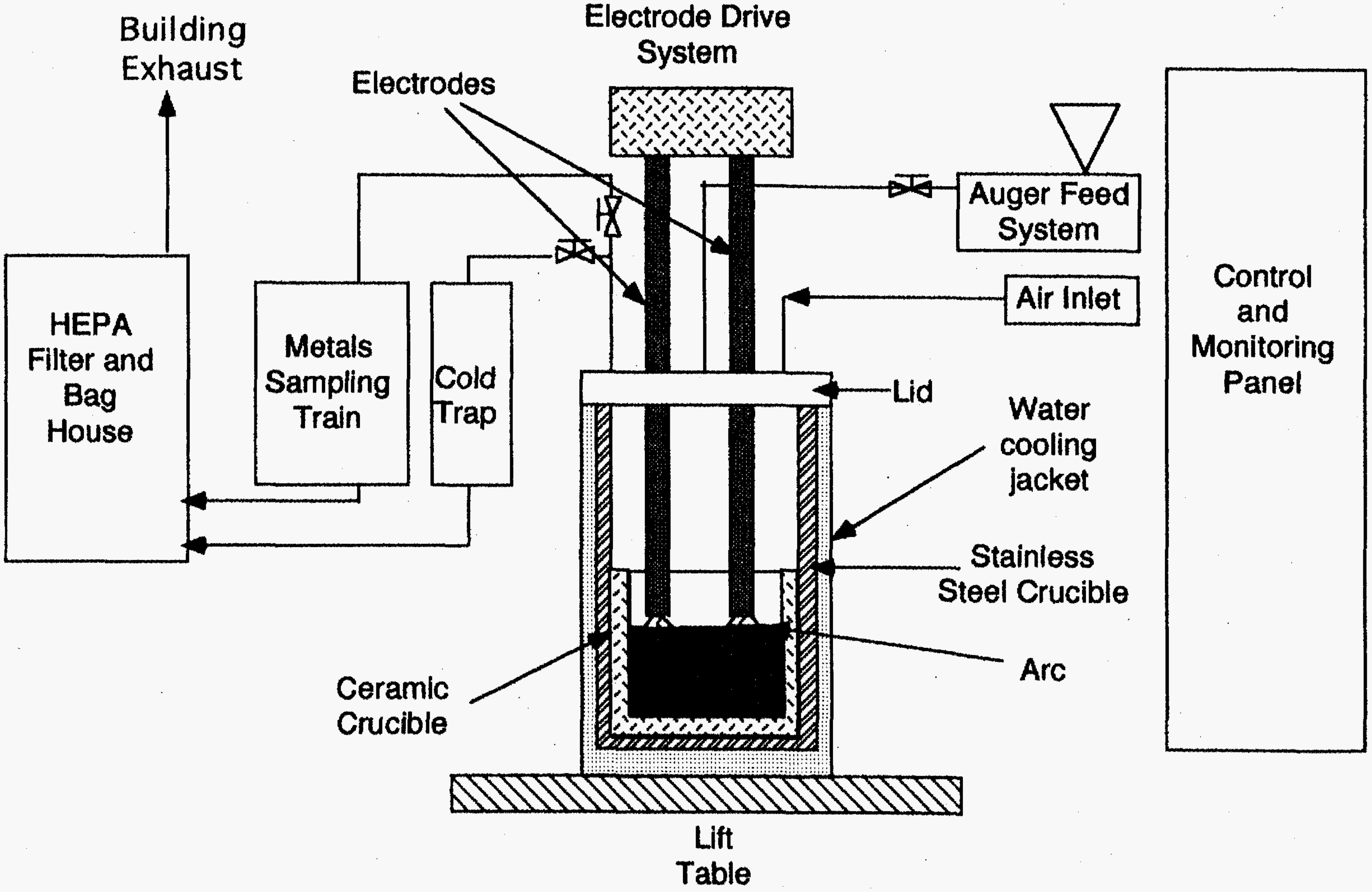

Figure 1. Schematic of the modified DC arc melter system.

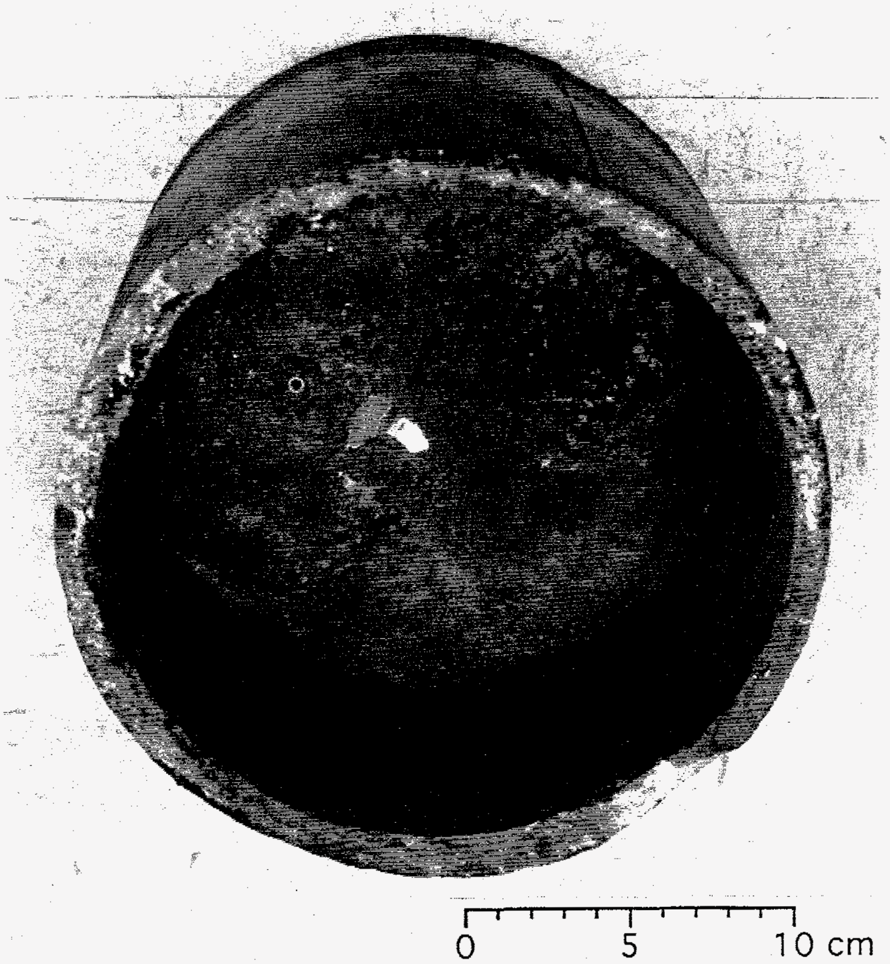

Figure 2. Photograph of IEB/A-40 (SC) waste form produced during the PSPI proof tests. The waste form is typical of all SC materials produced.

Table 6. IEB and IEB4 waste component compositions, as mixed (weight percent).

Waste component	SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	CeO_2	Sm_2O_3	Cr_2O_3	Cs_2O	CdO	PbO	ZnO
RWMC soil	65.4	12.5	4.8	9.6	2.5	1.5	2.9	0.7	---	---	---	---	---	---	---	---
IEB/A Waste Form (60 wt% waste loading)																
Avg. Waste (A) Comp.	38.0	7.4	34.5	8.3	4.6	4.8	2.4	---	---	---	---	---	---	---	---	---
IEB/A w/o additives	51.0	10.3	19.6	9.7	3.5	3.2	2.6	0.3	---	---	---	---	---	---	---	---
IEB/A w/ additives	47.4	9.6	18.2	9.0	3.3	3.0	2.4	0.3	---	1.0	1.0	1.0	1.0	1.0	1.0	1.0
IEB/S Waste Form (60 wt% waste loading)																
Series 743 (S) Comp.	35.4	4.8	40.9	14.7	3.5	0.3	0.4	---	---	---	---	---	---	---	---	---
IEB/S w/o additives	47.4	8.1	26.3	12.9	3.1	0.9	1.4	0.2	---	---	---	---	---	---	---	---
IEB/S w/ additives	44.1	7.5	24.5	12.0	2.9	0.8	1.3	0.2	---	1.0	1.0	1.0	1.0	1.0	1.0	1.0
IEB4/A Waste Form (60 wt% waste loading)																
Avg. waste (A) Comp.	38.0	7.4	34.5	8.3	4.6	4.8	2.4	---	---	---	---	---	---	---	---	---
IEB4/A w/o additives	45.9	9.3	17.6	8.7	3.2	2.9	2.3	5.0	5.0	---	---	---	---	---	---	---
IEB4/A w/ additives	42.7	8.6	16.4	8.1	3.0	2.7	2.1	4.7	4.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 6. (continued).

Waste component	SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	CeO_2	Sm_2O_3	Cr_2O_3	Cs_2O	CdO	PbO	ZnO
IEB4/H1 Waste Form (60 wt% waste loading)																
RFP Series 741 (HI) Waste Comp.	25.1	7.0	30.2	12.5	3.0	16.0	2.5	---	---	---	---	---	---	---	---	---
IEB4/H1 w/o additives	37.1	8.3	18.0	10.2	2.5	9.2	2.7	5.0	5.0	---	---	---	---	---	---	---
IEB4/H1 w/ additives	34.9	7.8	16.7	9.6	2.4	8.6	2.5	4.7	4.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0

A second approach for fabricating the monolithic samples involved extracting the molten slag from the melt via a quartz tube. However, the tube diameters required were too large to draw and maintain the sample. As a result, the test specimens had to be produced by remelting the fractured slag in quartz tubes in an electric resistance furnace.

Two different rates of cooling were used for the slag melts. For the fast cooling (FC) rate, the water continued flowing in the cooling jacket after the DC arc was turned off. This resulted in a cooling rate of about 1300°C/h between 1200 and 900°C.[a] For the slow cooling (SC) rate, the cooling water was drained from the jacket after the arc was extinguished. This resulted in a cooling rate of 780°C/h between 1200 and 900°C. Figure 3 shows the fast cooling rate for the IEB/S slag and the slow cooling rate for the IEB/A slag; similar slow cooling rates were used for the IEB4/A and IEB4/H1 slags. Both rates of slag cooling are higher than the conditions expected to be encountered in pilot-scale processing.

The monolithic waste form samples prepared in the electric resistance furnace were heat treated (HT) to increase the amount of crystallization in the samples and to relieve stress. The heat treatments are needed to promote the growth of durable crystals in IEB/IEB4 samples.[b] The heat treatment consisted of remelting the fractured slag at 1400°C for 1 h, followed by a 16 h soak at 1200°C, a slow furnace cool (180°C/h) to 700°C, a soak at 700°C for 2 h, and a furnace cool to ambient temperature. A schematic drawing of this schedule is shown in Figure 4. The 1200°C thermal soak temperature was selected based on previous studies.[19,20] The 180°C/h cooling rate between 1200 and 700°C is similar to the predicted cooling rate at the center of an uninsulated 55 gal drum of IEB, which was calculated to cool at 194°C/h through the 1200 to 900°C range.[c] As a result, the HT glass samples are expected to be more representative of actual FWF cooling conditions than either the FC or SC glass samples.

5.2.2.1 IEB/A

The mix was melted in a refractory liner in the DC arc melter for 70 min at 15 to 20 kW and slow cooled (see 5.2.2). A temperature of 1622°C was reached before cooling. After cooling, it was found that the slag had foamed, forming a porous crust without melting the entire oxide mixture. As a result, a second melter run (90 min at ~17 kW) had to be performed. This melt reached 1700°C, before it, too, was slow-cooled. The heat-treated samples were then prepared in a furnace from fragments of the second melt.

5.2.2.2 IEB/S

Ten kilograms of the IEB/S composition were melted without a refractory liner. The mix was heated for 43 min at 15 to 20 kW, and a temperature of 1600°C was attained. There was a large number of bubbles in the

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[a] This temperature range was selected because no crystals will grow until the liquidus is reached (estimated to be between 1250 and 1225°C) and crystal growth is slow below 900°C, so very little additional structural change was expected in the short time remaining until room temperature was reached.

[b] Because of the additional heat treatments, PCT testing was performed on the HT samples, as well as FC and SC samples, to evaluate how different cooling rates affect the leachability of the waste form.

[c] Private communication, J. E. Surma, PNL, April 5, 1994.

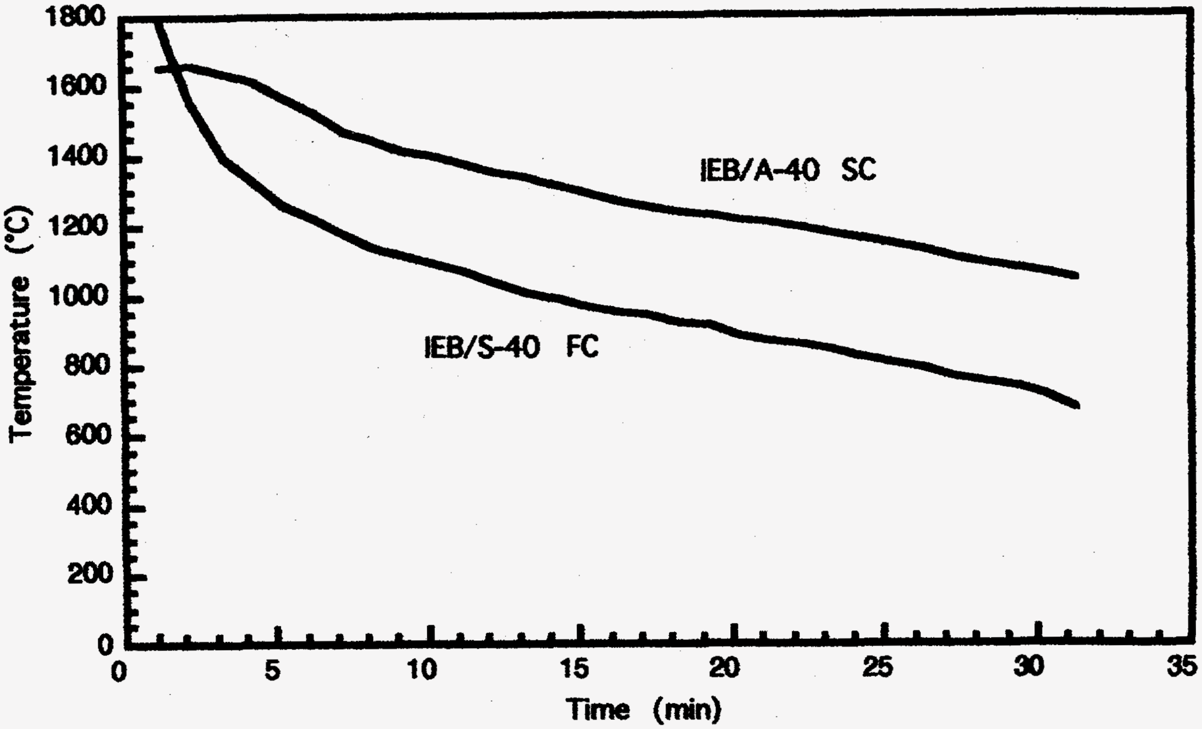

Figure 3. Comparison of the SC and FC rates for IEB/A-40 and IEB/S-40, respectively.

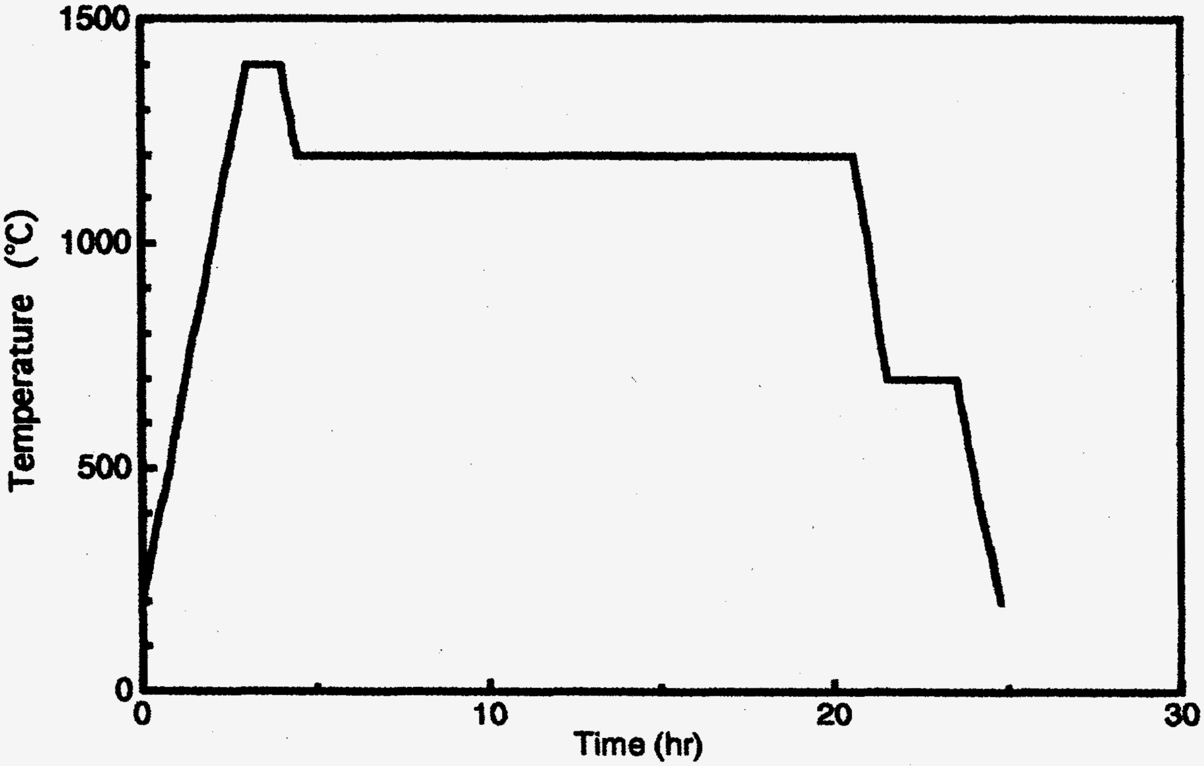

Figure 4. Schematic diagram of the heat treatment schedule used for the PSPI waste form preparation.

solidified slag, so it was fractured and remelted (105 min) at reduced power. The melt reached 1740°C during this run. The melt was fast cooled (see 5.2.2).

5.2.2.3 IEB4/A

The mixture (9 kg) was melted in a refractory liner. After 20 min, however, severe bubbling forced the shut down of the arc. The mixture was remelted. Upon cooling, it was found that the slag was still porous and contained unmelted material. Therefore, a third run of 135 min at 10 kW was performed. The resultant slag was slow cooled in accordance with Section 5.2.2.

5.2.2.4 IEB4/H1

Nine kilograms of the IEB-4/H1 composition were melted at 12.7 kW in a refractory liner. Foaming also interrupted this run. Several times the melter was turned off and the slag pushed back into the melt before continuing operation. After 2.5 h, foaming ceased and a total melt was achieved. The melt was slow cooled in accordance with Section 5.2.2.

5.2.3 Characterization of IEB and IEB4 Waste Forms

Scanning electron microscopy (SEM) was used to observe the microstructure of the waste forms. Microchemical information about the phases was obtained by energy dispersive x-ray (EDXS). X-ray powder diffraction (XRD) was used to identify crystalline phases in the waste forms. Ferrous-to-total iron ratios were determined to obtain information on the redox environment for each IEB and IEB4 waste form.

SEM and EDXS analyses were performed with an AMRY Model 1813 instrument. The samples were cut, polished, and carbon coated for both SEM imaging and microchemical analysis. EDXS spectra were collected using a Kevex Delta 5 spectrometer system. The spectral data were analyzed using the "Extended phi-roe-z" and "Magic V" software programs.

XRD was performed with an automated Philips Model 1729 diffractometer. Samples were prepared by grinding to <200 mesh. The data were automatically compared to the Powder Diffraction File by computer to identify the crystalline compounds present.

Ferrous iron was determined by dissolving one aliquot of a sample in a hydrofluoric/hydrochloric acid mixture, then titrating the solution with cerous sulfate to precipitate the ferrous iron. Total iron was determined on a second sample aliquot that was dissolved in a hydrofluoric/perchloric solution, then analyzed using ion-coupled plasma spectroscopy (ICP) analysis. The ferrous-to-total iron ratio was then computed from these data. These analyses were performed by CELS-Corning Laboratory Services, Corning, New York.

5.2.3.1 Melt Compositions

The bulk compositions of the vitrified melts differed somewhat from the reference compositions identified in Table 6, primarily due to the partially volatile nature of the Cs, Cd, and Pb additives during high temperature vitrification. A "general area" EDXS scan was used to determine an "average" chemistry of the area in view. Although relatively accurate, "general area" EDXS scans are only semi-quantitative and are not able to detect elements at concentrations below 0.10%. In addition, the scan covers a relatively small area. It is recommended that the more quantitative ICP compositional analysis, when available, be used to normalize the MCC-1 and PCT leach data.

The "semi-quantitative" data from EDXS scans of the IEB and IEB4 melt samples are given in Table 7. The "general area" scans are given in the top row of each block. With regard to specific oxides, SiO_2 is 18-29% higher than expected, FeO is lower, and CdO is relatively absent. Nevertheless, the balance of oxides are within the range expected, and the differences are not significant enough to affect waste form behavior. Table 7 also includes data from spot analyses of each waste form. These analyses, coupled with the XRD plots, enabled identification of the various crystal species that formed from the cooling melts.

5.2.3.2 Microstructure and Mineralogy

None of the crystalline phases identified had a precise compositional match with reference XRD patterns. Rather, the phases were identified based on their similarity to those patterns. The impurities in the crystalline phases may skew the XRD peaks so that the patterns only vaguely resemble those produced by a high-purity reference material. Examples of the phases are shown in Figures 5 through 8. The numbers in each figure indicate the locations of the spot analyses that are summarized in Table 7.

The samples exhibited similar phases regardless of the cooling conditions, with spinel, pyroxene (e.g., augite), and residual glass present in each case. Zirconia and zirconolite were present in IEB4, which was expected, but the amount of zirconolite was small and its presence could not be confirmed by XRD.

Plagioclase, a crystalline phase normally found in natural basalts, is desirable in glassy waste forms because it develops at the expense of the residual glass phase, forming a crystalline phase that has improved mechanical durability over glass.[33] In addition, it may induce zirconolite formation by increasing the concentration of zirconia and titania in the glassy phase of the waste form. However, plagioclase was not detected in any of the SC or FC specimens. Its absence was attributed to two factors: 1) the high temperatures attained during melting in the arc furnace, and 2) the excessive rate of cooling below the liquidus temperature (estimated at 1200 °C).

Normally, the crystals that remain in the liquid after heating serve as nuclei upon which new crystals may grow when cooling. Submicroscopic crystal remnants may persist above the liquidus temperature, but these remnants have dissolved completely at arc melting temperatures above 1300 °C.[34] After the remnants have dissolved, it is difficult to initiate crystallization unless the melt is cooled very slowly (<2 °C/h), or unless the resulting glass is reheated from room temperature to an elevated temperature suitable for crystal nucleation and growth.

While the rate of cooling was too rapid in each case to enable development of plagioclase, it was sufficiently slow to crystallize spinels and pyroxene. In general, the formation of spinels has little or no effect on leachability, while the formation of pyroxenes may cause a slight increase in the rate of dissolution of the remaining glassy components. Augite crystal formation may increase the concentration of sodium in the less durable glassy phase while decreasing calcium, thereby decreasing the residual glass phase durability. The effect of augite formation on IEB/IEB4 leach resistance needs to be quantitatively determined.

Most of the pyroxenes in Figures 5 through 8 appear to be dendritic crystals that developed during rapid cooling. Pyroxene will transform from dendrites into blocky crystals during long holding times or at slow

Table 7. EDXS and XRD analytical data for IEB and IEB4, after melting (weight percent).

Sample ID	Photo ID	SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	CeO_2	Sm_2O_3	Cr_2O_3	Cs_2O	ZnO
IEB/A-SC	**0036**	55.8	11.2	15.6	6.9	3.0	2.8	1.9	0.39	1.1	.55	.46	0.37	—	—
glass	(1)	58.8	13.9	14.6	2.6	??	2.7	2.6	0.48	1.8	1.6	1.0	—	—	—
augite	(4)	54.0	4.6	21.3	11.7	7.3	—	.31	0.27	—	.10	.50	—	—	—
chromite	(2)	1.9	7.4	31.2	0.21	4.6	—	—	0.45	—	—	—	53.5	—	.69
glass II	(3)	49.3	9.7	23.6	6.3	—	2.3	1.0	0.89	2.0	2.3	2.5	—	—	—
IEB/A-HT	**0087**	56.0	10.9	15.9	6.9	3.0	2.7	1.9	0.36	1.1	.51	.46	0.26	—	—
glass	(1)	59.5	15.7	11.9	1.8	—	3.3	2.9	0.50	1.9	1.7	.87	—	—	—
augite	(2)	54.2	6.4	19.0	10.7	6.8	—	.66	0.31	1.2	.26	.39	—	—	—
chromite	(3)	1.7	6.7	30.3	0.17	4.1	—	—	0.27	—	—	—	55.9	—	.85
glass II	(4)	44.2	9.1	35.3	1.0	—	.68	1.6	1.3	2.4	2.6	1.7	—	—	.18
IEB/S-FC	**0010**	54.3	8.5	21.6	11.4	—	.55	1.2	0.26	—	.41	.53	0.81	.41	—
glass	(1)	53.9	14.0	19.7	4.8	—	1.2	2.5	0.30	—	1.8	.70	—	.73	.39
augite	(2)	54.7	6.9	18.0	12.7	5.5	.34	.78	0.24	—	.25	.25	—	.18	—
Cr spinel	(3)	1.9	7.8	29.7	0.31	4.9	—	—	0.15	—	—	—	55.3	—	—
IEB/S-HT	**0095**	57.1	8.7	20.1	11.0	—	.46	1.3	0.21	—	.57	.43	—	—	—
glass	(5)	63.7	13.7	11.8	3.5	—	.62	2.6	—	—	.90	.51	1.3	1.3	.07
glass +? mix	(2)	59.3	13.2	12.3	3.7	—	1.0	2.3	—	1.3	3.2	1.3	1.7	.63	—
augite	(1)	53.7	4.5	18.0	16.4	6.7	—	.36	—	—	.12	.23	—	—	—
chromite	(3)	1.6	4.9	39.4	—	3.2	—	—	—	—	—	—	49.4	—	1.4
glass II	(4)	48.4	10.4	26.4	5.8	—	—	.61	0.58	1.7	3.0	2.0	1.0	—	.24
IEB/S-HT	**0050**	56.8	9.1	17.9	10.4	2.4	.56	1.2	0.23	—	.32	.30	0.54	.23	—
glass	(3)	61.8	11.3	14.5	7.4	—	.79	1.8	0.32	—	.92	.76	—	.37	—
augite	(2)	59.9	9.5	15.4	9.9	1.8	.38	1.2	0.17	—	.72	.56	—	.32	.07
magnetite	(1)	1.8	3.8	79.1	0.19	2.9	—	—	0.55	—	—	—	11.0	—	.61

Table 7. (continued).

Sample ID	Photo ID	SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	CeO_2	Sm_2O_3	Cr_2O_3	Cs_2O	ZnO
IEB4/A-HT	**0060**	52.0	9.3	13.5	6.6	2.2	1.6	1.6	5.6	6.4	.42	.23	—	.32	—
glass	(4)	59.6	12.4	11.4	4.0	—	3.0	2.2	3.2	2.7	.60	.28	—	.78	—
augite+glass	(1)	56.4	10.3	10.6	8.4	3.8	1.3	1.5	4.2	2.6	.36	.13	—	.47	—
augite	(6)	52.0	8.8	12.5	11.0	5.6	1.0	.9	5.0	2.6	.27	.30	—	—	—
chromite	(5)	1.7	6.8	28.5	—	4.4	—	3—	2.9	—	—	—	54.8	—	.88
zirconolite	(3)	12.9	2.3	6.6	4.4	—	—	.29	25.7	40.8	??	7.0	—	—	—
zirconia	(2)	—	—	0.76	—	—	—	—	4.9	94.3	—	—	—	—	—
zircon	(NP)*	37.7	—	—	—	—	—	—	—	62.4	—	—	—	—	—
IEB4/H1-HT	**0237**	41.1	10.4	14.8	9.0	2.1	7.3	1.9	5.6	6.0	.57	.44	0.41	.30	—
glass	(1)	43.9	10.8	14.1	9.9	2.2	7.1	2.0	5.1	3.6	.62	.39	0.00	.31	—
zirconia	(3)	—	—	3.6	3.2	—	—	—	3.7	86.0	.17	1.8	0.47	—	—
magnesio-chromite	(2)	—	7.1	28.7	—	4.8	—	—	3.7	—	—	—	55.8	—	—
IEB4/H1-HT	**0073**	42.3	10.8	13.5	8.8	1.9	7.4	1.8	4.8	7.3	.48	.20	0.65	.21	—
glass	(5)	52.8	13.4	12.4	4.0	—	8.6	3.4	1.5	2.4	.51	.07	—	.74	—
augite	(4)	48.0	9.5	10.2	17.1	7.4	1.5	.77	4.7	—	.61	.30	—	—	—
zirconolite	(1)	—	—	5.5	7.7	—	—	—	28.7	48.5	2.5	7.0	—	—	—
baddeleyite	(2)	—	—	0.84	0.61	—	—	—	1.4	97.2	—	—	—	—	—
ulvospinel	(3)	1.6	3.7	62.8	0.21	4.4	—	—	24.9	—	—	—	2.3	—	—

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* (NP) - Not pictured in report, but has been identified

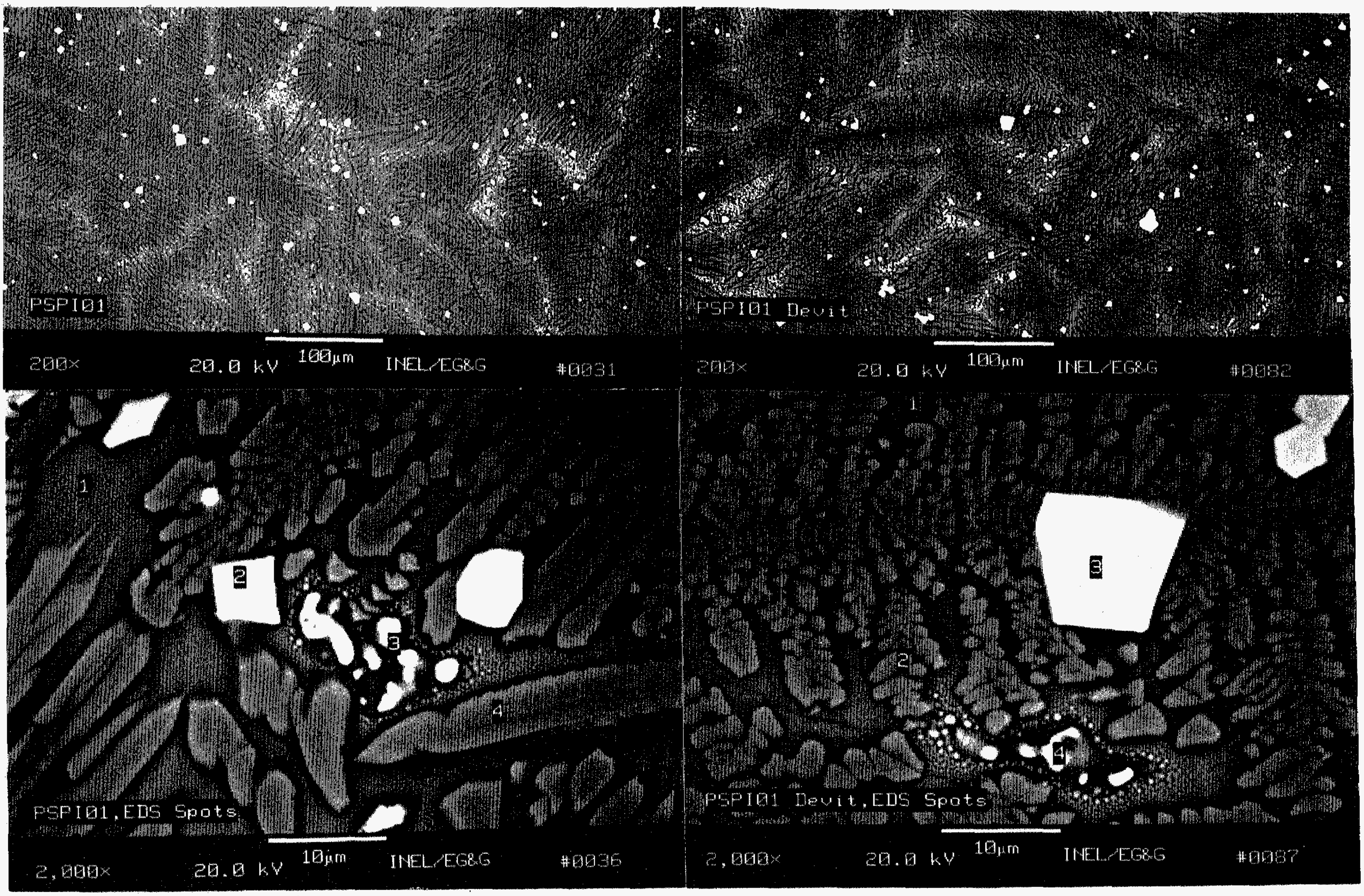

Figure 5. Microstructure of slow-cooled (#0036, left) and heat-treated (#0087, right) IEB/A-40. Photo numbers correspond to numbers given in Table 7.

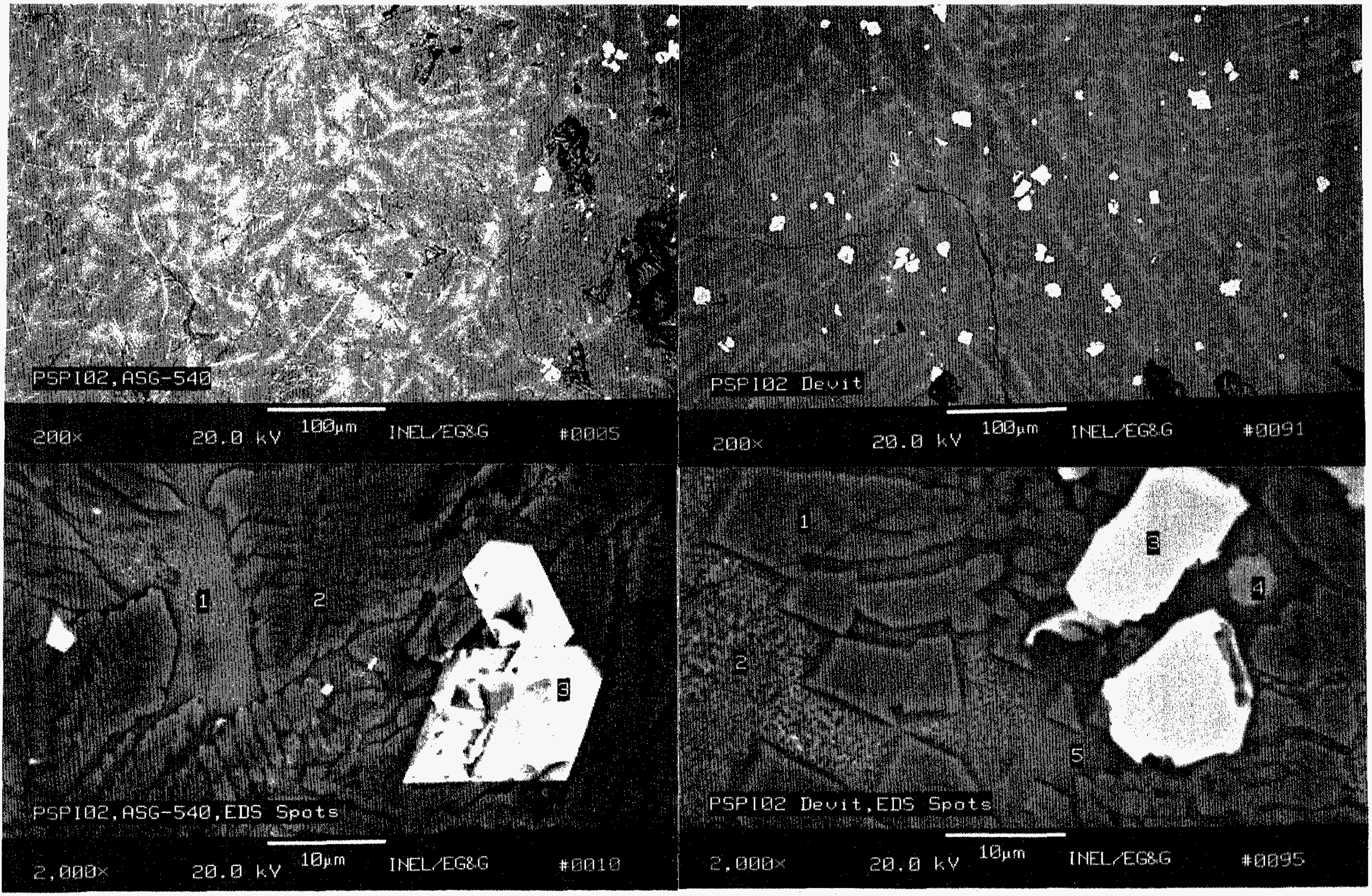

Figure 6. Microstructure of fast-cooled (#0010, left) and heat-treated (#0095, right) IEB/S-40. Photo numbers correspond to numbers given in Table 7.

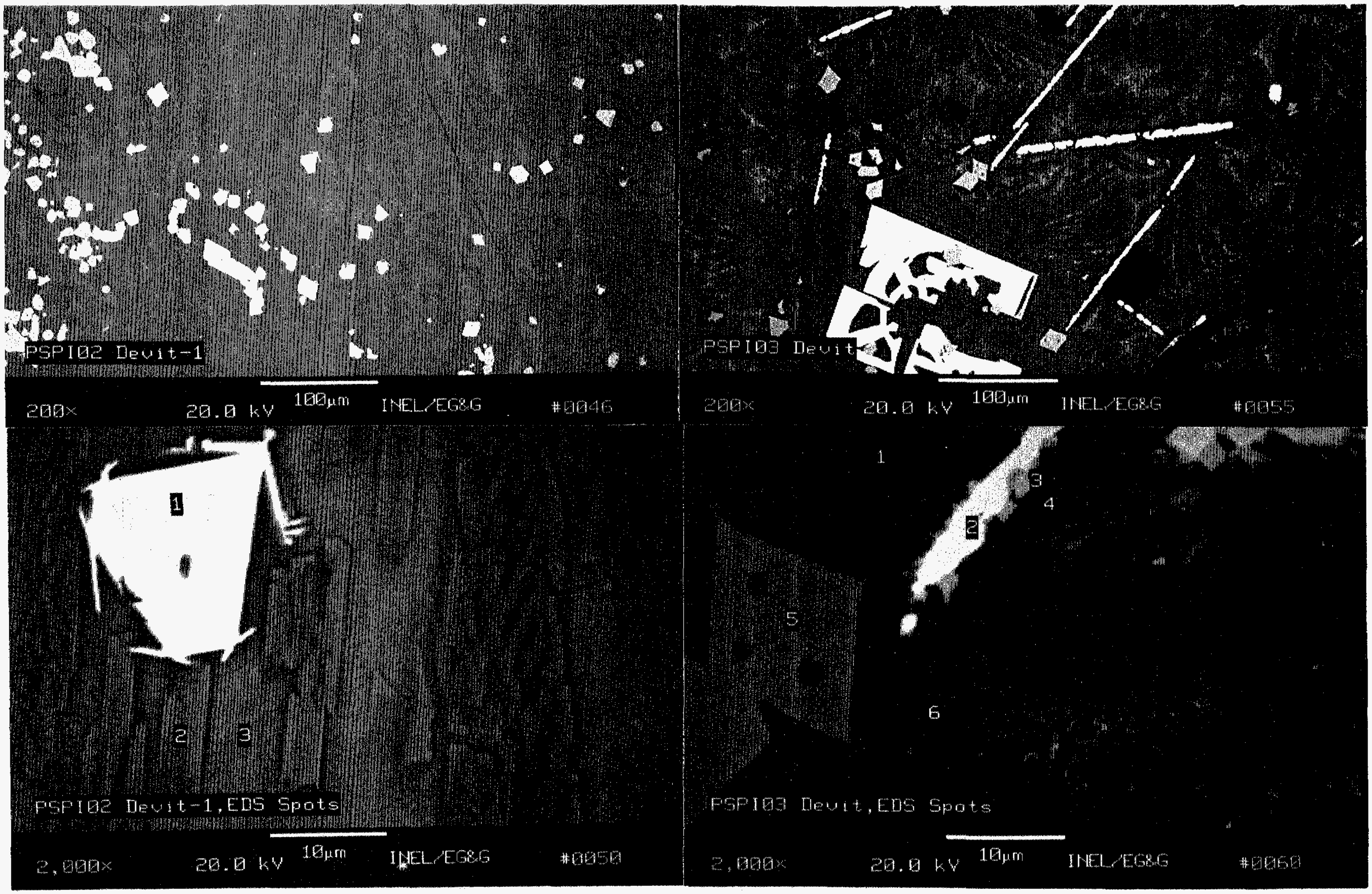

Figure 7. Microstructure of heat treated IEB/S-40 (#0050, left) and IEB4/A-40 (#0060, right). Photo numbers correspond to numbers given in Table 7.

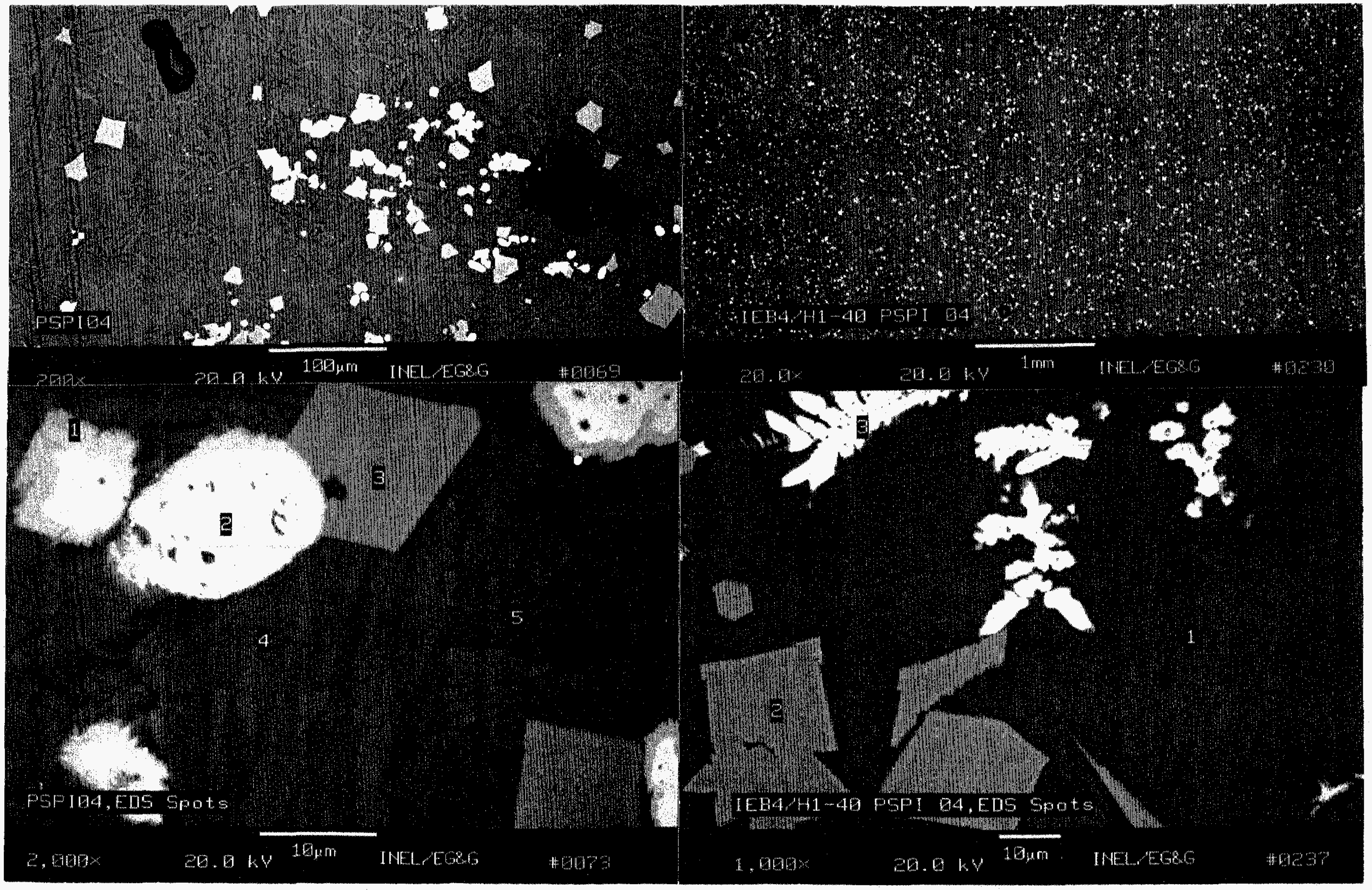

Figure 8. Microstructures of heat-treated IEB4/H1-40 (#0073, left, and #0237, right). Photo numbers correspond to numbers given in Table 7.

cooling rates below the pyroxene crystallization temperature. Examples of the blocky crystal morphology in the IEB/IEB4 waste forms are shown in Figures 6 and 7.

5.2.3.3 Redox Ratio Evaluation

The ferrous-to-total iron ratio was calculated for several specimens to determine the different redox ratios that resulted from the FC, SC, and HT melts. These results are presented in Table 8. Reduction to the ferrous ion is indicated by a ferrous-to-total iron ratio close to 1.0, while complete oxidation to the ferric ion is indicated by a ferrous-to-total iron ratio of zero. The ferrous-to-total iron ratios are markedly different depending on whether the samples were cooled in the melter (FC or SC) or heat treated. This is because the heat-treated (remelted) samples were held at elevated temperatures for prolonged periods in air, which oxidized ferrous ions (Fe^{+2}) to ferric ions (Fe^{+3}), thereby lowering the ferrous-to-total iron ratio to between 0.51 and 0.85. In contrast, the high temperature graphite electrode DC arc melter generally creates severe reducing conditions in the melt (ferrous-to-total iron ratios between 0.93 and 0.97), due to the limited amount of oxygen, and the carbonaceous materials in the electrode.

Table 8. Ferrous-to-total iron ratios for the various FC, SC, and HT samples.

	FC	SC	HT
IEB/A	---	0.97	0.51
IEB/S	0.95	---	0.56
IEB4/A	---	0.95	0.85
IEB4/H1	---	0.93	0.76

6. WASTE FORM DURABILITY TESTING

6.1 Mechanical Durability

The compressive strength of each waste form was measured using ASTM C-39.[27] This test was designed for concrete specimens, but it can be adapted for vitrified waste forms. The specimens used for these tests were cylindrical samples, 25.4 mm in diameter and 50.8 mm high. The tests were performed on three samples of each waste form; small variations in sample height were corrected for in the compressive strength calculations.

The compression test requires that the ends of the samples be within 0.05 mm of parallel and not more than 0.5 ° from perpendicular to the axis of the sample. Considerable difficulty was encountered in achieving this. The ends of the cylindrical samples were cut using a diamond saw. Then the sample was clamped in a V-block fixture and the ends were ground parallel with a 120 grit diamond surface grinding wheel. After grinding, the faces of all the samples were parallel to within 0.01 mm and perpendicular to within 0.5 °.

The samples were then loaded in a rigid frame between two 8 mm thick pieces of copper, which deformed easily and distributed the load uniformly across the face of the specimen. The specimen was compressed axially by a hydraulic ram at a rate of 10 μm/s until failure occurred. The compressive strength was calculated as the maximum compressive load divided by the cross-sectional area of the specimen.

Impact testing, for three samples of each waste form, was done according to the method given in Jardine, Reedy and Mecham.[28] Before impact, each specimen was measured and weighed. To determine actual sample volume, the diameter and length of each specimen were measured in three places. The volume of the specimen was then calculated based on the average of each dimension. The height of the drop weight was adjusted to provide the desired impact energy.

The specimens (25.4 mm in diameter and 25.4 mm high) were sealed inside a hardened steel chamber, with a hardened steel rod (slightly smaller diameter) placed on top of the sample (see Figure 9). The specimens were then impacted by a falling weight with the prescribed energy of 10 J/cm^3 (10.4 kg with an approximate drop height of 1.26 m).

The material collected from the impact chamber was weighed to ensure that no material had been lost. Then it was mechanically sieved to <250 μm. A sample of the <250 μm material was analyzed in a full range particle analyzer. The amount of respirable fines is of particular interest; since a respirable fine has been considered either a particle less than 10 μm in diameter[35] or less than 15 μm in diameter,[36] the amount of material below each of these limits was measured. The percent of fines was calculated from those values.

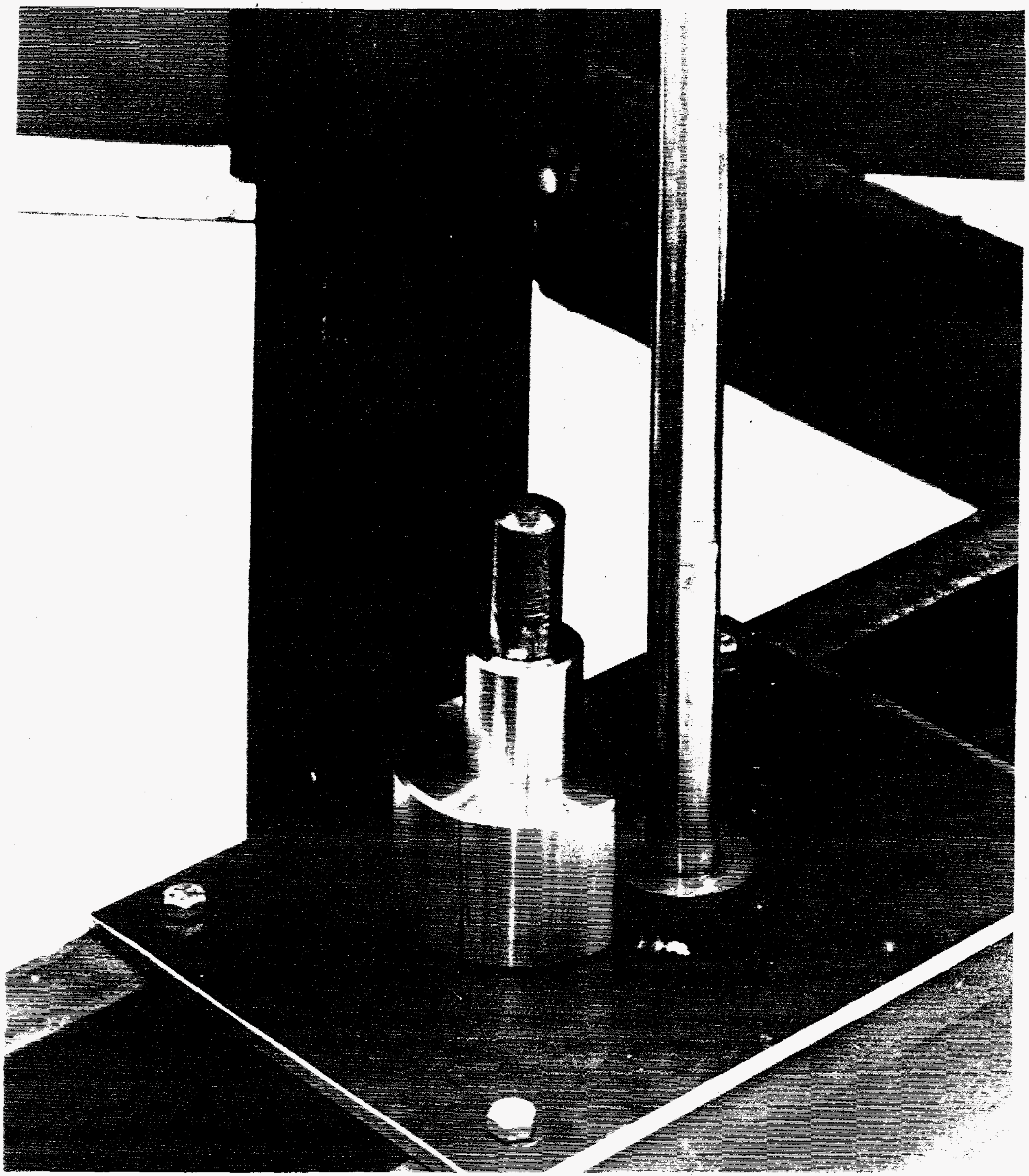

Figure 9. Specimen chamber used for the fines generation upon impact test.

6.2 Chemical Durability—Leach Resistance

To evaluate chemical durability, the primary property needed is leach resistance.[d] Leach tests that have been used in evaluating final waste forms are ANS 16.1, MCC-1, and PCT. A brief description of each of these is given below.

ANS 16.1[37] is an NRC procedure used to measure the leachability of various radionuclides from porous waste forms. The leachate is changed continually, in a manner that limits its change in pH. This test is primarily used on waste forms that have a significant potential for mass diffusion, such as PCC, FUETAP, or SPC.

MCC-1[38] measures the elemental mass loss from a sample as a function of surface area and time. The test uses a waste form monolith, of known surface area to volume ratio, that is immersed, without agitation, in silica water (pH=10), deionized water (pH=7), or brine (pH=4). The standard surface area to solution volume ratio for MCC-1 testing is 10 m^{-1}. In general, the leachates can be analyzed after 3, 7, 28, or 90 days. The 28-day, deionized water test was used in this study.

PCT[39] is a modification of the MCC-3 test[40] in which crushed material (approximate surface area to solution volume of 1855 m^{-1}) is leached for seven days in deionized water (pH=7) without agitation. Crushing the sample allows the leachate to become more quickly saturated than in the MCC-1 test, thereby approximating the waste form's long-term leach rate. The leachate is analyzed for bulk and hazardous components to determine their relative leachability. While the PCT test is the crushed-sample leach test of choice, it is acceptable to supplement the PCT data base with data from previously performed MCC-3 tests where necessary.

While it was desired, for comparison purposes, to find one leach resistance test that would be applicable to all of the final waste forms, a number of problems were identified which prevented this approach. For example, the results from MCC-1 and PCT testing of PCC and FUETAP would be biased by the extremely basic nature of the cement material, which causes precipitation of any previously dissolved leachates as the solution reaches a pH >10.5. Once the precipitated leachates have been filtered out (per MCC-1 and PCT standard test procedures), the results may erroneously indicate that the cementitious waste forms have a better product quality than the glassy ceramics, even though the cement waste forms are known to be more rapidly dissolving. The MCC-1 test is also inappropriate for PCC and FUETAP because of the large amount of mass diffusion that results from the porous nature of the cement waste forms (resulting in an unknown surface area to volume ratio, important in evaluating leachability). Conversely, PCT leach testing does not give an adequate representation of the product quality of SPC, FUETAP, or PCC, since crushing the material sample for the test eliminates the encapsulating effect of these waste forms, and thus biases their results negatively relative to those of the glassy ceramics. For these reasons, standard practice was followed in that MCC-1 monolithic leach testing was only used for the nonporous waste forms (SPC, BSG, and the ASGs [ISV glass, IEB, IEB4]), while PCT testing, also suitable for nonporous waste forms was only performed on the glass/ceramic materials that involve chemical incorporation of the waste (BSG and the ASGs) and not on

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[d] The waste form must also be able to pass TCLP requirements. However, the TCLP tests are environmental pass/fail tests and are not generally used for comparisons. Therefore, there is no need to include TCLP test results in this evaluation of final waste forms. It should be a requirement of all prospective candidates for the PSPI contract, however.

SPC (physical encapsulating media), and that ANS 16.1 was only used for the porous waste forms (PCC and FUETAP).

The elements that are typically recommended to be analyzed for when evaluating the leach resistance of waste form materials are Pu, U, actinide surrogates (Ce, Sm), Cs, Na, Ca, and Si. However, existing leach data from other components, such as K or Sr, may also be used to supplement the data when results for certain components, such as Na or Ca, are unavailable. The procedures used for this study are described below.

The MCC-1 leach tests were performed, in duplicate, on monolithic SPC samples and on heat-treated monoliths of IEB and IEB4. Testing was performed by Pacific Northwest Laboratory (PNL) in Richland, Washington. Each sample monolith was suspended in deionized water, within a sealed Teflon™ container, for 28 days at 90°C without agitation in accordance with the latest version of the MCC-1 test procedure. The dimensions of the SPC sample monoliths were 9.5 mm diameter x 9.5 mm long, while the dimensions of the IEB and IEB4 sample monoliths were 6.4 mm x 6.4 mm x 12.7 mm. Following leaching, replicate chemical analyses were performed on the leachate from each waste form sample by inductively coupled plasma atomic emission spectroscopy (ICP-AES). In addition, samples of each waste form were analyzed via either X-ray fluorescence (for the SPC samples) or ICP-AES (for IEB and IEB4 samples) to determine their initial bulk compositions. This was necessary to provide normalized leach data (in g/m^2 for 28 days) for various elements in each waste form.

PCT tests were performed by CELS-Corning Laboratory Services, in Corning, NY, on fast-cooled, slow-cooled, and heat-treated IEB and IEB4 samples. The leachates were analyzed using either ICP-AES or ICP-mass spectroscopy (ICP/MS) to determine the relative leachability of Cs, Na, Ca, Cd, Ce, Pb, Si, Sm, and Zn. The compositional analyses of the IEB and IEB4 waste forms performed for the MCC-1 tests were used to normalize the results of the PCT tests (in g/m^2 for 7 days).

6.3 Chemical Durability—Compositional Flexibility

Compositional flexibility addresses how variations in waste loading and composition affect the properties of the waste form. This issue is only applicable to IEB and IEB4. Due to their primarily encapsulating nature, the chemical compositions of the cementitious waste form materials (PCC, FUETAP, SPC) generally are not significantly affected by the composition of the encapsulated waste, so only maximum waste loadings need to be established (except for those cases where a chemical reaction may occur between the cementitious material and the waste materials). Although waste composition does affect all the glass/ceramic compositions, compositional variations were not evaluated for BSG and ISV glass in this study due to the known specific compositional definitions/constraints of their respective processes.

Determining the acceptable composition range and compositional flexibility relative to the range of potential waste feed compositions is important in evaluating the IEB and IEB4 waste forms because relatively high waste loadings are expected for these FWFs and the TSA waste is far from homogeneous. Compositional flexibility (allowable composition range) for IEB/IEB4 is primarily determined as a function of allowable (desired) leach resistance, though effects of composition on compressive strength and fines generation upon impact could potentially be factors.

The effects of waste stream composition and the addition of glass formers (soil) on IEB/IEB4 have been considered in previous studies.[1,11,41] Of the seven potential waste streams for evaluating IEB and IEB4 compositional variations, the only major waste streams needing to be considered were the A, S, and H1 compositions. The A-composition provides an evaluation of the average resulting waste form, while the S, and H1 compositions provide an evaluation of how spikes of inorganic and organic sludge (two of the major components in waste stored at TSA) affect the mechanical and chemical durability of the waste forms. The N-, M-, and P-compositions were not selected for evaluation due to their minimal volumes in the stored waste at TSA, while the H2 composition was not selected due to its similarity to the H1-composition. Project funding limited the number of compositions that could be evaluated in this scoping study to two IEB compositions (A and S) and two IEB4 (A and H1) compositions. Nevertheless, the compositional similarity of IEB and IEB4 is sufficient to allow a relatively complete scoping evaluation of potential effects of compositional variability on key indicator properties for both waste forms.

7. RESULTS OF CRITICAL PROPERTY TESTS

7.1 Compressive Strength

Compressive strength tests were performed on heat-treated samples of IEB/A, IEB/S, IEB4/A, and IEB4/H1. In addition, samples of the slow-cooled IEB/A slag were also tested to obtain an indication of the effect of cooling rate on compressive strength. Averages of the various compressive strength tests for each waste form and cooling condition are shown in Table 9 and Figure 10.

Most IEB and IEB4 waste forms tested had compressive strengths between 386 and 441 MPa. The exception was IEB/S, which at 119 MPa had only 27 to 31% of the compressive strength of the other IEB and IEB4 samples. The IEB samples also had slightly higher compressive strengths than the IEB4 samples, although the results are within a standard deviation of each other. Likewise, the heated-treated IEB/A had slightly greater compressive strength than the slow-cooled samples (430 vs. 386 MPa). The results are still close enough to be within the standard deviation of each sample, however.

A review of the raw data found that the IEB/S samples experienced more strain during testing than the other ASG samples. The increased strain implies more plasticity in IEB/S, which may have limited its stress buildup prior to failure. The results suggest that waste composition can be a significant factor in the compressive strength of IEB or IEB4.

The compressive strengths of IEB and IEB4 are significantly greater than the previously reported data for PCC (2-55 MPa), FUETAP (20 MPa) and SPC (12-69 MPa) (Table 1). The results are similar to the Koegler et al.[30] values for ISV glass (409 MPa) and slightly higher than the reported values for BSG (281-314 MPa).

7.2 Fines Generation on Impact

The initial fines generation upon impact tests were done on the SPC samples to verify the test procedure. The SPC was very resistant to impact loads because it is malleable and the impact tends to deform the SPC without pulverizing it. Particle collection was difficult because the SPC had a considerable static charge after impact and the particles tended to cling to the surfaces of the impact chamber. Dry brushing proved ineffective, so the SPC had to be collected with water.

After completing the initial impact tests, the remaining three SPC impact samples and PCC samples were tested; those results are given in Table 10. Results of the PCC impact tests are also shown in Figure 11. The heat-treated IEB and IEB4 waste forms were impact tested in the same manner. However, these waste forms appeared to be much more resistant to impact than SPC or PCC. In particular, no measurable respirable fines (<10 or 15 μm) were generated by the 10 J/cm^3 impacts. Rather, the majority of the specimens remained nearly intact and produced no particles that could be analyzed. One IEB4/H1 sample was even impacted twice, with over 11.5 J/cm^3 on the second impact (15% more than prescribed by the test). Nevertheless, very little damage was observed.

Table 9. Compressive strength of IEB/IEB4.

Waste form	Cooling rate	Compressive strength (MPa)
IEB/A	Heat treated	430
IEB/A	Slow cooled	386
IEB/S	Heat treated	119
IEB4/A	Heat treated	403
IEB4/H1	Heat treated	441

Table 10. Impact test summary for SPC and PCC.

Sample designation		weight % <15 μm	weight % <10 μm
	Sulfur polymer cement		
SPC-1		0.37	0.16
SPC-2		0.29	0.14
SPC-3		0.32	0.16
	Mean	0.33	0.15
	Standard Deviation	0.03	0.01
	Portland cement		
PCC-1		0.69	0.45
PCC-2		0.46	0.31
PCC-3		0.33	0.21
	Mean	0.49	0.32
	Standard Deviation	0.15	0.10

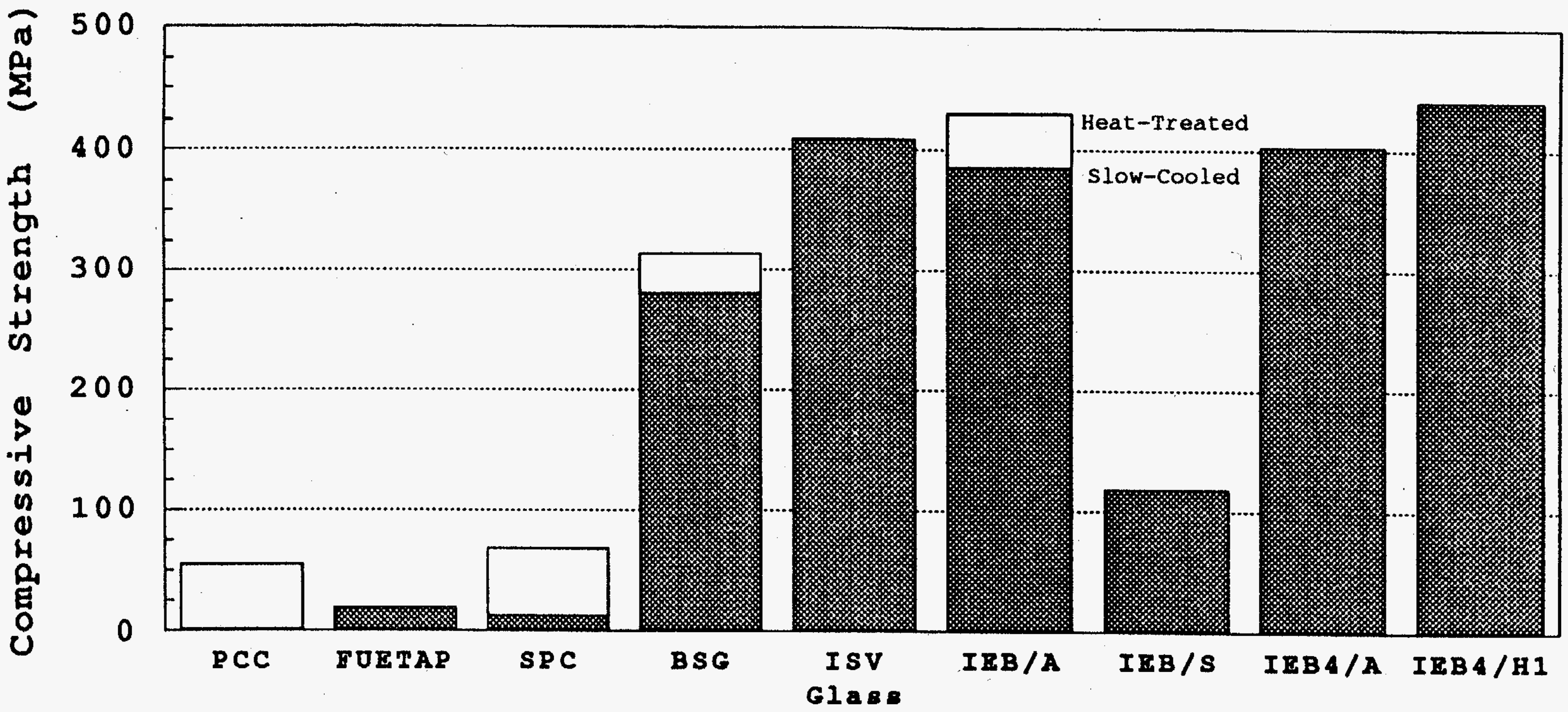

Figure 10. Compressive strength comparison.

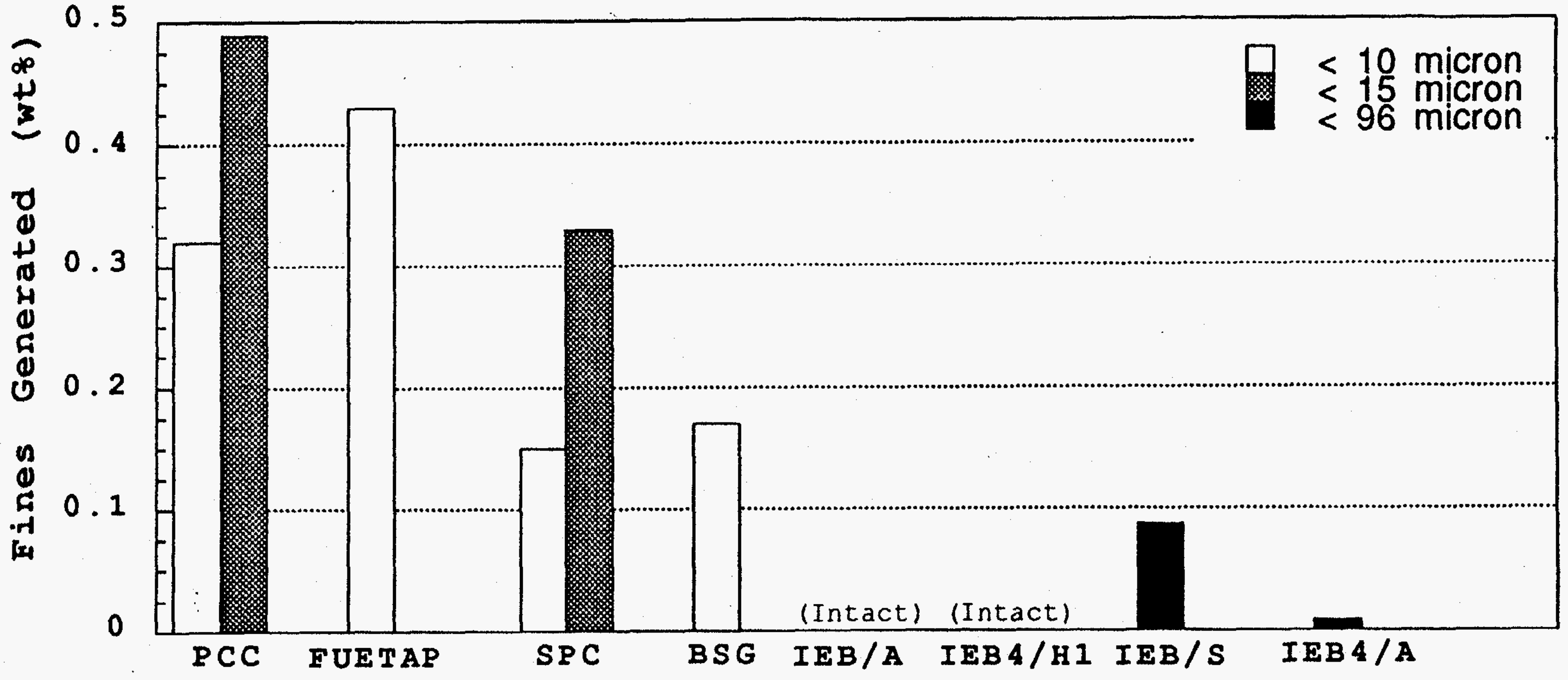

Figure 11. Fines generated upon impact.

To allow comparison of the IEB and IEB4 waste forms that did fracture on impact, the results of the impact tests are reported both as weight percent of particles below 96 μm and as the size of the smallest particle that resulted from the impact test. Results for these waste forms are shown in Table 11.

A fractured sample of each of the waste forms tested is shown in Figure 12. These test results, along with previously reported impact testing results for FUETAP and BSG,[28] showed that FUETAP and PCC were the least resistant to impact (0.43 and 0.32 wt% <10 μm, respectively), followed by BSG and SPC (0.17 and 0.15 wt% <10 μm, respectively), IEB/S (0.088% <96 μm), IEB4/A (0.008 wt% <96 μm), and IEB4/H1 and IEB/A (virtually intact). The only surprising results were the higher amount of fines generated by FUETAP than PCC, and the similar levels of fines generated by BSG and SPC. Very little is known about the previously-tested BSG and FUETAP samples, however, so the higher literature values for these waste forms may be due to differences in the way they were prepared. The PCC samples also have a relatively large standard deviation.

Table 11. Impact test summary for IEB and IEB4.

Sample designation		Weight % <96 μm	Smallest particle found (μm)
		IEB/A	
1		Intact	Intact
2		Intact	Intact
		IEB/S	
1		Intact	Intact
2		0.17	26.16
	Mean	0.088	
		IEB4/A	
1		0.0049	40.35
2		0.011	15.56
	Mean	0.008	
		IEB4/H1	
1		Intact	Intact
2		0.0000	124.45
3		Intact	

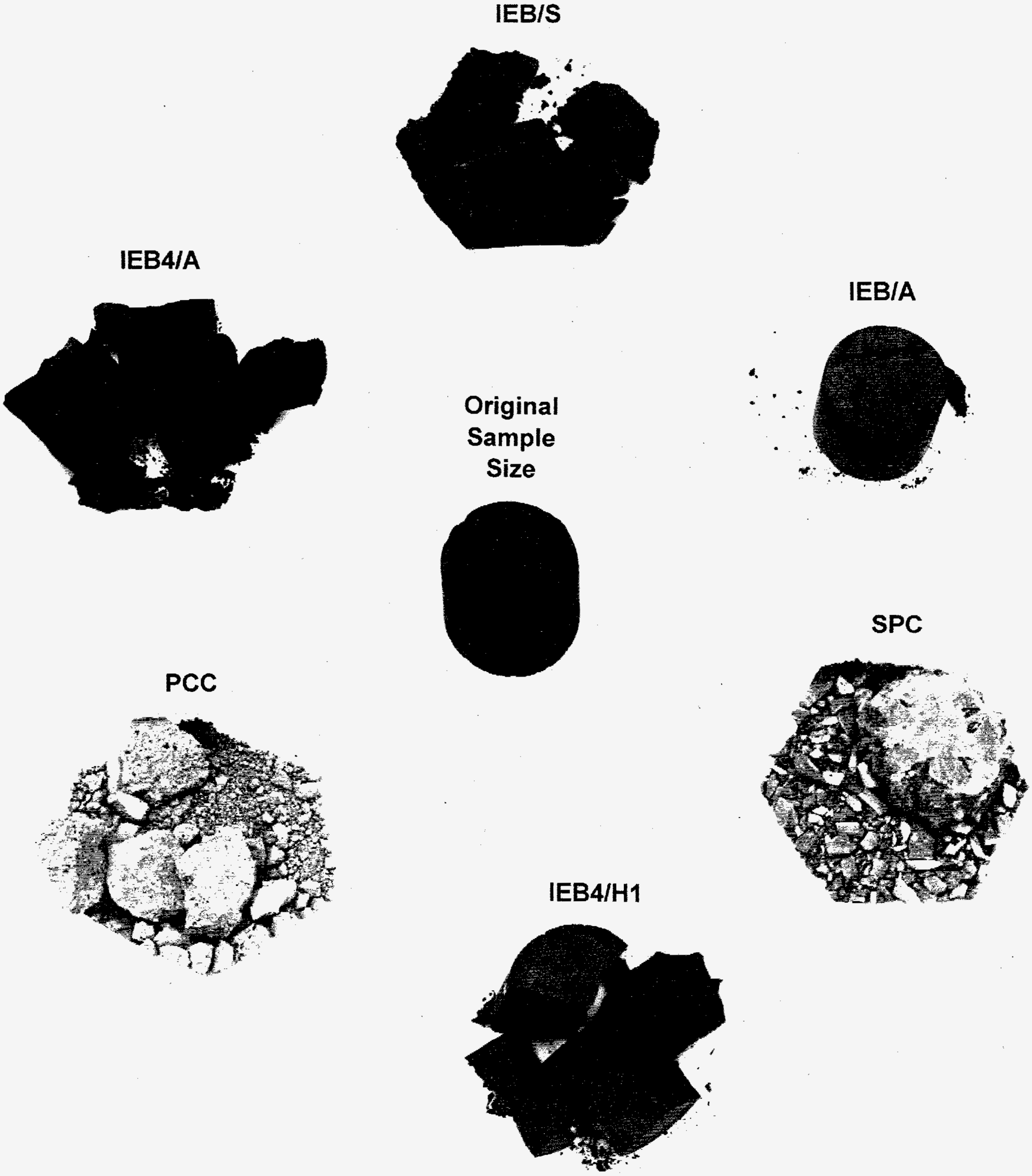

Figure 12. Final waste forms following fines generation upon impact testing.

7.3 MCC-1 Leach Test

The 28-day MCC-1 tests were conducted by Pacific Northwest Laboratory on SPC, heat-treated IEB and IEB4, and fast cooled IEB/S. The results were normalized to g/m^2 for 28 days. The MCC-1 analysis procedure used duplicate analysis of the leachates from two samples of each waste form, with a third sample used to determine the bulk composition of each waste form. However, with both the IEB/S (HT) and SPC waste forms, there was a significant difference between the leachate analyses of the two samples, indicating that the samples may have had significantly different compositions. To investigate this concern, portions of the leached IEB/S (HT) and SPC samples were submitted for compositional analysis. These results were used with the original leachate results to provide a more accurate indication of normalized MCC-1 leach rates. While it appears that there were slight compositional differences between the two samples, that is not the primary factor affecting the leach rates. Crystallization inhomogeneities may have influenced the MCC-1 leach rates for IEB/S (HT). A number of processing variables (e.g. cooling rate and redox ratio) also may have affected the results. Because of funding limitations, only a limited number of MCC-1 tests could be performed. As a result, any conclusions from this study are preliminary—further testing is needed for verification. Results of the normalized, 28-day MCC-1 leach tests are shown in Table 12; the Na and Si results are shown in Figure 13.

The IEB/IEB4 waste forms exhibited a leach resistance significantly better than that of SPC. In general, SPC leach rates are 3 to 470 times those of the IEB/IEB4 waste forms. The only discrepancies are Al (lower for SPC than IEB4/H1 and IEB/S [HT]) and Na (lower for SPC than IEB/S). Although not tested, PCC is expected to have a product durability similar to, and perhaps worse than, SPC. This conclusion is based on a comparison of ANS 16.1 leach indices for SPC and PCC (see Table 3).

Of primary interest in the IEB/IEB4 data are the relatively high leach rates of cesium and sodium compared to the literature values for IEB and ISV glass. In particular, the sodium results for the IEB/IEB4 waste forms (14-67 g/m^2) were closer to the values for SPC (74 g/m^2) and BSG (14-37 g/m^2)[6,7,8,9,10,12] than the values previously reported for IEB and ISV glass (1.4-7.8 g/m^2).[33,42] However, the IEB/IEB4 samples in this study had a waste loading of 60% and a heat-treatment schedule of 16 h at 1200°C, followed by a 180°/h cooling from 1200°C to 700°C. In contrast, the IEB samples described in the literature had waste loadings of 30 to 50 wt% and were held at temperatures of 800 to 1100°C for 19.5 to 21.5 h. Comparing the phase structures of our samples with those in the literature, it was observed that our samples contained augite (a virtually alkaline-free pyroxene), while the literature samples contained albite (an alkaline-rich plagioclase). The sodium in our samples remained in the vitreous phase, while the sodium in the literature samples was locked up in a crystalline matrix (plagioclase) that was more resistant to leaching. These results imply that a hold temperature of 1200°C is too high to form the Na-leach-resistant plagioclase in IEB/IEB4.[e]

The sodium leach rates of the IEB/S samples (both FC and HT) were significantly higher than those of the other IEB/IEB4 waste forms tested. In fact, the average sodium leach rate for the IEB/S (HT) samples (67 g/m^2) was closer to the leach rate of SPC (74 g/m^2) than the other IEB/IEB4 waste forms (14-48 g/m^2). However, the value for one of the IEB/S (HT) samples was over two times that of the other, casting doubt on

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[e] Phase structure and cooling rate information for the ISV glass literature values was unavailable. However, it can be assumed that the rate of cooling in an ISV glass melt is sufficiently slow to produce the type of crystalline structure necessary to inhibit alkaline leachability.

Table 12. Normalized MCC-1 leach rates for SPC, IEB, and IEB4 (mean g/m^2 for 28 days, standard deviation in parenthesis).

Waste form	Na	Cs	Si	Al	Ca	Ba	Pb	Mg	Fe	Ce	Zr
IEB/A (HT)	14.1 (1.1)	12.3 (8.3)	2.83 (.74)	4.82 (.32)	2.16 (.22)	2.90 (.09)	0.228 (.029)	0.09 (.11)	0.042 (.005)	0.247 (.006)	0.168 (.021)
IEB/S (FC)	48.4 (1.6)	21.8 (1.8)	3.50 (.76)	5.84 (.62)	2.15 (.21)	2.32 (.31)	0.262 (.061)	0.032 (.065)	0.03 (.01)	0.115 (.024)	---
IEB/S (HT)	67 (28)	19.8 (2.5)	6.0 (1.2)	8.26 (.49)	3.46 (.19)	4.02 (.59)	0.61 (.20)	0.022 (.026)	0.052 (.015)	0.42 (.14)	0.46 (.11)
IEB4/A (HT)	15.6 (1.9)	7.51 (.81)	3.1 (.1)	3.92 (.15)	3.01 (.03)	2.49 (.29)	0.096 (.064)	0.70 (.16)	0.09 (.12)	0.099 (.031)	0.017 (.013)
IEB4/H1 (HT)	27.6 (1.8)	20.6 (0.7)	7.8 (.5)	11.1 (.4)	3.92 (.48)	0.408 (.005)	0.43 (.01)	0.22 (.01)	0.06 (.01)	0.056 (.008)	0.02 (.004)
SPC	74.1 (6.9)	61 (14)	36 (22)	6.2 (.5)	52 (20)	---	12.0 (5.6)	10.4 (3.4)	1.92 (.59)	3.76 (-.--)	---

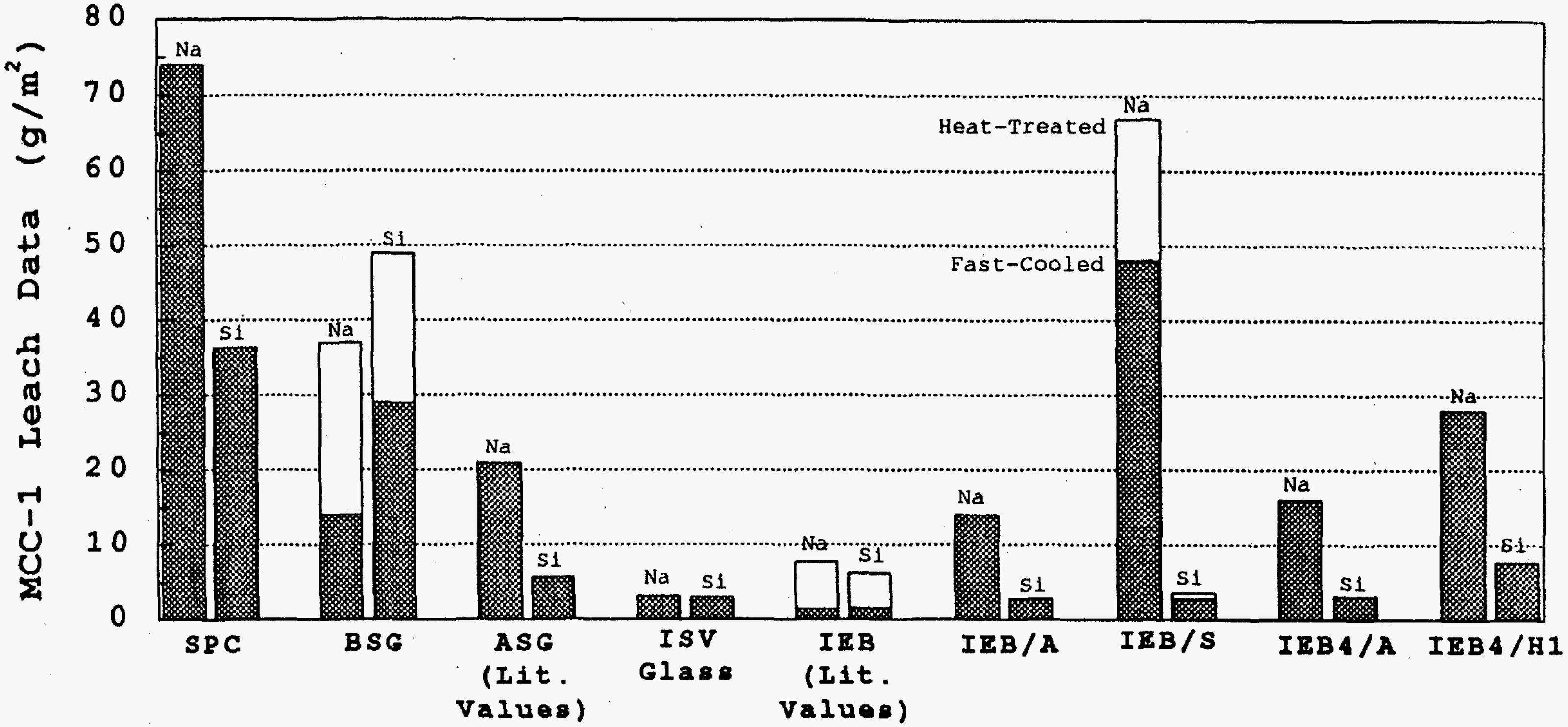

Figure 13. MCC-1 test results (28 day).

the data's validity. It is suspected that the Na leach rate is accurate for only the fast cooled IEB/S, which is still more than 50% higher than those of the other IEB/IEB4 waste forms, suggesting that compositional variations affect the leachability of IEB and IEB4.

The significant difference in sodium leach rate between the two IEB/S (HT) samples may be due to differences in the material exposed. Studies currently underway at PNL indicate that greater than 10% crystallization reduces waste form homogeneity.[f] Therefore, it can be supposed that the heat-treated IEB/S monolithic samples may have had different amounts of exposed glass. The presence of augite crystals in the waste form increase the concentration of alkaline elements in the more leachable glass.[43] Further investigation is required to confirm that this is the cause of the observed differences, however.

Another possible reason for the relatively high sodium leach rate for IEB/S-40 (HT) is the large number of bubbles or voids on the surface of the samples. Personnel involved with the MCC-1 tests reported that the bubbles/voids may have doubled the effective surface area. In contrast, the surface voids or bubbles on the other MCC-1 tested samples were estimated to increase the effective surface area by less than 50% (no change to IEB/A, <5% for IEB/S (FC), 25% for IEB4/A, and 50% for IEB4/H1).

A comparison of all the MCC-1 leach data for the heat-treated and fast-cooled IEB/S samples found that the leach rates were greater for the heat-treated samples. The heat-treated IEB/S had higher leach rates for Si, Ca, Ba, and Pb, with similar leach rates (within one standard deviation) for Na, Cs, Al, Fe, and Mg. Assuming that the heat-treated samples have more augite than either the fast-cooled or slow-cooled samples, the formation of augite may slightly degrade the durability of the IEB and IEB4 waste forms. However, the data were generally within two standard deviations, implying that the confidence level of this conclusion is less than 95%.

The leachabilities of both cerium and zirconium were generally lower for IEB4 than for IEB. The primary reason for this is the zirconolite crystals in IEB4, which act as crystalline matrix sites for both zirconium and cerium. However, the reduction in cerium leachability, though significant, was only 60%. A possible explanation is that cooling rates were insufficient to produce zirconolite in sufficient quantities to encapsulate all of the cerium, since most of the cerium still resided in the glass. Nevertheless, it is uncertain whether the reduction in actinide leachability is worth the 5 to 10% zirconia/titania additions and heat treatments necessary to create zirconolite. In addition, the IEB4 waste form had a significant increase in calcium and magnesium leachability (greater than two standard deviations from IEB). While the primary purpose of the zirconia/titania addition in IEB4 is to increase the leach resistance of TRU components in the waste, the results show that such additions can also affect the leachability of other components. This needs to be taken into account in deciding whether or not to add zirconia/titania to the waste.

The increased leachability of calcium in IEB4/A relative to IEB/A is of special interest for two reasons: 1) calcium leachability is a good indicator of the expected leachability of Sr-90 and, 2) calcium is one of the primary components in the relatively low-leaching zirconolite. However, the EDXS analysis for IEB/A (HT) and IEB4/A (HT) indicates that a higher concentration of calcium exists in the glassy portion of the IEB4 waste form (4 wt%), relative to the IEB waste form (1.8 wt%), (see Table 7). It is suspected that the lower concentration of calcium in the IEB glass is responsible for the apparently lower leachability of calcium. However, it is uncertain whether this phenomenon is a characteristic of all IEB/A glasses or just an

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f. Phone conversation with M. J. Schweiger (PNL), July 1994.

anomaly of this study. Based on the high concentration of calcium in the IEB/S glass, it appears that high calcium partitioning to the glass was not a function of zirconolite formation.

7.4 PCT Leach Test Results

The PCT tests were conducted on heat-treated samples of the different IEB and IEB4 compositions, as well as on fast-cooled or slow-cooled fragments from the original melts. Normalization was performed using a standard equation for converting PCT data (in micrograms per milliliter) to g/m^2 for seven days. The equation,

$$\mathrm{PCT}_{\mathrm{norm}}\ [\mathrm{g/m}^2 \text{ for 7 days}] = \frac{5.39 \times 10^{-2}\,(\mathrm{PCT}_{\mathrm{unorm}}\ [\mathrm{g/m}^3])}{\text{weight fraction}},$$

differs only slightly from the standard PCT equation in that a surface area to volume (S/V) ratio of 1855/m is used, rather than the standard 2000/m ratio. Nevertheless, the results should be relatively comparable to PCT data in the literature (within 8%).

The PCT results from CELS-Corning Laboratory Services were generally normalized using ICP compositional data from the heat-treated MCC-1 samples. Where ICP analysis was unavailable (IEB/A [SC] and the samarium results for all IEB/IEB4 compositions), EDXS composition data were used. ICP compositional data from HT samples were used for the SC samples (IEB4/A [SC] and IEB4/H1 [SC]) when neither ICP or EDXS analysis had been performed. This decision was based on the assumption that waste form elemental composition would not be affected by the type of cooling. Comparisons of ICP data for HT and FC versions of IEB/S indicate that the only significant change in waste form composition is with PbO, which is relatively volatile during the 16 h heat treatment at 1200°C. Normalized results of the seven-day PCT tests are shown in Table 13. A summary of the Na and Si results for the seven-day PCT tests is shown in Figure 14.

The PCT values for IEB and IEB4 (Table 13) are approximately one to two orders of magnitude smaller than the MCC-1 values (Table 12) for the IEB/IEB4 waste forms. This is consistent with previously reported data for both BSG and *in situ* vitrification glass. The reason for the lower values is that the PCT test uses a high surface area particulate sample, 100 to 200 mesh, while the MCC-1 test uses a monolithic sample with much smaller surface area. Because of its higher surface area to volume ratio for the leach period (S/V*t of 13,000 vs. 280 for the 28-day MCC-1 test), the PCT test is more representative of leach rates expected from longer-term, more saturated leaches than the MCC-1 test. The higher S/V ratio for the PCT test causes the leachants to become saturated much sooner than in the MCC-1 tests.[42] This slows the dissolution process, resulting in a lower calculated dissolution rate for the PCT data relative to the MCC-1 data.

Comparison of the PCT leach rates for the heat-treated waste forms with those of their fast-cooled or slow-cooled counterparts shows no significant trend. While the PCT results indicate a drop in sodium leachability for the heat-treated waste forms, the leach rates are higher for the cesium and calcium leachability of IEB4/A, the calcium leachability of IEB/A and IEB/S, and the cerium and samarium leachability of IEB4/H1. Studies by Eddy et al.[24] have suggested that the cooling cycle or heat treatment may not affect the leach resistance of IEB4/H1. The results from this study, including the MCC-1 leach rates for the HT and FC versions of IEB/S, appear to support this conclusion for the other compositions of IEB/IEB4. However, the variation in cooling rate between the heat-treated samples and the fast-cooled and slow-cooled samples may

Table 13. Normalized PCT values for the IEB/IEB4 waste forms (mean g/m^2 for 7 days, standard deviation in parenthesis).

Waste form ID	Na	Cs	Si	Ca	Pb	Ce	Sm
IEB/A							
Slow-Cooled	0.504 (.056)	---	0.0649 (.0004)	0.00214 (.00023)	---	0.00289 (.00068)	0.00190 (.00058)
Heat-Treated	0.488 (.024)	0.246 (.12)	0.0669 (.0014)	0.0036 (.0009)	0.0124 (.0002)	0.0016 (.0009)	0.00106 (.00008)
IEB/S							
Fast-Cooled	0.813 (.005)	0.228 (.002)	0.0498 (.0003)	0.00527 (.00025)	0.00429 (.00034)	0.0010 (.0004)	0.00041 (.00021)
Heat-Treated	0.282 (0)	0.0815 (.0005)	0.0496 (.0003)	0.0171 (.0001)	Neg	0.000208 (.000021)	0.000188 (.000024)
IEB4/A							
Slow-Cooled	0.809 (.071)	0.0119 (0)	0.0798 (.0019)	0.00212 (.00019)	---	0.00173 (.00022)	0.00174 (.00023)
Heat-Treated	0.435 (.005)	0.0776 (.0019)	0.0635 (.0006)	0.0055 (.0001)	0.00091 (.00011)	0.000812 (.000056)	0.000829 (.000096)
IEB4/H1							
Slow-Cooled	1.3 (.04)	0.306 (.006)	0.119 (.0004)	0.0058 (.0003)	---	0.000158 (.000008)	0.000195 (0)
Heat-Treated	0.0395 (.0002)	0.315 (.001)	0.143 (.001)	0.00262 (0)	0.0138 (0)	0.00517 (0)	0.00518 (.00014)

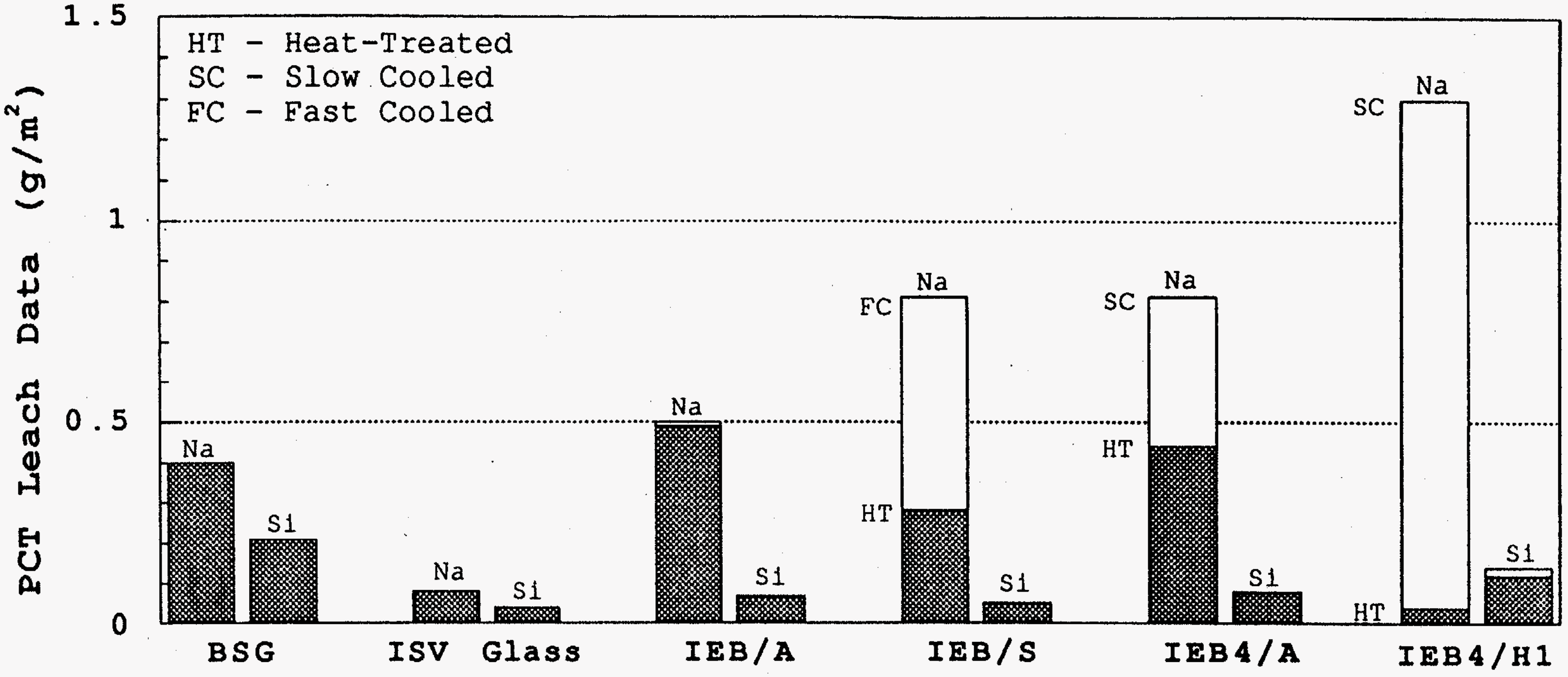

Figure 14. Sodium and silicon PCT test results (7 day) for the vitrified waste forms.

be too limited to make a definitive statement on cooling rate effects. Furthermore, comparison of the MCC-1 results of this study with previously reported IEB literature values suggests that significant variations in cooling rate do affect waste form durability.

The PCT leach testing results for IEB/A and IEB4/A are similar, except for the rare earth data, which showed that IEB4 leaching was reduced 40 to 50% for cerium and 9 to 22% for samarium (see Figure 15). These results are similar to those for MCC-1 leachability of cerium, and are due to the presence of zirconolite crystals in the IEB4 waste form. The results also showed that the heat-treated waste forms exhibited a slightly higher leach resistance for cerium and samarium than the slow-cooled ones. This implies that the heat treatment may have increased the amount of zirconolite that formed, increasing the leach resistance of the TRU surrogates.

The leach resistance of the other components of interest differed among the waste forms without any specific trends. For example, IEB4/S had the lowest leachability of silicon and lead, IEB4/A the lowest leachability for cesium, IEB/A the highest leachability for lead, and IEB4/H1 the highest leachability of cesium and silicon. However, the results were generally similar for each of the IEB and IEB4 waste forms, with most of the values within an order of magnitude.

The IEB/S generally exhibited the highest PCT leach resistances (particularly for the heat-treated samples), while IEB4/H1 and IEB/A exhibited the lowest leach resistances. This is contrary to the results from the MCC-1 tests, which showed a high leachability for IEB/S and a low leachability for IEB/A. A possible explanation is that the PCT data represent the long-term leach rate (after saturation), while the MCC-1 data show the initial leach rate. Thus, a low MCC-1 test result with a high PCT result would indicate that the waste form is more susceptible to leaching if the environment is relatively stagnant (which leads to a saturated leaching solution situation). Likewise, a high MCC-1 test result coupled with a low PCT result would imply that the waste form is more susceptible to leaching if the environment is relatively free flowing (the leaching solution does not become saturated). However, the results are too limited to reach a definitive conclusion. The apparent differences may also be a result of differences in the exposed crystallinity of the heat-treated samples or the locations for the sampled material taken from the crucibles.

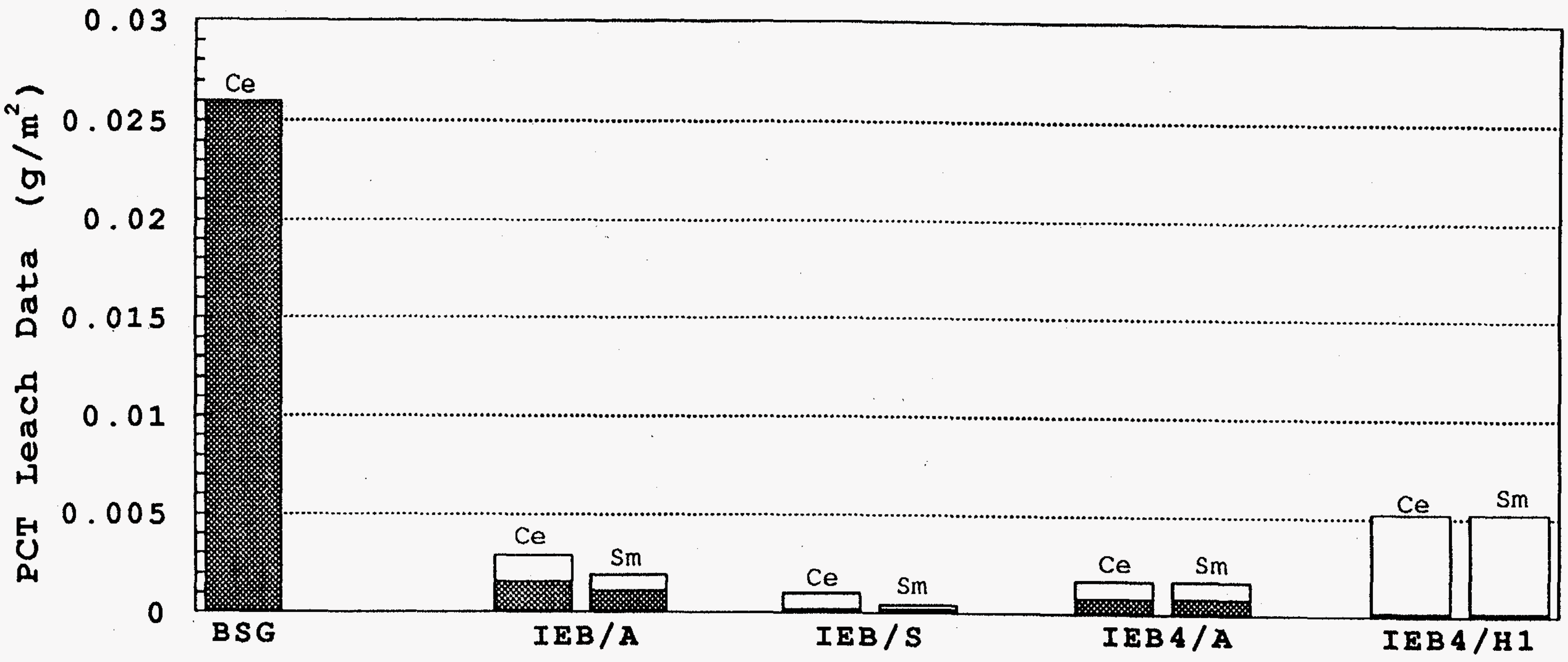

Figure 15. PCT results for simulated TRU components.

8. SUMMARY OF FINAL WASTE FORM KEY INDICATOR PROPERTIES

A summary of the key indicator property data for all of the selected waste forms is given in Tables 14 and 15. The tables include all the data compiled from literature (Tables 2 and 3), as well as the additional results from the MCC-1, PCT, compressive strength, and fines generation upon impact tests summarized in Section 6.

Table 14. Mechanical durability data for each of the final waste forms.

Final waste form	Compressive strength[27] (MPa)	Density (g/cm^3)	Fines generation upon impact[28] (wt%)
Portland Cement Concrete	1.6-14.1 (ion-x)[29] 20.6-55.2 (conc)[30], 3.5-40[3]	~ 1.5	0.32 (< 10 µm)[a] 0.49 (< 15 µm)[a]
FUETAP	20[12]	~ 2[12]	0.43 (< 10 µm)[12,28]
Sulfur polymer cement	12.6-44.4[6,7] 41.4-69 (w aggregate)[3]	1.4-2.1[6,7]	0.15 (< 10 µm)[a] 0.33 (< 15 µm)[a]
Borosilicate glass	281-314[30]	2.6[12]	0.17 (< 10 µm)[12,28]
Alumino-silicate glass (generic)	No data available (not needed, however)	2.7-3.0[12]	No data available (not needed, however)
ISV Glass	409[42,30]	2.7-2.9	No data available (not needed, however)
Iron enriched basalt	430 (IEB/A[HT])[a] 386 (IEB/A[SC])[a]	2.9-3.0[31]	Intact (IEB/A)[a] 0.088 (<96 µm) (IEB/S)[a]
Iron enriched basalt-IV	403 (IEB4/A[HT])[a] 441 (IEB4/H1[HT])[a]	3.0-3.1[31]	0.008 (<96 µm)[a]; 0.0 (<15 µm)[a] (IEB4/A)

a. Data from this report.

Table 15. Chemical durability data for each of the final waste forms.

Final waste form	MCC-1 (28 day) (g/m^2)	PCT (7 day) (g/m^2)	ANS 16.1 leach index
Portland Cement Concrete	Data not applicable	Data not applicable	Cs-137, 6.0-10.6 ; Sr-90, 7.0-10.7; Co-60, 9.7-13.0; C-14, 12.9-14.2; H-3, 7.4-9.0 [3]
FUETAP	Data not applicable	Data not applicable	IAEA Data:[5] Cs, 12.2; Sr, 8.2; Pu, 16.2
Sulfur polymer cement	Na, 74.1; Cs, 60.7; Si, 36.4; Ca, 52.5; Pb, 12.0; Mg, 10.4; Cd, 9.4; Al, 6.2; Cr, 2.4; Fe, 1.9[a]	Data not applicable	Co-60, 10.7-14.6; Cs-137, 9.7-11.2[7,b]
Borosilicate glass	Na, 14-37; Si, 11-28; Cs, 29-49; B, 15-39; Fe, 0-.2; blk, 12; Sr, 1.0-2.1; (Ce, <.1; Ca, 1.9-7.2; Mo, 39; U, 1.3-1.5[8,9,12,14,c]	Na, .40; Si, .21; Cs, .13; Al, .12; B, .44; Cr, .0086; Li,.49; Ca, .041; Mg, .25; Zr, .027; Ni, .12; La, .029; Nd, .027; Mo, .43; Mn, .20; Ce, .026[8,9,c]	Data not applicable
Alumino-silicate glass (generic, from literature)	U, 1.5; Cs, .8; Ce, .39[14] Na, ~21; Si, 5.8; Ca, 6.4; Sr, 4.7; Ba, 1.8; Mo, 6.1[12]	No Data	Data not applicable
Iron enriched basalt (literature values)	Na, 1.4-7.8; Si, 1.6-6.2; Al, .35-6.4; Fe, .03-.8; Ca, .8-5.3; Mg, 1.6-5.9; K, 3.4-7.3; blk, 2.2-4.0; U, .02-.25; La, .02; Cs, 1.7; Sr, 1.6[12,17,18]	No Data	Data not applicable
ISV Glass	Na, 3.2; Si, 3.0; Al, 2.8; B, 2.8; Ca, 8.7; Fe, .56; K, 3.7[30]	Al, .01; B, .09; Ca, .29; Fe, .00; K, .06; Na, .08; Si, .04; V, .25[30]	Data not applicable
IEB/A (SC) (60 wt% WL)	No data	Na, .50; Ca, .0021; Si, .065; Ce, .0029; Sm, .0019[a]	Data not applicable
IEB/A (HT) (60 wt% WL)	Na, 14; Cs, 12; Si, 2.8; Al, 4.8; Ca, 2.2; Ba, 2.9; Pb, .23; Mg, .090; Fe, .042[a]	Na, .49; Cs, .24; Si, .067; Ca, .0036; Pb, .067; Ce, .0016; Sm, .0011[a]	Data not applicable

Table 15. (continued).

Final waste form	MCC-1 (28 day) (g/m^2)	PCT (7 day) (g/m^2)	ANS 16.1 leach index
IEB/S (FC) (60 wt% WL)	Na, 48; Cs, 22; Si, 3.5; Al, 5.8; Ca, 2.2; Ba, 2.3; Pb, .26; Mg, .032; Fe, .028[a]	Na, .81; Pb, .0043; Si, .050; Ca, .0053; Cs, .23; Ce, .0010; Sm, .00041[a]	Data not applicable
IEB/S (HT) (60 wt% WL)	Na, 67; Cs, 20; Si, 6.0; Al, 8.3; Ca, 3.5; Ba, 4.0; Pb, .61; Mg, .022; Fe, .052[a]	Na, .28; Cs, .082; Si, .050; Ca, .017; Ce, .00021; Sm, .00019[a]	Data not applicable
IEB4 (from literature)	Pu, .006; Cs, 20[12]	No Data	Data not applicable
IEB4/A (SC) (60 wt% WL)	No Data	Na, .81; Ce, .0017; Si, .080; Ca, .0021; Cs, .012; Sm, .0017[a]	Data not applicable
IEB4/A (HT) (60 wt% WL)	Na, 16; Cs, 7.5; Si, 3.1; Al, 3.9; Ca, 3.0; Ba, 2.5; Pb, .096; Mg, .70; Fe, .086[a]	Na, .44; Pb, .00091; Cs, .078; Ca, .0055; Si, .064; Ce, .00081; Sm, .00082[a]	Data not applicable
IEB4/H1 (SC) (60 wt% WL)	No Data	Na, 1.3; Ca, .0058; Cs, .31; Ce, .00016; Si, .12; Sm, .00020[a]	Data not applicable
IEB4/H1 (HT) (60 wt% WL)	Na, 28; Cs, 21; Si, 7.8; Al, 11; Ca, 3.9; Ba, .41; Pb, .43; Mg, .22; Fe, .062[a]	Na, .040; Cs, .32; Si, .14; Ca, .0026; Pb, .014; Ce, .0052; Sm, .0052[a]	Data not applicable

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a. Data taken from this report

b. For 20-40 wt% sodium sulfate/incinerator ash

c. 2000/m MCC-3 data for PCT

9. SUMMARY AND CONCLUSIONS

Seven different waste forms were selected for comparative evaluation: Portland cement concrete, concrete formed under elevated temperature and pressure (FUETAP), sulfur polymer cement, borosilicate glass, ISV glass, iron-enriched basalt, and iron-enriched basalt with zirconolite crystals. The properties selected for evaluating the mechanical durability of each waste form were compressive strength (per ASTM C39) and fines generation upon impact. The properties selected for evaluating the chemical durability were leach resistance (per ANS 16.1, MCC-1, or PCT) and compositional flexibility. Based on a literature search for existing mechanical and chemical durability data for these FWFs, it was determined that the following properties data were still needed:

Compressive Strength (ASTM C39) - IEB-A (average waste composition), IEB4-A (average waste composition), IEB-S (Series 743 sludge composition), and IEB4-H1 (Series 741 sludge composition), all at 60 wt% waste loadings.

Fines Generation Upon Impact - PCC (average waste composition) and SPC (average waste composition) at 40 wt% waste loadings; IEB-A, IEB4-A, IEB-S, and IEB4-H1, 60 wt% waste loadings.

MCC-1 and PCT - SPC (MCC-1 only), 40 wt% waste loading; IEB4-A, IEB-A, IEB-S, and IEB4-H1, 60 wt% waste loadings.

Compressive strengths of the vitrified waste forms (BSG and the ASGs, including ISV glass/ceramics, IEB, and IEB4) are indicated to be 6 to 26 times greater than those of the cementitious waste forms (PCC, FUETAP, and SPC). However, it appears that waste composition can affect the IEB glass/ceramic compressive strength significantly, as evidenced by the relatively lower compressive strengths of the IEB/S samples as compared to the other IEB samples (29% of that of the other IEB/IEB4 samples).

The fines generation upon impact tests indicated that the IEB and IEB4 waste forms are significantly more resistant to impact than the other waste forms. No respirable fines (<10 μm) were created from impact testing of any of the IEB or IEB4 waste forms, compared to respirable fine levels of 0.15% for SPC, 0.17% for BSG, 0.32% for PCC, and 0.43% for FUETAP.

A direct comparison of leach resistance based upon a common test procedure cannot be performed between PCC or FUETAP and the vitrified waste forms (BSG and the ASGs) due to the basic, porous, and diffusion-driven nature of PCC and FUETAP during leaching. Therefore, the relative leachability of PCC and FUETAP was evaluated using the ANS 16.1 procedure, while the leachability of the nonporous vitrified waste forms was analyzed using the bulk dissolution MCC-1 and PCT procedures. Because of SPC's nonporous character and acidic nature during leaching, however, MCC-1 procedures are applicable and a direct comparison can be made between SPC and the vitrified waste forms using MCC-1 data. MCC-1 results show that the leach resistances of the vitrified waste forms were generally much greater than that of SPC. Although generally more leach resistant than nonvitrified materials, the leach resistance of the multiphase glass/ceramic materials (IEB/IEB4), for some elements, can be significantly affected by both waste composition and the degree of heat treatment during cooling, as evidenced by the relatively high normalized leach concentrations of sodium in the IEB/S samples; the leach rates of the silica and TRU surrogate (cerium) were consistently low.

The MCC-1 test results show that IEB/A and IEB4/A were generally more leach resistant than IEB4/H1 and IEB/S. However, the order was reversed in PCT leach testing results. These results imply that the H1 and S waste forms leach at faster initial rates (when leaching solution is unsaturated) than the A waste forms, but more slowly after the solutions become more saturated (long term leaching rate).

For the IEB/IEB4 waste forms, the 16-h heat treatment is more representative of expected waste processing conditions than slow or fast cooling in the arc melter. The heat-treated samples cooled from 1200 to 700°C at a rate of approximately 180°C/h, compared with cooling rates of 780°C/h and 1300°C/h for the slow-cooled and fast-cooled IEB/IEB4 waste forms. The predicted centerline cooling rate between 1200 and 900°C for an uninsulated 55-gallon FWF is 194°C/h. It is expected that even slower rates of cooling (via insulation or a furnace-controlled environment) may improve the durability of the IEB/IEB4 waste forms via the formation of highly durable crystals such as plagioclase or zirconolite. This conclusion was reached by comparing the durabilities of the IEB/IEB4 waste forms tested with previously reported data. Based on PCT data for the HT, SC, and FC samples, it appears that cooling rates of 180°C/h or higher do not affect waste form leachability.

The MCC-1 leach rates of the IEB/IEB4 waste forms tested were indicated to be significantly greater than those previously reported in the literature for IEB, ASG, and ISV glass. The probable reason for this discrepancy is the different heat treatments and resulting phase structures that were experienced. While the IEB/IEB4 samples in this study were held 16 h at 1200°C and cooled to 700°C at 180°C/h, the samples in the literature were held at 800 to 1100°C for 19.5 to 21.5 h. As a result, a durable plagioclase phase rich in sodium was formed in the literature IEB, ASG, and ISV glass/ceramics but not in the IEB/IEB4 slags created in this study. The results suggest that slower cooling rates (<180°C/h) would improve the durability of the IEB/IEB4 waste forms.

Finally, the MCC-1 and PCT results show that zirconolite crystals in IEB4 improve the leach resistance of simulated TRU contaminants (cerium and samarium). The leachabilities of cerium and samarium in the IEB4/A samples were lower than in the IEB/A samples (40-60% and 9-22% lower, respectively). At these levels, it is uncertain whether the slightly improved leach resistances are worth the additions of zirconia, titania, and (possibly) calcines to the wastes. Slower cooling rates (<180°C/h) may increase the effects of zirconolite formation in the IEB, however. Additional research is still needed.

Although some scoping level indications of the expected relative mechanical and chemical durability behavior of the most likely final waste form materials have been obtained based upon the selected indicator materials properties available in the literature, and from a limited number of supplemental tests on several materials, it is clear that quantitative prediction of final waste form materials performance behavior at any reasonable confidence level will require considerable additional well planned and controlled testing and analysis of data.

It is also clear that final waste form chemical durability, as primarily indicated by the property of leachability which is obtained through a particular test method, is a complex function of a large number of potential variables. These include the nature of the product material chemical composition and material structure and phases (which are dependent upon waste composition and treatment process conditions), and the nature of the leach test (leach fluid type and ph, time, temperature, surface area to volume of sample, fluid saturation conditions), and the selection (location) and number of the product materials samples. It is suggested that, although absolutely necessary, additional testing and simple correlation attempts for these multi-material (in the case of encapsulated waste material forms like PCC) and multiphase microstructure materials (in the case of glass/ceramics) alone will be insufficient, and prohibitively expensive, to develop the quantitative performance prediction capability needed to support licensing, public acceptance, and ALARA process optimization. It is recommended that a set of simple, predictive analytical models be developed in order to help plan and properly interpret data from future multiphase materials testing and observed properties behaviors. Once validated the models can be used for performance prediction to extend/relate the fixed base of empirical performance data to the variable future in-service performance conditions.

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