DOE/CH-9504
Distribution Category:
General, Miscellaneous, and
Progress Reports (UC-600)

DEVELOPMENT AND TESTING OF THE MINIMUM ADDITIVE WASTE STABILIZATION (MAWS) SYSTEM FOR FERNALD WASTES

Phase I Final Report
Contract No. 21402401

by

Sabrina S. Fu, Keith S. Matlack, Robert K. Mohr,
Marek Brandys, Hamid Hojaji, Sarah Bennett,
Jacqueline Ruller and Ian L. Pegg

GTS Duratek, Inc.
8955 Guilford Road, Suite 200
Columbia, MD 21046
Phone: (410) 312-5100
Telefax: (301) 621-8211

and

Vitreous State Laboratory, The Catholic University of America
Washington, DC 20064

December 1994

Prepared For

Office of Research and Development
Technology Development, Environmental Restoration and Waste Management
U.S. Department of Energy
1000 Independence Avenue
Washington, DC 20585-0002

Research and Development Program Coordination Office
Waste Management and Technology Development, Chicago Field Office
U.S. Department of Energy
9800 S. Cass Avenue
Argonne, IL 60439

MASTER

Office of Waste Management Programs
Chemical Technology Division, Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439
under Prime Contract W-31-109-Eng-38 to the U.S. Department of Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DLC

Acknowledgements

Many dedicated people at GTS Duratek and The Vitreous State Laboratory (VSL) contributed towards the success of this project. The following people and their respective staffs are due special thanks: M. Adel-Hadadi (Analytical Lab); A. Alhedai (ICP-MS); K. Matlack (Special Analysis, Off-gas Sampling); A. Buechele (SEM-EDS); Z. Djordjevic (XRD, DSC); I. Muller (Glass Melting, Hot Labs); N. Balitactac (Viscosity, Conductivity, Ion Exchange Testing, and Physical Measurements); S. Lai (Glass Leach Testing); R. Mohr, B. Bowan, and M. Brandys (Melter System Design and Construction); H. Hojaji (Melter Operations); R. Clemmer, J. Burns, P. Wasserman, T. Clemmer, F. Brown, P. Baker, M. Tangeman, B. Djurkovic, (Melter System Construction and Operation at Fernald), P. Macedo, W. Greenman, M. Nohe, and R. Prince (Facility and Contract Management). Many people worked above and beyond the call of duty to ensure the success of the Duramelter™ 10 and Duramelter™ 100 campaigns. These people include G. Del Rosario, M. Boroomand, M. Leontiev, T. Labuda, K. Chiu, H. Kuang, E. Wang, Q. Yan, F. Perez-Cardenas, W. Guo, F. Duan, H. Cheng, and S. Kaptsan. Special thanks are due to M.C. Paul of the VSL for preparation of the manuscript and the extensive graphics and tables included in this report.

Thanks are also due to C. Tellez, D. Soderstrom and S. McKeag of Lockheed Environmental Services Corporation for providing the necessary information and samples from soil washing activities, N. Beskid, D. Bugielski, and G. Edgell of Argonne National Laboratory for contract management and coordination, and to the many people at the Fernald site that were essential to the success of this project; R. Gimpel, N. Akgunduz, R. Stocker, and R. Warner deserve special mention.

This work was supported by the United States Department of Energy, Office of Environmental Restoration and Office of Technology Development.

DISCLAIMER

Table of Contents

List of Tables

List of Figures

List of Acronyms

ANL	Argonne National Laboratory
ANSI/ASME	American Nuclear Standards Institute/American Society of Mechanical Engineers
ARAR	All Relevant and Applicable Requirements
ASTM	American Society for Testing and Materials
BSM	Boat Sampling Module
CIS	Characterization Investigation Study
CUA	The Catholic University of America
DOE	United States Department of Energy
DCP-ES	Direct Current Plasma Emission Spectroscopy
EPA	Environmental Protection Agency
FEMP	Fernald Environmental Management Project
HEPA	High Efficiency Particulate Air
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IC	Inorganic carbon
JHCM	Joule-Heated Ceramic Melter
LESC	Lockheed Environmental Services Corporation
MAWS	Minimum Additive Waste Stabilization Program
NIST	National Institute of Standards and Technology
NRC	Nuclear Regulatory Commission
OSHA	Occupational Safety and Health Act
OU	Operable Unit
pCi/g	Picocuries/Gram
PCT	Product Consistency Test
PLC	Programmable Logic Controller
PPB	Parts Per Billion
PPM	Parts Per Million
QA	Quality Assurance
QAO	Quality Assurance Officer
RCRA	Resource Conservation and Recovery Act
RI/FS	Remedial Investigation/Feasability Study
SRL-EA	Savannah River Laboratory - Environmental Assessment
SEM/EDS	Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy
S/CM	Siemen Per Centimeter
S/V	Ratio of Glass Surface Area to Solution Volume
TC	Total Carbon
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total Organic Carbon
VSL	Vitreous State Laboratory
WEMCO	Westinghouse Environmental Management Company

Executive Summary

This report presents the results from a treatability study for the evaluation of the Minimum Additive Waste Stabilization (MAWS) process as a treatment technology for wastes stored at the Fernald Environmental Management Project (FEMP) site. The work was conducted by GTS Duratek, Inc. and its subcontractors the Vitreous State Laboratory of The Catholic University of America, and Lockheed Environmental Services Corporation. The wastes included in the study were FEMP Pit 5 sludges, soil-wash fractions, and ion exchange media from a water treatment system supporting a soil washing system. Characterization of these streams was directed specifically at the data needs for application of vitrification process technologies to the remediation of these wastes in a MAWS integrated system. Results from soil-washing studies are presented in a separate report.

The MAWS approach offers the potential for the treatment of a variety of waste streams to produce a more leach resistant waste form at a lower overall cost than has proved possible with competing treatment technologies such as cement stabilization. The key concepts that are applied in the MAWS approach are as follows:

- Increased volume reduction translates into lower life-cycle treatment costs due to the generally high volume-based costs of disposal.

- The need for non-waste additives should be minimized since these materials must be purchased, processed, and disposed (since they form part of the final waste form) and consequently impact treatment costs from all three perspectives.

- Waste streams are resources for the treatment process since by blending available waste streams of different compositions, the requirements for additives can frequently be reduced considerably.

- In general, no single treatment technology will fulfill the diverse requirements that are typical of site remediation activities. Thus, a portfolio approach is used to combine the benefits obtained by blending waste streams and integrating treatment subsystems in order to bring a variety of appropriate technologies to bear on the waste treatment problem.

- Focus on optimizing the performance of the complete system, not the individual subsystems since, in general, the optimum system performance is not obtained by optimizing the performance of the components individually.

- Produce a highly leach resistant waste form that meets or exceeds treatment requirements (to the extent that these are defined) and offers the best possible prospects of long-term stability. Such a waste form should, in addition, offer the best prospects for delisting which would result in additional cost savings for listed wastes.

- The system should be designed to produce minimal, and ideally zero, sidestream wastes.

Vitrification was selected as the best available technology around which to build this system for a number of reasons including: the well-developed technology base that exists from high-level waste programs and the commercial glass industry; large volume reductions achievable; destruction of organic contaminants by thermal processing; the ability of glass to chemically incorporate a wide range and large amounts of hazardous and radioactive components; production of a stable homogeneous wasteform that can be made highly resistant to aqueous corrosion; and similarity of the wasteform material to many natural minerals whose long-term corrosion resistance has been demonstrated by the geological record.

The general MAWS approach could be manifested in a variety of system configurations and process flows depending on the quantities and compositions of the waste streams that are available at a given site. The system developed for the MAWS demonstration at the Fernald site integrates vitrification, soil-washing, and water treatment systems to treat blends of Pit wastes and contaminated soils.

Fernald pit wastes are rich in fluxes (such as calcium, magnesium, and fluorine) that reduce the melting temperature and viscosity of silicate glasses but are not, by themselves, glass forming. However, the large volume of uranium-contaminated soils (and in later stages of the program other wastes such as fly ash, asbestos, transite, etc.) provides an available source of glass-forming materials (mostly silica and alumina). Volume reduction is maximized and the flux:glass-former ratio is improved by pretreating the contaminated soils in a soil washing process. Soil washing studies on Fernald soils using the Lockheed TRUclean process have produced an approximately 80%:20% split between the decontaminated fraction and the contaminant-enriched fraction. The contaminated minor fraction is then blended with the pit wastes to produce a glass-forming feed for the vitrification process. The uranium contamination in the soil washing process water is removed by a supporting ion exchange water treatment system. A regeneration cycle is employed to strip the uranium from the ion exchange media and direct it to the vitrification system. Several GTS Duratek joule-heated glass melters and supporting off-gas treatment systems have been used in the development and demonstration activities in this program. The unique off-gas system employed permits capture of not only the hazardous and radioactive components but also the significant amounts of hydrogen fluoride produced in vitrifying these wet high-fluoride wastes. The off-gas system operates in such a way that no side-stream wastes are generated since off-gas sludges are recycled to the feed batch.

The MAWS development and demonstration program for the Fernald site is presently scheduled to proceed in two phases. Phase I of the MAWS program began in June 1992. This includes lab development and testing studies; lab proof of concept; design, procurement, and construction of system components; documentation and permitting; FEMP Plant 9 facility modifications to house the MAWS system; operator training; installation and operation of system components through radioactive soil washing and water treatment tests and non-radioactive vitrification system tests. Phase II began in April 1994 and is expected to include on-site system integration and proof of concept using Pit 5 waste; process control development; evaluation of equipment performance; evaluation of waste form performance; runs specifically designed to accumulate data in support of a delisting application; and incorporation of other FEMP wastes.

The major objectives of Phase I of this program are:

- Develop glass formulations that will fulfill the key MAWS concepts listed above, as applied to Fernald wastes, and satisfy the processability requirements of the Durameter joule-heated vitrification system.
- Demonstrate, with actual Fernald waste, that these formulations can be processed in laboratory continuous melter systems and use the test data that is collected in the detailed design of the on-site system.
- Demonstrate, with actual Fernald waste, that the Duramelter off-gas system captures fluoride emissions from the melter and produces a recyclable sludge. Demonstrate that the off-gas sludge can be recycled to the melter feed.
- Collect and analyze process data, off-gas data, system performance data, and waste form quality data from the continuous melter test runs.
- Demonstrate a lab-scale soil washing process that will decontaminate Fernald uranium-contaminated soils to below 35 pCi/g and provide sufficient contaminant-enriched soil-wash fractions for the lab-scale vitrification tests.
- Demonstrate a lab-scale ion-exchange process that will remove uranium from actual soil-wash water produced in the lab-scale soil washing tests.
- Demonstrate a lab-scale ion-exchange regeneration process in which the captured uranium is directed to the vitrification process.
- Deploy a system at the Fernald site which consists of: a GTS Duratek Duramelter glass melter and supporting off-gas treatment system capable of a minimum glass output rate of 300 kg/day; a Lockheed TRUclean soil washing system capable of processing at least 0.25 yd^3/hr; and a GTS Duratek ion exchange water treatment system capable of processing at least 100 gallons/minute.

- Demonstrate the operation of the on-site system by treating at least 100 yd^3 of contaminated soil in the soil washing system with supporting water treatment.

- Demonstrate the operation of the on-site vitrification system by processing a borosilicate glass test feed.

All of these objectives have been met in Phase I of the MAWS program. (Note: in addition, a major Phase II milestone has also been achieved with the successful completion of a sustained test run of 75 hours using a non-radioactive but fluoride-containing surrogate feed corresponding to the feed formulations developed for actual Fernald wastes.) This report presents and discusses the results that were obtained under Phase I of the MAWS program with the exception of the soil washing results which are presented in a separate report.

Extensive characterization data (chemical and radionuclide composition, particle size distributions, water content, density, etc.) are presented for several 55-gallon drum samples of Fernald Pit 5 sludge and a variety of soil-wash fractions generated from lab-scale soil washing tests on contaminated Fernald soils. Six 55-gallon drum samples of Pit 5 waste were selected by FEMP personnel and shipped to the Vitreous State Laboratory over the course of Phase I of this work. Due to delays in shipping subsequent drums, much of the development work was performed on Pit 5 material from the homogenized contents of the first 55-gallon drum that was received. Later samples showed lower contents of magnesium fluoride and greater contents of sulfates than did the first samples. Discussions with FEMP personnel concerning process knowledge of the generation of the Pit 5 material indicated that the overall sulfate content of Pit 5 was expected to be low and consequently the Phase I studies have concentrated on the low-sulfate material. By the end of Phase I, however, three of the six drums received showed sulfate contents of 10-13 wt% on a dry basis. Phase II work will therefore address further the variability in the Pit 5 sludge composition, an important factor for any treatment technology, as well as broadening the compositional envelope of acceptable glass formulations accordingly.

A total of 31 crucible melts were made from six different samples of Pit 5 sludge and seven different soil-wash fractions. Characterization of the resulting glasses included determination of the melt viscosity and electrical conductivity as functions of temperature; determination of their phase stability including the amounts and types of secondary phases that are produced on heat treatment and estimated liquidus temperatures; and measurement of their leach resistance by the EPA TCLP procedure and the high-level nuclear waste glass Product Consistency Test (PCT). These results were used to select the optimal formulation for continuous melter tests using the requirements for processability, leach resistance, and economics (primarily waste loading and cost of additives).

A step-wise approach was used for the continuous melter tests, progressing from tests on 10 kg/day and 100 kg/day laboratory Duramelter systems up to the on-site 300 kg/day system. Each step provides more realistic information and approaches more closely the process that would occur in a production-scale system. The continuous melter tests provide information, such as off-gas emissions and processing rates, that cannot be obtained from crucible melts. Information learned in the small-scale melter tests provides an important basis for the design and selection of larger, production-scale systems.

Data collected in these tests included production rates, power requirements, off-gas composition, distribution of chemical components between various parts of the system (glass, off-gas scrubber solution and sludge, filtered particulates, and off-gas emissions), off-gas sludge recycle, and characteristics of the resulting glass product.

The results obtained to date provide strong support for the viability of the MAWS approach, as outlined above, for the treatment of Fernald waste streams. Extremely high waste loadings (up to 96%) in the feed formulations were obtained and these feeds were successfully processed in the 10 kg/day and the 100 kg/day continuous melter systems using actual Fernald wastes. The resulting glasses pass the TCLP test and exhibit performance comparable to high-level waste glasses on the PCT test. While the continuous melter tests performed to date have been relatively short, the overall performance of the systems has been very good and showed no indications of any major problems which might preclude scale-up to production-scale systems. The very large volume reductions obtained by this approach (approximately seven-fold), as compared to a volume <u>increase</u> of about a factor of three on cement stabilization, coupled with the large volume-based disposal costs results in very large potential cost savings (about 56% by independent estimates made by Fernald site personnel) in the treatment and disposal of these wastes.

Recommendations that can be made on the basis of Phase I testing results include the following: Continue the phased scale-up of the testing activities from laboratory tests to on-site system tests; conduct significantly longer system test runs under steady-state conditions; conduct test runs on laboratory and on-site systems to better define the system operational envelope (limits for key operating parameters) for these wastes; conduct test runs to confirm the extent of the compositional envelope identified by crucible studies; evaluate other FEMP waste streams to broaden the MAWS waste stream blend and maximize the benefits of this approach; evaluate the variability of Pit 5 sludge composition, particularly with regard to sulfate and particularly on the feed-batch scale (presently, a few thousand gallons); expand the compositional envelope as appropriate to whatever additional characterization data suggest is the "mean" Pit 5 sludge composition and variability; batch-by-batch analysis is clearly necessary for process control and therefore alternative analytical methods with rapid turnaround times should be evaluated; the long-term effects of FEMP melts (especially with respect to the high fluoride content and low viscosities) on melter components should be evaluated.

SECTION 1.0
Introduction

This report presents the results from a treatability study for the evaluation of the Minimum Additive Waste Stabilization (MAWS) process as a treatment technology for wastes stored at the Fernald Environmental Management Project (FEMP) site. The work was conducted by GTS Duratek, Inc. and its subcontractors the Vitreous State Laboratory of The Catholic University of America, and Lockheed Environmental Services Corporation. The wastes included in the study were FEMP Pit 5 sludges, soil-wash fractions, and ion exchange media from a water treatment system supporting a soil washing system. Characterization of these streams was directed specifically at the data needs for application of vitrification process technologies to the remediation of these wastes in a MAWS integrated system. Results from soil-washing studies are presented in a separate report.

The MAWS program is an innovative program involving the development and demonstration of an integrated, multiple-technology system to treat blends of waste streams to achieve significant reductions in treatment and disposal costs at the Fernald Environmental Management Project site in Fernald, Ohio. The three primary technologies integrated in the MAWS system are vitrification, soil washing, and water treatment. All contaminant streams are directed to a final stabilized glass waste form using a Duramelter vitrification system (as shown in Figure 1.1). Vitrification was selected as the stabilization technology due to the superior leach resistance of the wasteform and the large volume reduction compared to many alternative technologies; this increased volume reduction leads to significantly reduced life-cycle remediation costs.

The MAWS concept is innovative in several respects: the available waste streams are viewed as resources for the process; the chemical properties of these resources are fully exploited to minimize the need for the purchased additives usually required for stabilization, and a portfolio approach is adopted to maximize the economic benefits of blending the optimum proportions of multiple waste streams in an integrated system composed of an appropriate combination of treatment technologies.

Vitrification was selected as the best available technology around which to build this system for a number of reasons including: the well-developed technology base that exists from high-level waste programs and the commercial glass industry; the large volume reductions achievable; the destruction of organic contaminants by thermal processing; the ability of glass to chemically incorporate a wide range and large amounts of hazardous and radioactive components; production of a stable homogeneous wasteform that can be made highly resistant to aqueous corrosion; and similarity of the wasteform material to many natural minerals whose long-term corrosion resistance has been demonstrated by the geological record.

The potentially very high leach resistance of a glass-based waste form for FEMP mixed and low-level wastes is especially attractive in light of the fact that several of the pit wastes are Resource Conservation and Recovery Act (RCRA) listed wastes. In these instances it is likely that a very strong case can be made for delisting the vitrified wastes which would result in significant further savings in disposal and monitoring costs.

Thus, the MAWS approach offers the potential for the treatment of a variety of waste streams to produce a more leach resistant waste form at a lower overall cost than has proved possible with competing treatment technologies such as cement stabilization. The key concepts that are applied in the MAWS approach are as follows:

- Increased volume reduction translates into lower life-cycle treatment costs due to the generally high volume-based costs of disposal.
- The need for non-waste additives should be minimized since these materials must be purchased, processed, and disposed (since they form part of the final waste form) and consequently impact treatment costs from all three perspectives.
- Waste streams are resources for the treatment process since by blending available waste streams of different compositions, the requirements for additives can frequently be reduced considerably.
- In general, no single treatment technology will fulfill the diverse requirements that are typical of site remediation activities. Thus, a portfolio approach is used to combine the benefits obtained by blending waste streams and integrating treatment subsystems in order to bring a variety of appropriate technologies to bear on the waste treatment problem.
- Focus on optimizing the performance of the complete system, not the individual subsystems since, in general, the optimum system performance is not obtained by optimizing the performance of the components individually.
- Produce a highly leach resistant waste form that meets or exceeds treatment requirements (to the extent that these are defined) and offers the best possible prospects of long-term stability. Such a waste form should, in addition, offer the best prospects for delisting which would result in additional cost savings for listed wastes.
- The system should be designed to produce minimal, and ideally zero, sidestream wastes.

The general MAWS approach could be manifested in a variety of system configurations and process flows, depending on the quantities and compositions of the waste streams that are available at a given site. The system developed for the MAWS demonstration at the Fernald site integrates vitrification, soil-washing, and water treatment systems to treat blends of Pit wastes and contaminated soils.

Fernald pit wastes are rich in fluxes (such as calcium, magnesium, and fluorine) that reduce the melting temperature and viscosity of silicate glasses but are not, by themselves, glass forming. However, the large volume of uranium-contaminated soils (and in later stages of the program other wastes such as fly ash, asbestos, transite, etc.) provides an available source of glass-forming materials (mostly silica and alumina). Volume reduction is maximized and the flux:glass-former ratio is improved by pretreating the contaminated soils in a soil washing process. Soil washing studies on Fernald soils using the Lockheed TRUclean process have produced an approximately 80%:20% split between the decontaminated fraction and the contaminant-enriched fraction. The contaminated minor fraction is then blended with the pit wastes to produce a glass-forming feed for the vitrification process. The uranium contamination in the soil washing process water is removed by a supporting ion exchange water treatment system. A regeneration cycle is employed to strip the uranium from the ion exchange media and direct it to the vitrification system. Several GTS Duratek joule-heated glass melters and supporting off-gas treatment systems have been used in the development and demonstration activities in this program. The unique off-gas system employed permits capture of not only the hazardous and radioactive components but also the significant amounts of hydrogen fluoride produced in vitrifying these wet high-fluoride wastes. The off-gas system operates in such a way that no side-stream wastes are generated since off-gas sludges are recycled to the feed batch.

The MAWS development and demonstration program for the Fernald site is presently scheduled to proceed in two phases. Phase I of the MAWS program includes lab development and testing studies; lab proof of concept; design, procurement, and construction of system components; documentation and permitting; FEMP Plant 9 facility modifications to house the MAWS system; operator training; installation and operation of system components through radioactive soil washing and water treatment tests and non-radioactive vitrification system tests. Phase II is expected to include on-site system integration and proof of concept using Pit 5 waste; process control development; evaluation of equipment performance; evaluation of waste form performance; runs specifically designed to accumulate data in support of a delisting application; and incorporation of other FEMP wastes.

The major objectives of Phase I of this program are:

- Develop glass formulations that will fulfill the key MAWS concepts listed above, as applied to Fernald wastes, and satisfy the processability requirements of the Duramelter joule-heated vitrification system.
- Demonstrate, with actual Fernald waste, that these formulations can be processed in

laboratory continuous melter systems and use the test data that is collected in the detailed design of the on-site system.

- Demonstrate, with actual Fernald waste, that the Duramelter off-gas system captures fluoride emissions from the melter and produces a recyclable sludge. Demonstrate that the off-gas sludge can be recycled to the melter feed.
- Collect and analyze process data, off-gas data, system performance data, and waste form quality data from the continuous melter test runs.
- Demonstrate a lab-scale soil washing process that will decontaminate Fernald uranium-contaminated soils to below 35 pCi/g and provide sufficient contaminant-enriched soil-wash fractions for the lab-scale vitrification tests.
- Demonstrate a lab-scale ion-exchange process that will remove uranium from actual soil-wash water produced in the lab-scale soil washing tests.
- Demonstrate a lab-scale ion-exchange regeneration process in which the captured uranium is directed to the vitrification process.
- Deploy a system at the Fernald site which consists of: a GTS Duratek Duramelter glass melter and supporting off-gas treatment system capable of a minimum glass output rate of 300 kg/day; a Lockheed TRUclean soil washing system capable of processing at least 0.25 yd^3/hr; and a GTS Duratek ion exchange water treatment system capable of processing at least 100 gallons/minute.
- Demonstrate the operation of the on-site system by treating at least 100 yd^3 of contaminated soil in the soil washing system with supporting water treatment.
- Demonstrate the operation of the on-site vitrification system by processing a borosilicate glass test feed.

As we discuss in detail below, Phase I activities have successfully met all of the above objectives.

1.1 The MAWS System

Figure 1.1 shows the principal process flows between system components for the FEMP MAWS demonstration. The GTS Duratek Duramelter vitrification system used has a nominal glass production rate of 300 kg/day and is based on standard joule-heated ceramic melter

(JHCM) technology as employed in high-level waste vitrification applications but includes a number of proprietary innovations to enhance throughput rates and expand the operating envelope, as discussed further below. The off-gas treatment system is also based on existing commercial technology with a number of proprietary improvements. These changes related to the need to capture not only the hazardous and radioactive components but also the significant amounts of hydrogen fluoride produced in vitrifying these wet high-fluoride wastes. The off-gas system operates in such a way that no side-stream wastes are generated since off-gas sludges are recycled to the vitrification feed batch and the majority of the fluoride is retained in the glass on each cycle.

Soil washing is provided by Lockheed Environmental Services Corporation's (LESC) TRUclean system which has a processing rate of about 0.25 yd^3/hr and combines physical and chemical processes such as density and particle size separations and uranium leaching by mild oxidation and carbonate extraction. This system is supported by a GTS Duratek ion exchange water treatment system with a 100 gallon/min throughput capacity.

FEMP Pit 5 sludge has a high water content (about 71 wt%) and a major objective is to target high waste loadings with respect to sludge which leads to feed blends with a high water content; a slurry feed system to the melter was therefore selected although a dry feed system may also be tested later in the program. The waste streams are blended in 4000 gallon mixing tanks to produce a feed batch which is then fed to the melter continuously. Batch preparation and feeding alternate between the two tanks. Characterization data on the waste streams are used to determine the requisite quantities of each stream, and samples from the mixing tank are taken to determine chemical additive requirements. These analytical data are used for process control by comparison with models for the effects of composition on key glass processing parameters determined from supporting laboratory studies. Thus, process and product control is effected through control of the feed (and therefore the glass) composition. Determination of the operating envelope is discussed further below.

1.2 Schedule Overview

Phase I of the MAWS program began in June 1992. This includes lab development and testing studies; lab proof of concept; design, procurement, and construction of system components; documentation and permitting; FEMP Plant 9 facility modifications to house the MAWS system; operator training; installation and operation of system components through non-radioactive vitrification system tests. Phase II is expected to include on-site system integration and proof of concept using Pit 5 waste; process control development; evaluation of equipment performance; evaluation of waste form performance; runs specifically designed to accumulate data in support of a delisting application; and incorporation of other FEMP wastes.

1.3 Laboratory Support

Development and demonstration of the MAWS approach is supported by a variety of laboratory studies as illustrated in Figure 1.2. Figure 1.3 shows the interrelationships between the various laboratory activities in support of the on-site system installation and demonstration. The VSL is responsible for the wasteform design by glass composition optimization, and for a variety of analytical, glass melting, characterization, and modelling activities. Small-scale Duramelter vitrification systems are installed at VSL for laboratory tests with actual radioactive FEMP wastes. These systems have nominal glass production rates of 10 kg/day and 100 kg/day. Thus, a step-wise approach is used, including crucible melts, laboratory system tests, and on-site tests, in order to extract the maximum benefit from the necessary compromise between the relatively low cost of small-scale tests and the increased realism of larger-scale tests. The laboratory Duramelter systems are used to obtain process related data, especially on off-gas emissions, that cannot be obtained from crucible melts but are critical in expediting the startup of the on-site system. Furthermore, a number of design changes have been made in the on-site system as a result of these tests.

LESC soil laboratory is responsible for the soil characterization and lab-scale testing necessary for process development and design and construction of the on-site TRUclean system. These tests also produce the soil-wash concentrates necessary for laboratory vitrification tests at VSL. A GTS Duratek ion exchange water treatment system is installed at LESC to support these tests. Loaded ion exchange columns were provided for regeneration and vitrification tests at VSL.

Samples of the vitrified waste were provided for additional leach testing at Argonne National Laboratory (ANL). These studies employ standard (e.g. Product Consistency Test (PCT)) as well as non-standard (e.g. vapor-phase hydration) tests to study the effects of a range of conditions on the waste form and its ability to immobilize the contaminants of concern. Particular attention will be paid to alteration phases that are formed under very extreme reaction conditions. Identification of such phases can be helpful in modelling efforts.

This report presents the results obtained during Phase I of this program with the exception of the data collected from studies at ANL and from soil-washing testing which are presented in separate reports.

1.4 Waste Materials Used in the Study

The FEMP identification numbers for the various Pit 5 sludges used in this study are listed in Table 3.1 of Section 3. The VSL identification numbers of the Lockheed soil-wash fractions are listed in Table 3.2 of Section 3.

1.4.1 Pit 5 Sludges

A total of six 55-gallon drums of Pit 5 sludge were received at the VSL. The drums were given VSL identification numbers FE1, FE14, FE15, FE16, FE51, and FE52, in the order in which they were received. The FE prefix was used to identify material for Fernald Environmental Management Project studies. FE1 was received in March of 1992; FE14, FE15, and FE16 were received in February of 1993; and FE51 and FE52 were received in July of 1993. As discussed in Chapter 3, these Pit 5 samples all consisted mainly of Ca, Si, and Mg, but varied greatly in their fluoride and sulfate contents. Crucible melts were made from all six 55-gallon drums of Pit 5 material, 10 kg/day melter runs were made using only FE1, and 100 kg/day melter runs were made using FE14, FE15, and FE16 Pit 5 drums. Radionucleide concentration data on Pit 5 sludge provided by FEMP (Roy Weston CIS) are summarized in Table 1.1.

1.4.2 Lockheed Soil-Wash Fractions

A total of 31 5-gallon pails of soil-wash fractions were received from Lockheed between October of 1992 and June of 1993. These samples were identified by Lockheed as either "cyclone underflow" (SiO_2 rich, inorganic) or as various organic fractions retained on various mesh sizes (for example, +20M for the soil fraction retained on mesh #20). A number of 5-gallon pails were shipped with the same label. For example, there were six 5-gallon pails which were identified as +20M. After giving each 5-gallon pail a unique VSL identification, the soil samples were combined to produce mixtures from three or four separate 5-gallon pails. The reason for mixing some of the soil samples was to reduce the number of analyses from 31 samples to something more manageable. Seven different soil samples were used for crucible melts, one type of soil sample was used for the 10 kg/day melter runs, and eleven different soil samples were used for the 100 kg/day melter runs.

Table 1.1
Radionuclide Content of Pit 5 Sludge
(FEMP, Roy Weston CIS)

Isotope	Activity, pCi/g	Isotope	Activity, pCi/g
^{230}Th	3080-20200	^{99}Tc	423-2990
^{238}U	387-1230	^{234}U	310-1250
^{226}Ra	235-999	^{228}Th	41-191
^{232}Th	21-90	^{235}U	14-79
^{137}Cs	2-76	^{106}Ru	13-35
^{237}Np	0.3-23	^{90}Sr	0.8-23
^{239}Pu/^{240}Pu	0.1-13	^{238}Pu	0.1-4.4

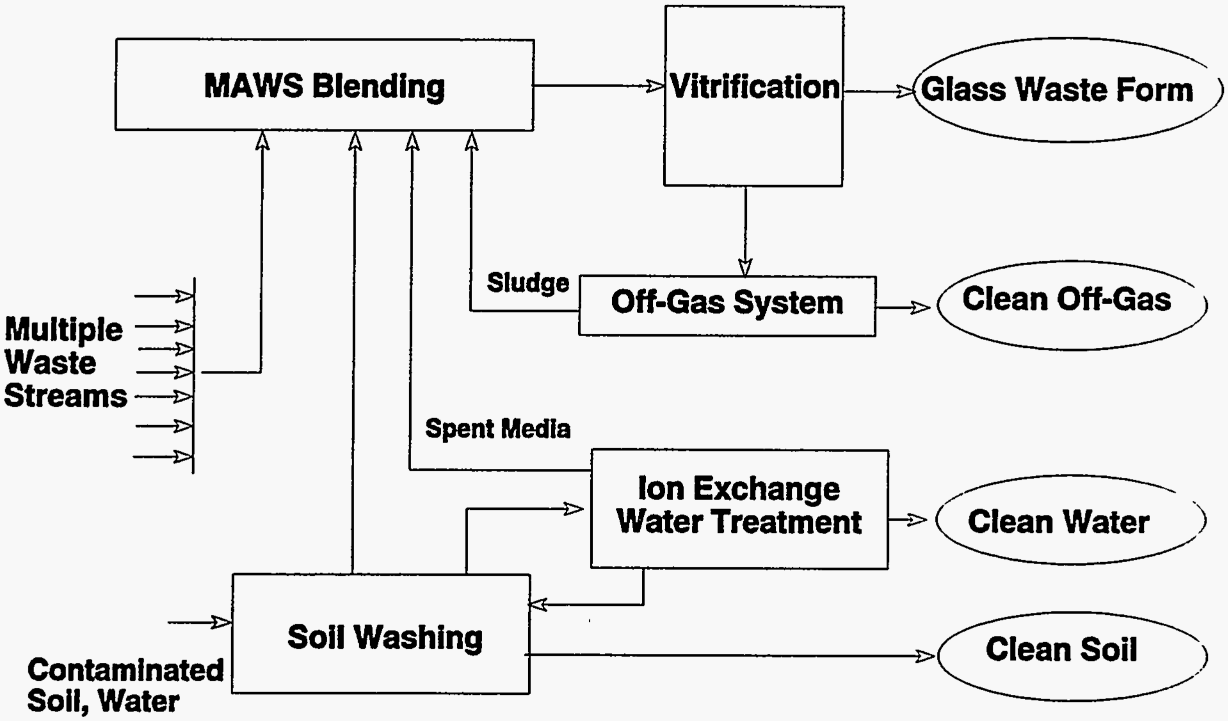


Figure 1.1
The MAWS system process flow.

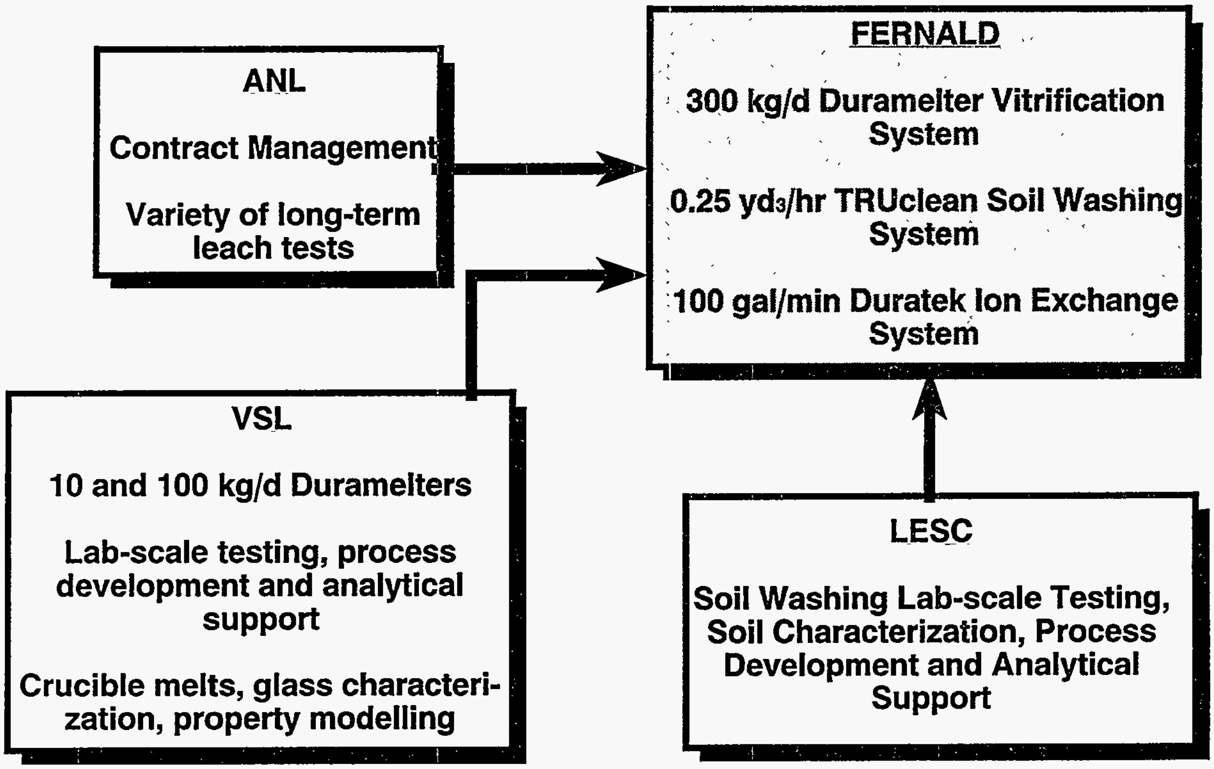


Figure 1-2.
MAWS system components and off-site support.

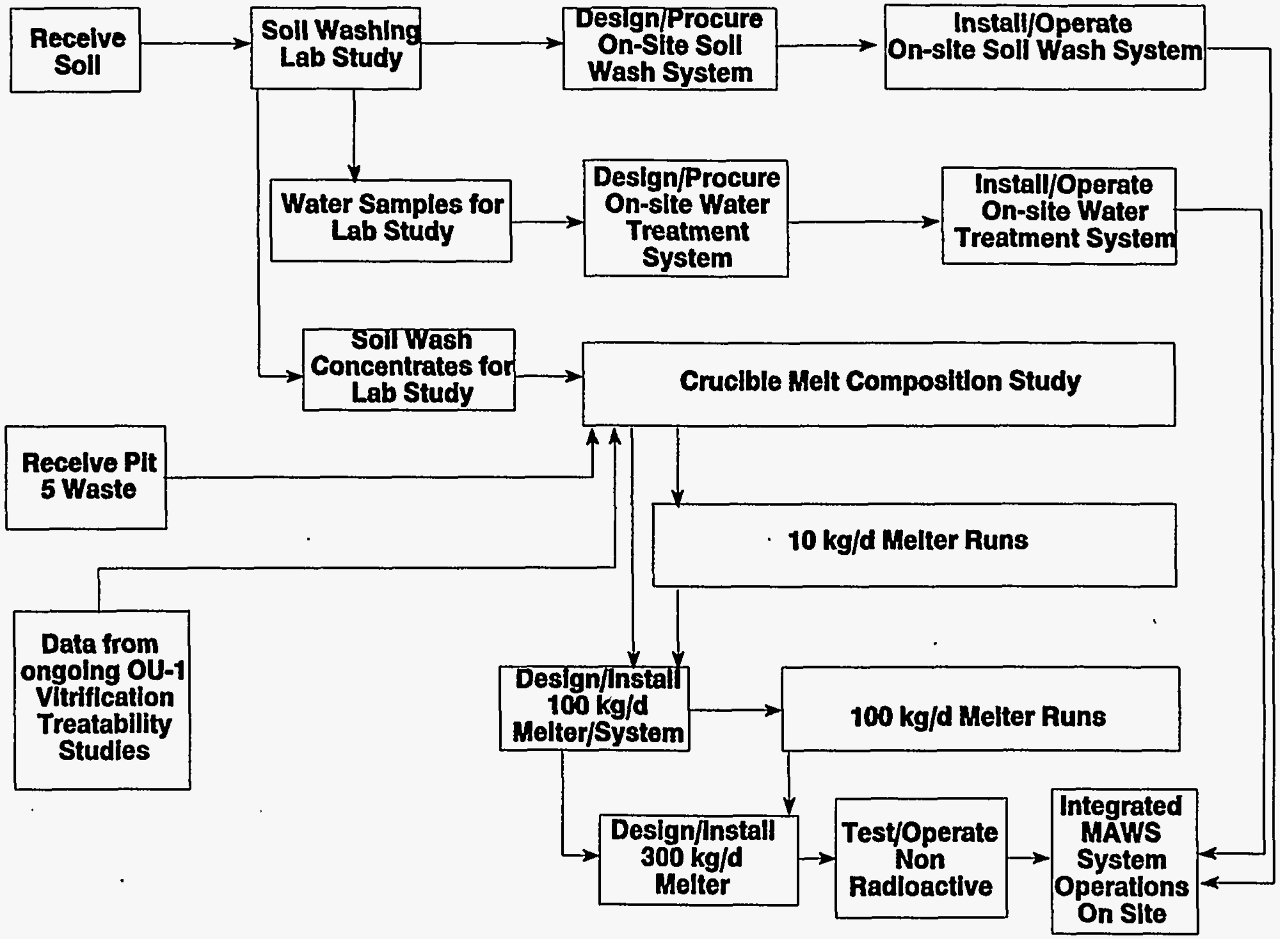


Figure 1.3
Relationship between laboratory support activities and the installation and demonstration of the MAWS system at Fernald.

SECTION 2.0
Methodology and Approach

2.1 Introduction

The objectives of the present laboratory-, bench- and pilot-scale study include development and demonstration of the major principles on which the MAWS approach is based and the accumulation of process and product characterization data necessary for the development and evaluation of the suitability of the approach for larger-scale applications.

A schematic diagram of the vitrification development activities in the MAWS program is shown in Figure 2-1. The glasses produced are then characterized to obtain data on key process parameters and waste form performance parameters, as shown schematically in Figure 2-2. An objective of this study is to obtain an understanding of the relationship between glass composition and these key parameters since this permits selection of optimum formulations for treatment by vitrification. Melt viscosity as a function of temperature is an important factor in determining processing temperature since a high viscosity results in slow throughput rates and very low viscosity melts are often more corrosive. A similar compromise is necessary with the electrical conductivity of the melt for acceptable processing by joule-heated melting; high conductivity melts lead to electrode current density limitations whereas low conductivity melts increase the conduction through the melter refractories. Phase stability and glass microstructural data are necessary to determine the lower limit of processing temperatures beyond which melt crystallization occurs, since this could cause melter clogging.

Leach resistance is obviously an important performance criterion since the role of the glass waste form is to immobilize the hazardous and radioactive constituents and minimize their release into the environment. Two leach tests were used in this study: the Environmental Protect Agency Toxicity Characteristic Leaching Procedure (EPA TCLP) test procedure and the Savannah River Product Consistency Test (PCT). The EPA TCLP test is an 18 hr test at 22°C for release of hazardous components to the leaching solution. Since these are rather benign conditions for glass, the Savannah River PCT test (Jantzen and Bibler, 1989), which is the present standard for high-level nuclear waste glasses, was also employed. The PCT test is a seven-day test at 90°C using 75-150 μm glass powder and is usually significantly more aggressive than the TCLP test. In addition, data from the PCT test permit direct comparison of the glass leaching behavior with that of high-level nuclear waste glasses.

Finally, there are also important economic factors involved in identifying the best formulations for vitrification of any given waste stream. These are primarily the waste loading that is achievable, since increased waste loading decreases overall treatment costs, the cost of the chemical additives that are used in the formulation, and disposal costs.

Glass composition development then is a problem in multi-parameter constrained optimization and a true optimal solution would require a huge number of experiments.

Fortunately, however, a practical solution can usually be obtained with a manageable number of experiments through the application of known principles from glass chemistry and the use of composition-property modelling.

Viable glass compositions are selected on the basis of crucible-melt studies for further testing in continuous melter systems. A step-wise approach is used progressing from the 10 kg/day and 100 kg/day laboratory Duramelter systems up to the on-site 300 kg/day system. Each step provides more realistic information and approaches more closely the process that will occur in the production size system. The continuous melter tests provide information, such as off-gas emissions and processing rates, that cannot be obtained from crucible melts. Information learned in the small scale melter tests provides an important basis for the design and selection of larger, production-scale systems.

2.2 Waste Stream Characterization

The starting point in evaluation of the suitability of vitrification as a treatment method for a particular waste stream is characterization of the waste material. The characterization data are also essential in the development of optimum glass formulations for the particular problem. The primary data requirements are for chemical composition, with particular emphasis on the major components. It is often the case that detailed data on contaminant concentrations have been collected for regulatory purposes, but only very gross information is available on the bulk constituents; it is the latter data that are most important for vitrification development since precise information on trace constituents is of little benefit for that purpose.

In a broad sense, waste streams can be classified on a spectrum of "silica-rich" (or more generally "glass-former rich") to "flux-rich", with these extremes having opposite effects on melting temperature and melt viscosity. The characteristics of the waste then determines the types and amounts of additives that are required in order to meet the design objectives (see below). Generally, flux-rich wastes will not form acceptable glasses due to either poor leach resistance or crystallization. Similarly, glass-former rich wastes will only form glasses at high temperatures and typically require the addition of fluxing agents to reduce the processing temperature.

Waste stream compositional information should include all components present at greater than about the 1 wt% level on a dry basis for glass development purposes. This should include anions as well as cations. Total carbon content is useful for assessment of potential redox effects, as is the content of metallic components. Thermogravimetric measurements (weight loss versus temperature) and particle size analyses also provide useful data from a process perspective. Since it is ultimately necessary to determine the fate of all of the contaminant species of concern, the concentrations of these species in the waste must be determined but are not critical in the glass design process.

While there are many classes of glass forming systems including chalcogenides, heavy metal fluorides, and oxynitrides, only two - silicates and phosphates - have found significant applications in waste treatment. However, silicates are by far the most commonly used due mainly to the ubiquity, and therefore low cost, of silicon-bearing minerals in nature. Silicate glasses can be formulated to incorporate a very wide range of concentrations of the majority of the elements of the periodic table.

2.3 Glass Formulation Development

Development of viable glass formulations for any given waste stream is basically a problem in constrained multivariate optimization. As such, it is therefore essential to recognize and state clearly both the imposed constraints and the key variables in the problem. The constraints can usually be summarized in three categories: Economics, Processability, and Product Performance.

Economics

The process should operate as economically as possible, for obvious reasons. Some of the major factors that influence the overall economics are the following:

(i) Waste loading, or conversely stated, minimum addition of non-waste additives in order to produce the stabilized waste form. Additives impact the overall economics from several perspectives. First, is the direct cost of the additives themselves. Second, is the cost associated with running the non-waste additives through the process, which will include a combination of additional operating costs (labor, utilities, etc.) and increased capital costs, depending on whether the additives are accommodated by increasing the size of the process or the length of the production run. Third, is the increased disposal costs since a certain fraction of the volume of the waste form is comprised not of waste but of purchased additives. Waste loading is discussed further below.

(ii) Volume reduction. Since disposal of the final stabilized waste form invariably incurs a per-unit-volume disposal cost, the volume change upon stabilization is an important economic factor. Processes in which the volume is decreased upon stabilization are therefore favored over those in which the volume is increased. Similarly, high density waste forms are favored, as are processes in which innocuous components (e.g. water, carbon dioxide, etc.) are removed, rather than contained within the waste form. Volume reduction is discussed further below.

(iii) Process specific factors. Processes will differ in their operating and capital costs between each other and depending on the waste volume to be treated and the completion time required.

Processability

Viable glass formulations must be capable of being processed through the particular type of system under consideration. Systems differ in the types of constraints that they impose on the feed formulation; those of importance for joule-heated melter processing are:

(i) Phase Stability. Many systems involve a molten glass bath into which the waste feed is dissolved. If a homogeneous molten liquid is produced at the processing temperature, draining of the melt and long-term operation is facilitated. Conversely, if crystalline phases are formed, sedimentation can occur which may ultimately lead to clogging as those materials accumulate. Thus, the liquidus temperature - the highest temperature at which crystals will form from the melt - is an important processing parameter. It is desirable to operate the process at a temperature above the liquidus temperature. The liquidus temperature is, in general, strongly composition dependent and is determined by different crystalline phases in different composition regions. Nominal feed formulations must therefore be selected such that the liquidus temperature remains below the processing temperature for all reasonable variations in feed composition.

(ii) Melt Viscosity. Many of the factors which determine the processability of a particular feed in a given vitrification system, have an underlying dependence on the viscosity of the melt. Mixing and reaction processes, including convection, diffusion, and the effect of active stirring, depend on the melt viscosity and can also determine throughput rates. The melt viscosity is strongly dependent on the melt composition and temperature. Understanding and quantifying this dependence is an important factor in the determination of optimized feed formulations and also plays a role in the selection of the processing temperature through the interplay between system constraints and glass formulation constraints.

(iii) Electrical Conductivity. The electrical conductivity of the melt is an important factor affecting processability in vitrification systems that rely on electrical conduction through the melt in order to produce power dissipation into the melt by the joule heating effect. The conductivity determines such parameters as electrode sizes and spacing and power supply specifications. Again, the electrical conductivity of the melt is strongly dependent on its composition and temperature. Therefore, this dependence must be quantified in order to select target feed formulations for a particular system design and in order to determine acceptable ranges of variation in feed composition.

Note that there is an additional requirement of compatibility between the molten glass, the feed, and the off-gas with the materials of construction of the various vitrification system components. This is, however, more appropriately addressed as an engineering design issue.

Product Performance

The objective of the stabilization process is to change the physical and chemical form in such a way that specific performance criteria are met. Typical criteria of concern are the following.

(i) Leach Resistance. Generally, the most important requirement from a product performance perspective is that the waste form be highly resistant to leaching of the contaminants of concern, since a major objective of the remediation process is to effectively isolate those contaminants and prevent their release into the environment. As with other properties, glass leach resistance is strongly dependent on composition. However, it differs significantly from other properties, such as the viscosity, in that it is rather more subjectively defined. The observed rate of reaction of glass with water is highly dependent on the conditions that are imposed. Important factors include the temperature, the composition of the leachant (e.g. pure water, a natural groundwater, a pH-buffered solution, etc.) the time elapsed since the start of the reaction (initial rates are typically greater than later rates), and the ratio of the surface area of the glass to the volume of leachant. Standardized leach test methods have been developed which attempt to fix these factors at well-defined values so that meaningful comparisons between glasses can be made. The more relevant question is, however, "How will the waste form perform in the environment?", and in that respect data from some leach test procedures may be more relevant than others. In fact, efforts have been made to perform tests under the conditions expected to obtain in a given disposal site and to perform tests in an actual location - so called *in situ* tests. Other tests have grown out of the need to regulate waste and waste forms based on leachability, such as the EPA Toxicity Characteristic Leaching Procedure (TCLP).

Phase stability can also impact the leach resistance of the resulting waste form due to the formation of secondary phases as the molten glass cools after exiting the process. The leach resistance of a homogeneous glass can be easily controlled by careful control of the glass composition. However, if secondary phases are formed to any significant extent, the problem becomes more complicated since the secondary phases could be more soluble than the glass or may sequester constituents from the host glass which could degrade its leach resistance. The extent of these concerns obviously increases with the amount of secondary phases present. In particular, for a more soluble minority phase, an important question is whether that phase forms contiguous pathways (i.e. is "percolated") throughout the matrix. It should be emphasized, however, that extremely leach resistant waste forms can be formed from partially or extensively crystallized glass melts. When significant phase separation is present, it is simply another variable which must be controlled and understood, since the types and amounts of secondary phases and the waste form microstructure are all factors that can influence the leach resistance.

It is important to appreciate the critical dependence of the leachability measurement on the imposed test conditions. For example, if leachant pH is considered, the TCLP test is conducted under slightly acidic conditions and, therefore, by that measure, a glass formulation that shows good acidic leach resistance is favored. This may be of little relevance in terms of actual performance if the disposal conditions are likely to be alkaline. Unfortunately, disposal conditions are often unknown or poorly defined during the waste form development phase, and that is indeed the case at FEMP. We have, therefore, used a combination of both the TCLP and the PCT procedures since these evaluate leachability under two quite different sets of conditions.

(ii) Compressive Strength. The compressive strength of the waste form is important for land disposal due to the possibility of subsidence. If subsidence should occur, it provides a means for water collection and pooling, rather than run-off, which would tend to increase contaminant release. Glass-based waste forms have extremely high compressive strengths and this is rarely a constraining factor for these materials.

(iii) Volume reduction. While volume reduction was considered as an economic factor above, it should also be included as a performance consideration since there is an additional non-economic incentive to minimize the size and number of the disposal facilities that are required to store the treated waste.

The role of glass formulation development is then to arrive at the optimum compromise between these competing factors by variation of the target glass composition. It should, however, be emphasized that the selection of a particular process or set of operating conditions should not be divorced from the glass formulation development and *vice versa*; good communication between these activities is essential to arriving at the most efficient and effective solution, and, we believe, one of the keys to the success of Phase I of the MAWS program.

2.4 Facilities, Equipment, and Experimental Methods

The major operations performed at VSL to support this development and demonstration program included glass melting; standard leach tests on the vitrified product; analysis of the raw materials, the vitrified product, and leachates; and product characterization. Standard glass characterization techniques including viscosity, conductivity, Direct Current Plasma (DCP) analysis, and microstructure determination using Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) were performed at VSL. A short description of the techniques used are given below. Each of these techniques are described in detail in VSL technical procedures.

Specific Gravity: The specific gravity of soils, sludges, and fly ashes were determined using a pycnometer and the procedure specified in American Society for Testing and Materials (ASTM) D854-83. At least two measurements were made for each sample and the expected uncertainty in the specific gravity measurement is, as described in ASTM D854-83, within a standard deviation of 0.021 g cm^{-3}.

Carbon Content: The carbon content of sludge and soil samples was measured using a Dohrmann DC-80 Carbon Analyzer fitted with a 183 Boat Sampling Module (BSM). This system is capable of measuring the total carbon (TC), total organic carbon (TOC), and the inorganic carbon (IC) contents of wastewater, slurries, sludges and solid samples. Each liquid sample is measured at least five times and the measurements typically agree to within ±10%. We estimate the error of measuring the carbon content of solids to be also within ±10%. These errors are purely analytical, however, and do not include sampling errors which can be quite significant when sampling very small quantities of FEMP wastes.

Sieve Analysis: The distributions of particle sizes in soil and sludge samples were determined using ASTM procedure D422-63. The major sources of error for these measurements are: accuracy of sieve size, particles left on the sieve which should have passed through, and weighing errors. We estimate the accumulation of these errors to be about ±10%.

Weight Loss: The weight loss data were obtained by heating representative samples of sludges and soils as follows: 110°C for 18 hours; 450°C for 4 hours; 850°C for 4 hours; and 1150°C for 4 hours. Programmable Deltech furnaces (DT-28-12 and DT-28-06) were used for the weight loss measurements and consequently the time and heating rates could be easily controlled. The major source of error in our weight loss measurements is due to errors in weighing which we estimate to be ±5%. Uncertainties from sample-to-sample variations (sampling errors) are estimated to be ±15%.

Particle Size Analysis: ASTM D422-63 procedure was used to determine the particle-size distribution of soils and sludges.

Gamma Spectroscopy: A Canberra Gamma Spectroscopy system coupled to a personal computer was used to obtain gamma spectroscopy measurements. Only qualitative measurements were made on Fernald sludges and soils due to calibration difficulties relating to geometric and self-screening corrections for such materials.

Glass Melting: Crucible melts were made with various Pit 5 sludges dried at 450°C for four hours (except F5-54B, F5-55B, F5-57B, and F5-58B), soil-wash fractions produced at Lockheed's soil laboratory which we dried at 1150°C for four hours, and additives. The FEMP wastes and additives were manually mixed by shaking in a plastic container and transferred to a crucible (platinum-gold or clay). The crucible was then placed in a furnace at 1150°C, and the blend was typically melted at 1150°C for one hour, with stirring during the last half hour.

Heat Treatments: Approximately two-gram samples of various FEMP glasses were heat treated for specified times and temperatures. Unless otherwise stated, each sample was premelted at 1100°C for one hour before the heat treatment in order to dissolve any pre-existing crystals or crystal nuclei which may have been present in the as-melted glass.

Viscosity Measurement: The viscosity was calculated from measurements of the torque and rotation speed of a calibrated spindle attached to a Brookfield viscometer. Measurements were made over a range of temperatures, usually from 1000°C to 1200°C, and the data interpolated to standard temperatures. The equipment was calibrated using standard oils of known viscosity and checked using a National Institute of Standards and Technology (NIST) standard reference glass (SRM711). The precision and accuracy of the viscosity measurements are estimated to be within ±10%.

Conductivity Measurement: The electrical conductivity of the glass was determined by measuring the resistance of the glass melt as a function of frequency using a calibrated platinum electrode probe. The results were extrapolated to zero frequency to obtain the DC conductivity. These measurements are taken over a temperature range of typically 1000-1150°C, and the data interpolated to standard temperatures. The equipment was calibrated using salt solutions of known concentrations. Estimated uncertainties in the conductivity measurements are ±5%.

<u>TCLP Test</u>: The TCLP leach test was used to determine the leach resistance of the glasses that were produced by measuring the leachate concentrations obtained after 18 hours at 22°C in a sodium acetate buffer solution. The leachate concentrations were measured by both DCP and Inductively Coupled Plasma Mass Spectrometry (ICPMS). The overall uncertainty is estimated to be ±20%.

<u>PCT Test</u>: The PCT test evaluates the relative chemical durability of glasses by measuring the concentrations of the chemical species released from crushed glass (75-150 μm) to the test solution (deionized water in this case) at 90°C. All tests were conducted in triplicate (except where noted) with a standard glass (West Valley Reference 5) included in each test set. The overall uncertainty in the test results is estimated to be ±15%. The leachates were (or will be) sampled after 7, 28, 56, 120, 240, 360, 540, and 720 days; data extending to 120 days are included in this report. At each sampling date, 4.0 ml of the leachate is removed for analysis from each test vessel and is replaced by 4.0 ml of deionized water.

<u>Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)</u>: Scanning electron microscopy was used to characterize the microstructure of the glasses and permits analysis of the glassy and crystalline phases using energy dispersive x-ray spectrometry. This equipment permits determination of both the volume fractions and compositions of crystalline phases in both as-melted and heat treated glasses. The percentage of crystals is estimated by examining several regions of a ~1 cm^2 sample, and is accurate to about ±20%. The identity of major crystalline phases was also confirmed by X-ray diffraction measurements.

<u>Heat Dissolution of Sludges, Soils, and Glasses</u>: Various combinations of acids (HF, HCl, HNO_3, and H_2SO_4) are used to dissolve sludges, soils, and glasses, depending on the composition of the sample. The samples are dissolved completely by heating (typically 100 mg in 200 ml of solution) in a sand bath at 70±10°C for several hours. Further volumes of one or more acids were added as necessary to complete dissolution.

<u>Microwave Dissolution of Glasses</u>: In addition to heat dissolution, microwave dissolution in HF/HNO_3 solutions was used. Microwave dissolution, in general, permits faster dissolution than heat dissolution, and it is therefore becoming the dominant mode of dissolution in our labs.

<u>Solution Analyses</u>: Direct Current Plasma Emission Spectroscopy (DCP-ES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ion chromatography, and ion selective electrode techniques were used for solution analyses. The overall uncertainty associated with DCP-ES analysis is ±5%, that for ion chromatography and ion selective electrode analyses is ±10%, and for ICP-MS, the uncertainty is estimated to be ±30% for semi-quantitative analysis and ±15% for quantitative analysis.

<u>Fluoride Analysis</u>: The fluoride content was determined by a modified Environmental Protection Agency (EPA) SW846 procedure which involves microwave dissolution of the glass in a two-step process using NaOH then aqua regia. Once the fluoride is in solution, a fluoride electrode is used to determine its concentration. The experimental reproducibility of our fluoride analysis

is within ±15%.

2.5 Quality Assurance

FEMP treatability studies were conducted at VSL under a Quality Assurance program in order to ensure the reliability, verifiability, and traceability of data obtained in the laboratory. The program established at VSL strictly complies with the applicable quality assurance program requirements for nuclear facilities outlined in American Nuclear Standards Institute/American Society of Mechanical Engineers (ANSI/ASME) NQA-1. The implementation of the Quality Assurance program was effected for this project as follows:

(1) Both a Project Specific Quality Assurance Plan and a Work Plan were developed for this work.
(2) A full-time Quality Assurance Officer (QAO) supervised the implementation of the QA program throughout the duration of the project.
(3) Technical procedure requirements were reviewed and several new Standard Operating Procedures were developed. These include specific procedures for characterization of wastes, fluoride analysis, analysis of TCLP extracts, and dissolution of glass.
(4) In addition to the regular internal surveillance activities by the VSL QAO, and audits by other Department of Energy (DOE) project sponsors, FEMP QA representatives conducted an audit (Westinghouse Environmental Management Company/Fernald Environmental Restoration Management Company (WEMCO/FERMCO) Supplier Evaluation) of VSL QA program activities during the period September 24-25, 1992 and subsequently made a follow-up visit on February 25, 1993. The Evaluation Team concluded that "VSL is capable of providing analytical analyses in accordance with requirements, as currently specified, for FEMP Analytical Support Levels A, B, and E." The Evaluation Team closed out the audit by verifying the implementation of the corrective actions carried out by VSL in response to the Evaluation Team's observations.
(5) Data obtained at each stage of the project were reviewed by the competent Laboratory Managers, the Project Manager and the Principal Investigator for accuracy and reproducibility. Periodic validation by the QAO and statistical quality controls in place at VSL ensured the reliability of the data and the results.

In addition to the above, VSL's QA program continuously monitored and addressed the training needs of the personnel involved in order to ensure that all project activities fully complied with the QA requirements and stringent safety standards.

2.6 Safety Considerations

The activities performed in this project involve materials, equipment and procedures which, as is always the case, have potential hazards associated with them. Training, planning and design were employed to minimize or eliminate these potential hazards. The present discussion of safety issues primarily addresses the operations at the VSL, but the basic design of the melter system and mode of operation at Fernald is similar except for matters of scale and the requirements of operating at the Fernald site.

Both GTS Duratek and the VSL have established training programs which specifically and address safety issues. The VSL program involves the Catholic University of America's Chemical Hygiene plan, general laboratory safety training, and job-specific training which address chemical and laboratory safety. In addition, workers involved with radioactive materials take a two-day course in general radiation safety and receive job-specific training as needed. The handling of radioactive materials at the VSL requires approval of plans and procedures by an independent campus Radiation Safety Committee which is chaired by a full-time health physicist. For radioactive melter operations this committee requires procedure reviews and Operational Readiness Reviews before the approval and commencement of new activities. GTS Duratek personnel received HAZWOPER, radiation, and site-specific training as required for operators at the Fernald site. Certain GTS Duratek employees also received melter operation training at the VSL on the Duramelter™ 10 and 100 melters.

In addition to general operating and laboratory hazards, this project involves potential specific hazards and therefore these received further attention. Some of the major areas of concern are listed here and discussed below. The melter is electrically heated and the power supplies involve high currents and moderate voltage levels. The melters operate at temperatures in excess of 1150°C, and certain exposed components and molten glass can cause burns to skin if contact is made. Refractory materials used in the construction of the melters pose potential dust hazards during certain operations. Fluorine, a reactive gas, vaporizes from Fernald-type glass and feeds at high temperature and, in the presence of water vapor, forms HF, a corrosive and hazardous acid. The scrubber uses highly caustic (3M) NaOH solutions to neutralize the HF. The Fernald feeds are primarily mixed waste sludges and soils requiring careful handling to prevent laboratory and personnel contamination. These potential hazards were addressed via planning, specific training and design of the equipment.

The radiation levels and hazardous material levels of the Fernald sludges and soil wash fractions are relatively low (< 0.5 mrem/hr at the surface of the drums) and similar to materials which have been handled in many previous projects at the laboratory. Laboratory personnel involved with these radioactive materials received training as discussed above and were provided with film badges to monitor exposures. Exposures recorded are essentially background.

Although the waste materials exhibit low activity, there is concern with the handling of sludges and soils due to the potential for dust contamination, ingestion or inhalation. Where there is the potential for dust contamination, samples are handled in glove boxes or hoods. Several glove boxes were constructed with special bottom ports capable of accepting and sealing against the upper section of 55 gal drums. This construction permits the opening of drums, withdrawal and mixing of materials, etc. without directly exposing the laboratory or personnel to the material. Materials can be withdrawn from the glove boxes by pumping, in the case of slurry feeds, or in sealed containers through a pass-through, in the case of bulk samples. The glove boxes are operated under negative pressure with the exhausted air being filtered by two HEPA-filters in series before release to the atmosphere above the roof of the laboratory.

Crucible melters which involve small amounts of waste samples (a few hundred grams) are operated in hoods with High Efficiency Particulate Air (HEPA) filtered exhausts. The hoods accommodate the melting and glass pouring operations. The glasses do not have appreciable volatile radioactive components but do volatilize fluorine. Other high temperature operations with the glass, such as viscosity and conductivity measurements, also have exhaust hoods for personnel protection.

Maintenance and construction of furnaces and melters require the handling of insulation materials such as fiberboard. These materials are respiratory irritants and possible carcinogens. Cutting of the materials is done in a room with a baghouse dust collector. Personnel wear disposable protective clothing and respirators for dust protection when handling and cutting the materials. HEPA vacuum cleaners are used to clean the work area.

The Duramelters and associated feed, off-gas, and glass product discharge are designed as sealed systems and/or are operated under negative pressure to prevent the escape of hazardous materials. A schematic diagram of a melter system is shown in Figures 10.1a-c to illustrate the major features.

During normal operations the melter is vented via the main exhaust port through a scrubber system. If the main exhaust path becomes blocked and the melter pressure rises above a setpoint, an emergency exhaust line is opened by an automatic valve. This action keeps the melter under negative pressure. An audible alarm is also activated and any feeding to the melter is interrupted. The emergency line bypasses the scrubber but is cooled by dilution air and HEPA filtered before exhaust to the atmosphere. For further isolation, at the VSL, the melters are enclosed in their own room, with the operators and controls located outside. In the unlikely event of complete failure of the exhaust system and pressurization of the melter, forced air respirators are provided for personnel protection during emergency operations.

As stated above, HF vapor is produced in the melter. This vapor is potentially hazardous if not contained and neutralized. The sealed design and negative pressure operation isolate the melter gasses from the laboratory. The exhaust line materials are chosen to be resistant to HF vapor. Monel 400 and 316 stainless steel were chosen to ensure continued integrity. Inspections have found no indications to date of significant corrosion in the melter parts. The length of operating campaigns has been rather limited, however, and critical parts will receive continued scrutiny. After a short section of exhaust line, the gasses enter the first off-gas treatment unit which serves as a quencher and solid recovery scrubber. In the entrance pipe the first of a series of nozzles spray concentrated NaOH solution to cool and neutralize the exhaust gasses as quickly as possible. The spray from additional nozzles in the quencher column continue the quenching and neutralization process. The result is that the majority (~ 97% in initial tests) of the fluorine is trapped and rendered harmless in the quencher and is further reduced in the more efficient packed bed scrubber that follows. The amount of fluorine after passing through the system HEPA filter was below our detection limit of 25 ppb. The principal scrubbing product is NaF which is relatively harmless (it is an ingredient in toothpaste). The high concentrations of NaOH and NaF in the scrubber solutions, however, require resistant seals in the pumps such as tungsten carbide to prevent premature failure and leakage. The plumbing lines for the scrubber solutions are 316 stainless steel and are operated at pressures well below their design strengths. Because of the caustic nature of the concentrated NaOH solutions, personnel wear protective gloves and face shields when drawing samples or replenishing the scrubber solution supply.

The design of the melter operation is such that no net secondary wastes are generated. They are either released as clean gas and water vapor or recycled with the collected NaF solids. The water is vaporized from the scrubber sumps by controlling the temperature of the sump liquid via the amount of cooling provided. The NaF is pumped directly from the first solid recovery scrubber to the feed preparation glove box as a slurry in the Duramelter™ 100 and 300 systems. Both of these operations avoid direct operator handling of the secondary streams and thus operator hazards.

As mentioned above, the feed materials received in drums at the VSL are accessed from a glove box. All of the mixing and blending of the wastes is done in this closed environment. The feed tank is located in the glove box and is connected to the feed pump directly with a stainless steel pipe. The feed line is stainless steel and is fitted with several flush lines to allow clearing the lines without manual cleaning.

The melter has three drain ports. The primary drain is an air lift controlled drain trough or spout in a sealed discharge chamber held at negative pressure. Glass is discharged into containers which are sealed against the bottom of the discharge chamber. When it is necessary to change a container, the glass discharge is stopped and the opening of the discharge chamber is sealed with a gate valve. The filled container is removed and covered during cooling. An empty container is placed, sealed to the chamber and the gate valve is opened. Discharge can then be restarted. For handling the hot glass containers, metal tongs and heat resistant gloves are provided. Personnel also use reflective face shields for protection. The other drains consist of a bottom drain which is used to completely empty the melter and a surface drain that can be used to drain off a surface layer. These are normally sealed with frozen glass. The drain is opened by heating the drain pipe with an electric heater and resealed by cooling the drain pipe. These drains are not routinely used but safety considerations are similar to those of the main drain.

In addition to the hot glass, there are other high temperature hazards associated with the melter. The exhaust line can be very hot (> 400°C) before reaching the quencher. This line is relatively inaccessible during normal operations. During maintenance operations operators wear protective clothing and/or use insulation to avoid contact. Other hot surfaces exist near ports etc. and operators are made aware by signage and instruction that the melter has hot surfaces.

The melter is electrically heated and high current sources at moderate voltages are present. The electrodes may be supplied with currents in excess of 1000 amps and voltages as high as 140 volts. The primary voltage for the power supply is 277 Volts. Electrical connections are enclosed to prevent contact. When connections must be maintained, inspected or changed, procedures require de-energizing the equipment. Absence of voltage is confirmed by a test device prior to working on connections.

The status of pressures, temperatures, flows, power, etc. are monitored by both automatic devices and manually by operators. Critical parameters are connected to alarms which indicate departure from normal ranges. Most alarms require an operator response with the exceptions of the emergency exhaust mentioned earlier and the melter temperature controller alarm which automatically cuts power if power or temperature exceeds preset limits. A number of the system parameters are automatically monitored by computer and recorded or printed out periodically or as desired.

The constantly changing nature of the work at the VSL, as a research oriented development laboratory, requires a consistent level of effort to produce a safe working environment. The working conditions and requirements are frequently changing and safety requires special attention. The record to date bears testimony to the commitment to providing a safe working environment.

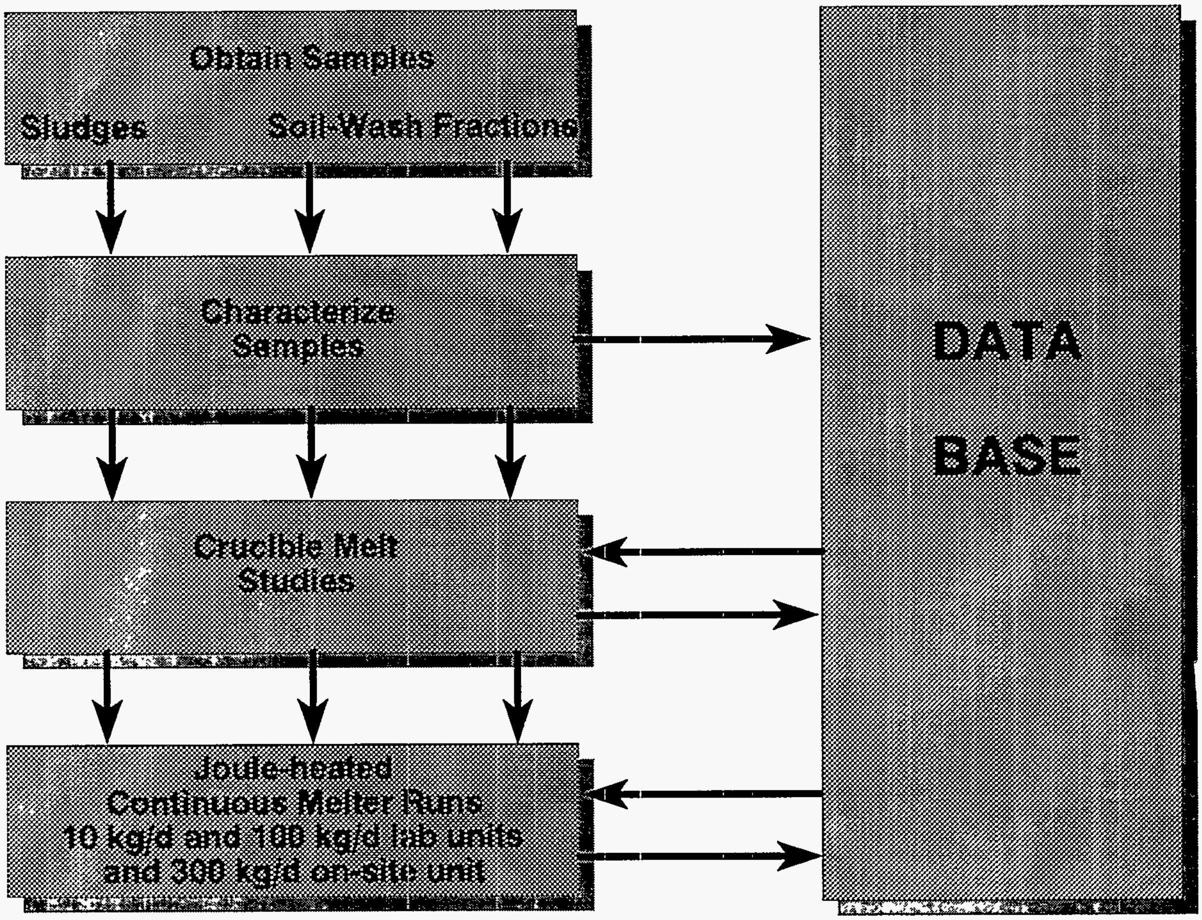


Figure 2-1. A schematic diagram of the study.

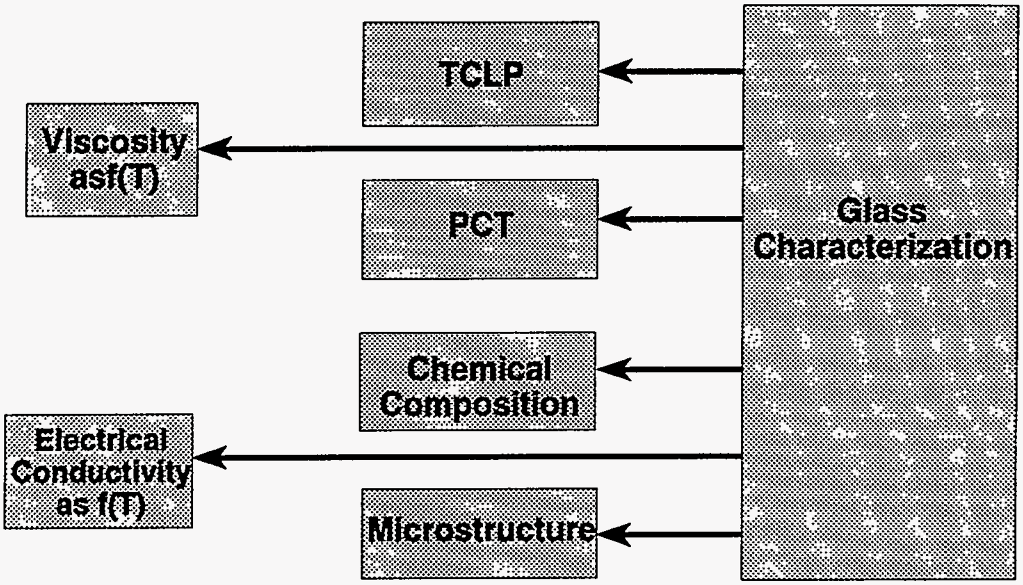


Figure 2-2. A schematic diagram of glass characterization activities

SECTION 3.0
Characterization of FEMP Sludges and Lockheed Soil Fines

3.1 Introduction

In this section, we present the characterization results for the six 55-gallon drums of FEMP Pit 5 sludges and the 31 5-gallon drums of soil fractions received from Lockheed Environmental (from lab-scale soil washing tests) and characterized at the VSL. The samples of Pit 5 material received from Fernald, their corresponding Remedial Investigation/Feasability Study (RI/FS) numbers, and VSL identification codes are shown in Table 3.1. Note that FE51 and FE52 did not arrive at VSL with RI/FS numbers. The samples received from Lockheed are listed in Table 3.2. Also shown in Table 3.2 are the blends of individual soil fractions that were made in order to decrease the number of analyses needed. We will use the VSL identification code when referring to the various materials since there are many samples with the same common name.

3.2 Composition Summary

For convenience and easy reference, a summary of our compositional conclusions for the Fernald sludges is given in Table 3.3. A compositional summary of the Lockheed soil-wash fractions is shown in Table 3.4. Both DCP-ES and ICPMS were used to analyze the Lockheed soil fines. The analyses of the sludges are more involved since they contain significant amounts of fluorides and sulfates. The top portion of Table 3.4 presents DCP-ES analysis (cation analysis) in oxide form while the bottom two portions present ICPMS analysis results for some radionucleides and heavy metals. The assumptions leading to the conclusions on the sludges will be discussed in the following subsections.

3.3 Sample Description

Six 55-gallon drums of FEMP Pit 5 material (each weighing ~200 kg) and 31 5-gallon drums of Lockheed soil fines (each weighing 7 to 17 kg) were received at VSL. Visual examination of the Pit 5 materials, as-received, showed that all of the 55-gallon drums contained approximately 20 vol% standing water and appeared to have a similar range of particle sizes. All of the Pit 5 materials were stratified, some more extensively than others. Once the Pit 5 materials were homogenized, the overall color of the sludges differed greatly. FE1, FE15, and FE16 were all brownish in color while FE14, FE51, and FE52 were pinkish. The origin of this color difference is not clear from our analyses but it does correlate with the sulfate and fluoride levels and the weight loss data for these samples.

Initially, each drum was stirred from 30 to 120 minutes depending upon the difficulty experienced in producing a homogeneous sludge. After the initial mixing of the material in the 55-gallon drums, less time was subsequently required to produce a homogeneous mix. Typically, each time samples were taken from a drum, the contents were first thoroughly stirred with an electric mixer for about 10-20 minutes or until the contents looked and felt homogeneous. This was done by stirring from top to bottom of the 55-gallon drum until similar resistance was felt throughout and no further color changes were observed.

The soil fractions received from Lockheed varied extensively in physical appearance. Some appeared to be dried clay while others appeared to be sludge-like; one 5-gallon drum contained standing water. Each of the 5-gallon drums were completely mixed by hand before sampling.

The physical characterization and carbon content results, the compositional analysis, and the radionuclide results from gamma spectroscopy and ICPMS analysis will be discussed in the following sub-sections.

3.4 Physical Characterization and Carbon Content

The specific gravity of ten of the Lockheed soil samples is shown in Table 3.5. Measurements were made on both as-received samples and samples that were dried at 110°C for 18 hours. All measurements were made using a pycnometer. The soils, as-received, varied in density from 1.4 to 2.5 g/cm^3. This variation in density is in part due to the variation in water content of the soil fines. Once the soil fractions were dried at 110°C for 18 hours, their density ranged from 2.1 to 2.8 g/cm^3. This is consistent with the fact that the soil is mainly composed of SiO_2 (density of SiO_2 ranges from 2.2 to 2.6 g/cm^3 depending on its structure).

As mentioned previously, the amount of water in the as-received soil fractions varied greatly. This is illustrated in Table 3.5 with weight loss data for samples dried at 110°C and 450°C. The samples dried at 110°C reflect a loss of non-structural water molecules while the samples dried at 450°C have lost structural water as well. The amount of weight loss upon heating to 110°C varies from 0.4 to 29 wt.% while the amount of weight loss upon heating to 450°C varies from 5.5 to 34 wt.%. There is a great variation in both the amount of non-structural and structural water contained in the soil fractions. The most important weight loss measurement for the vitrification of the soil fractions is the weight loss from room temperature to 1150°C; this measurement was made for all of the soil samples so that all of the soil fractions could be used for melter runs. The large variation in weight loss at all four temperatures for

Lockheed soil fractions is shown graphically in Figure 3.1, where weight loss as a function of drying temperature is plotted.

In addition to the specific gravity and the weight loss, the total carbon content and the total organic carbon content of the soil fractions were measured, as presented in Table 3.5. Lockheed labelled their soil fractions as "cyclone underflow" for the inorganic fractions. For the initial soil fractions received from Lockheed, the amount of carbon found corresponded to an inorganic fraction and an organic fraction. The later soils, however, contained between 2-3 wt% carbon regardless of whether they were labelled as organic or inorganic fractions. None of the soil fines analyzed, except FE6, FE11, and FE12 show more than 4 wt.% total carbon. Since soil loadings on an as-received basis compose less than 20 wt.% of the feed, none of the soils should present a redox problem since it is expected (and later confirmed) that sufficient oxygen is available to the melt in the Duramelter vitrification systems in order to maintain oxidizing conditions in the presence of this level of organics.

We did not obtain specific gravity measurements and weight loss measurements below 1150°C for a number of soil fines. This is because those data were not essential for use of the soil-wash fractions in subsequent melter runs; the key data are the weight loss at 1150°C, carbon content, and the composition of soils dried at 1150°C.

The majority of the Pit 5 sludge materials received at VSL were used for melter operations. The essential physical data for the use of Pit 5 material in the continuous melter tests is the weight loss at 1150°C. Table 3.6 shows the amount of various Pit 5 materials lost upon heating to 1150°C. Consequently, the variation in the amount of solid contributed from the Pit 5 samples on vitrification at 1150°C is from 8.3 wt.% to 22.6 wt.% (due to weight loss variation of 77.4 to 91.7 wt.%). This corresponds to about a factor of three difference in the amount of Pit 5 material which is converted to glass. The weight loss of Pit 5 materials was measured at 450°C as well as 1150°C. The weight loss data at 450°C were needed for crucible melts since we dry the sludge at 450°C prior to vitrifying with additives. The amount of solid left after drying at 450°C (which includes carbonates and hydroxides) varies from 10 to 29.4 wt.%. These weight loss data, presented in Table 3.6, are plotted in Figure 3.2. Note the similarity of the weight loss of FE14, FE51, and FE52 to each other and the weight loss of FE1, FE15, and FE16 to each other. We will see in the next sub-section that not only does the weight loss vary greatly but so too does the chemical composition.

3.5 Compositional Results by DCP-ES, Ion Chromatography, and Fluoride Analysis

The results from the analyses of the soil-wash fractions after total dissolution followed by DCP-ES emission spectroscopy are summarized in the upper portion of Table 3.4. Most of the analyses were obtained by dissolving three separate soil-wash sub-samples and then analyzing the solution by DCP-ES; thus three analyses are presented for most soil samples. All samples were dried at 1150°C for four hours before dissolution and all of the analyses recovered 93-104 wt.% as oxides. Anion analysis by ion chromatography and ion selective electrode showed from 0.1 to 0.5 wt.% sulfates, below our detection limit of 1 wt.% fluoride, and below our detection limit of 0.2 wt.% chloride for the soil fractions analyzed, as illustrated in Table 3.7.

The compositional analysis of the Pit 5 sludges is considerably more complicated than that of the soil samples. Initially, we attempted to analyze the Pit 5 sludges by the same method as that of the soils; taking 100 mg sub-samples of dried materials and dissolving them in acid followed by DCP-ES emission spectroscopy analysis. We discovered two problems with this method when applied to Pit 5 sludges: first, the unnormalized data for cations converted to oxide form added up to less than 90 wt.% and second, different sub-samples of the same drum of Pit 5 material had vastly different compositions. On the other hand, glasses made from 100-300 g sub-samples gave consistent results for the sludge composition of each 55-gallon drum. This implies that if we dissolved 100-300 g sub-samples of sludge and then analyzed the resulting solution, we would obtain a representative analysis of the sludge. But this would require dissolving the 100-300 g sub-sample in about 200 l of acid. This type of analysis is clearly both impractical and undesirable in that it creates large amounts of secondary waste streams, as each sludge analysis would produce 200 l of radioactive acid. Therefore, we developed an alternate method for analyzing the sludge samples which can be summarized in the following steps: 1) Analyze glasses produced from 100-300 g samples of sludge and known amounts of additives and deduce the cation composition of the sludge from the cation composition of the glass. 2) Since there is fluoride loss by volatilization from the melt above about 1000°C, the amount of fluoride in the sludge should be checked by analyzing sludges dried at 450°C for fluoride. By combining these analyses, we obtained the data presented in Table 3.3.

We have found that one of the more reliable methods of obtaining fluoride content in the sludge is by examining many sub-samples of sludge dried at 450°C. Table 3.8 shows the results of these analyses. Though the measurements of samples heated to 450°C represent no loss in fluoride, the samples heated to 450°C still contain carbonates, hydroxides, etc., which are irrelevant to the composition of the vitrified product. Conversely, samples heated to 1150°C have lost all CO_2 and H_2O, but have also lost some fluoride. By correcting for the amount of fluoride loss when heating to 1150°C, we can determine the true amount of fluoride that should be in the glass with no loss due to vitrification. This requires fluoride data at both 1150°C and 450°C in addition to the weight losses at 1150°C and 450°C. We do not have fluoride data for all the sludges dried at 1150°C, but can approximate the true fluoride content by taking the fluoride measurement and dividing by the weight retained between 450°C and 1150°C. This is accurate as long as the amount of fluoride loss relative to the total weight loss between 450°C and 1150°C is small. We have compared this approximate correction for fluoride loss to the most accurate correction for fluoride loss. Our approximate method gives 25.1 wt.% fluoride for FE1 (first FEMP Pit 5 sludge received at VSL) while our more accurate method (taking into account the inaccuracy of our weight loss due to fluoride loss) gives 22.9 wt.% fluoride, a difference of 9.6 relative percent (the difference between 25.1 and 22.9 divided by 22.9). We believe that this difference is insignificant since our ability to analyze the average fluoride in the sludge is ± 20 wt.%. In addition, FE1 (for which we do have the more accurate determination) should have the greatest error due to this approximation because that 55-gallon drum of Pit 5 sludge contains the greatest amount of fluoride of all the Pit 5 sludges analyzed at VSL. Table 3.8 shows the amount of fluoride analyzed for sludges dried at 450°C, the corrected fluoride for samples dried at 1150°C, and the corresponding MgF_2. Often, multiple fluoride analyses are performed for the same 55-gallon drum due to possible unrepresentative sampling in dissolving and analyzing 100 mg sub-samples. The highest fluoride value found for samples dried at 450°C were then converted to the nominal fluoride content of samples dried at 1150°C. That is shown in the fourth column of Table 3.8. Usually there are more moles of magnesium (found by DCP-ES) per sample than there are fluoride so that the remaining magnesium is reported as MgO. In Table 3.8, the amount of MgF_2 deduced to be in the various Pit 5 sludges by the above procedure is then compared to the amount of MgF_2 deduced to be in those same Pit 5 sludges by analysis of the resulting glass melts. By comparing those two columns in Table 3.8, we see that the two methods of deducing the MgF_2 content in the sludges are consistent with each other. Although this is a complicated method for analyzing MgF_2 content in sludge, it is necessary if we are to obtain an accurate sludge analysis. Note that we do not determine the speciation of the fluoride (or any other component) in the raw sludge by this procedure. We have presented the fluoride concentration as MgF_2 in order to preserve charge balance using the most likely species based on FEMP process knowledge. Whether the fluoride exists as MgF_2, CaF_2, AlF_3 or any other form in the sludge is essentially irrelevant to vitrification since the fluoride will be redistributed into the glass matrix upon vitrification.

In addition to fluoride analysis, the various Pit 5 samples were analyzed for sulfates and chlorides. The results, presented in Table 3.9, show that the amount of chloride is consistently below 1 wt.%, while the amount of sulfate varies widely from 3 to 13 wt.%. Though we detect sulfate (SO_4^{2-}) by ion chromatography, it is convenient (and conventional) to report the sulfur content as SO_3; hence, we have converted the SO_4^{2-} to SO_3 in a column of Table 3.9, and have reported the sulfur as SO_3 in our summary of compositional results in Table 3.3. Note that since some of our data for sulfates were obtained only for samples dried at 450°C, the amount of sulfate found at 1150°C had to be converted to what would have been found for samples dried to 1150°C by dividing by the amount of solid retained when heating from 450°C to 1150°C. Some of the sludges were dried at 450°C and 1150°C, dissolved completely in acid, and then analyzed by DCP-ES. However, since 100 mg subsampling of sludges tends to be unrepresentative, most of the oxide results were deduced from subsequent analysis of glass melts. We combined our fluoride and sulfate analyses with our DCP-ES analysis of sludges and glasses made from those sludges to produce Table 3.3. All of the data presented in Table 3.3 are unnormalized. By combining anion and cation analyses, we obtained recoveries of 98 to 102 wt.% for the six Pit 5 sludges analyzed which lends further confidence to our procedure.

3.6 Gamma Spectroscopy

The gamma spectra obtained for six of the Lockheed soil-wash fractions are presented in Figures 3.3 to 3.8, along with the background (Figure 3.9). The three main peaks in the spectra are the Th-234 peaks at 92.4 KeV and 92.8 KeV (unresolved in our spectra) and the U-235 peak at 143.7 KeV. In contrast to these spectra is the gamma spectrum of FE1 (Figure 3.10), the first 55-gallon drum of Pit 5 received at VSL from Fernald. The main differences are: (1) The activity between 200 KeV and 400 KeV, due largely to Pb-212 and Pb-214 present in the FE1 Pit 5 spectrum, is absent in the soil spectra, and (2) The activity between 70 KeV and 100 KeV, present in the FE1 Pit 5 spectrum, is simplified to mainly the Th-234 peak at 92 KeV for the soil-wash fractions. The clutter between 70 and 100 KeV in the FE1 Pit 5 spectrum led us to use the peak at 63.3 KeV to identify Th-234 instead of the peak at 92 KeV. Th-234 emits energy at 63.3 KeV, 92.4 KeV, and 92.8 KeV in the amounts of 3%, 2%, and 2% respectively.

Quantitative analysis by conversion of the gamma spectra to absolute activities was not possible due to the difficulty in making geometrical and self-screening corrections for these materials. But qualitatively, we see that FE8 is about ten times greater in activity than FE9 and that FE6 has more than twice the U-235 content of FE7.

3.7 Analysis of Lockheed Soil Fines by ICPMS

Twenty-two samples of Lockheed soil-wash samples were mixed into nine separate samples, dried at 1150°C for four hours, subjected to total acid dissolution, and the solutions were then used for analysis by ICP-MS. The results are presented in Table 3.10. As expected, the organic fractions, in general, contain greater amounts of radionucleides than the inorganic fractions. In all of the soil fractions examined, less than 2 ppm of mercury was detected. The concentration of lead varied from 30 to 120 ppm, the concentration of barium, from 430 to 1110 ppm, and the concentration of chromium, from 49 to 127 ppm.

3.8 Summary and Discussion

Six different 55-gallon drums of Pit 5 material along with the majority of the 31 5-gallon drums of soil fractions have been analyzed. From the weight loss analysis, we saw that both sludges and soil fractions vary greatly in water content from one drum to the next. This indicates that we cannot assume a specific solid content when working with Pit 5 material and washed soils and underscores the need for batch-by-batch analysis for control of the vitrification process. The carbon content measurements for the sludges and the soil fractions indicate that reduction should not be a concern in the melt except perhaps for the FE6, FE11, and FE12 soil, and even for these, there would not be a reduction problem unless FE6, FE11, and FE12 constituted a large fraction of the feed. Specific gravity measurements are generally consistent with the composition of the sludges and soils. Both the specific gravity and weight loss at 1150°C will be used to determine the volume reduction for vitrification of Pit 5 sludges and soil-wash fractions.

The compositional analyses of the soil-wash fractions were relatively straightforward: dissolve 100 mg samples in 200 ml of acid and analyze the resulting solution for cations and anions. The sludge, on the other hand, is inhomogeneous on the 100 mg scale. We found, however, that the sludge from a given drum was quite homogeneous on a 100 g scale, which then presents the options of either dissolving 100 g of sludge in 200 l of acid solution or making a glass out of 100-300 g of sludge and the dissolving 100 mg of the glass for analysis. We chose the latter option since it is obviously more practical. Vitrification at 1150°C, however, introduces the additional problem of fluoride loss, and to take this into account, many fluoride analyses had to be made from sludges dried at 450°C. Comparing fluoride analysis of sludges to fluoride analysis of glasses made from these sludges, we obtained consistent results for the sludge composition. We will see in the next section on crucible melts that the sludge compositions presented in this section are consistent with the analyzed composition of all of the crucible melts, further corroborating this approach.

Table 3.1
Samples Received from Fernald and their Corresponding VSL ID Code and RI/FS Numbers.

Common Name of Sample	VSL ID Code	RI/FS Numbers
Pit 5 Sludge	FE1	100204
Pit 5 Sludge	FE14	098538
Pit 5 Sludge	FE15	098539
Pit 5 Sludge	FE16	098540
Pit 5 Sludge	FE51	-
Pit 5 Sludge	FE52	-

Table 3.2
VSL ID of Lockheed Soil-Wash Fractions

VSL ID	Composed of:			
FE6	FE6 (Organic)			
FE7	FE7 (Inorganic)			
FE8	FE8 (Mixed)			
FE9	FE9 (Mixed)			
FE10	FE10 (Inorganic)			
FE11	FE11 (Organic)			
FE12	FE12 (Organic)			
FE13	FE13 (Inorganic)			
FE44	FE44 (MLW)			
FE47	FE47 (Organic)			
FE48	FE48 (Mixed)			
FE49	FE49 (Organic)			
	Cyclone Underflow (Inorganic)			
FE22+	FE22	FE25		FE23
FE26+	FE26	FE33		FE29
FE27+	FE27	FE28		FE31
FE34+	FE34	FE35	FE36	FE46
	+20M (Organic)			
FE30+	FE30	FE37		FE41
FE42+	FE42	FE43		FE45
	+50M (Organic)			
FE38+	FE38	FE40		FE50
	+100M (Organic)			
FE24+	FE24	FE32		FE39

Note: The "+" indicates a mixture of soil fines. For example, FE22 is one 5-gallon drum of soil fines while FE22+ is equal amounts of FE22, FE25, and FE23 mixed together.

Table 3.3

Composition of Six Pit 5 Materials. Analyses Derived from Combinations of Fluoride and Sulfate Analyses of Sludges Dried at 450°C and DCP-ES Analyses of Sludges and Glasses Made from these Sludges.

Components (wt.%)	FE1	FE14	FE15	FE16	FE51	FE52
Al_2O_3	2.11	3.5	5.00	4.30	3.8	2.9
B_2O_3	0.08	3.00	0.01	0.00	0.4	0.4
BaO	1.90	1.87	1.87	1.00	NA	3.3
CaO	37.2	44.0	36.80	53.70	46.0	47.2
Fe_2O_3	3.14	5.0	6.00	4.00	7.1	4.7
K_2O	0.27	1.00	0.23	0.25	0.3	0.3
Li_2O	0.34	0.20	0.33	0.23	0.4	0.4
MgO	1.33	10.0	10.5	5.4	16.73	17.56
MgF_2	37.6	6.00	14.8	10.2	0	0
MnO_2	0.12	0.12	0.15	0.10	NA	NA
Na_2O	0.92	1.0	1.00	1.40	1.4	1.5
NiO	0.07	0.03	1.03	0.0	NA	NA
P_2O_5	0.24	0.75	3.63	0.53	0.9	0.8
SiO_2	13.98	14.0	16.00	13.10	9.2	10.0
SrO	0.06	0.04	0.03	0.06	NA	NA
TiO_2	0.22	0.30	0.19	0.20	0.2	0.25
U_3O_8	0.6	0.5	1.94	1.3	0.5	0.4
SO_3	2.2	10.0	2.5	5.5	11.2	10.7
Other	0.0	0.0	0.0	0.0	1.87	0.0
Total	102.38	101.31	102.01	101.27	100.0	100.41

NA = Not Analyzed.

Table 3.4
Composition of Lockheed Soil-Wash Fractions after Drying at 1150°C for Four Hours

Oxide (wt.%)	FE6 (Organic)	FE7 (Inorganic)	FE8 (Mixed)	FE9 (Mixed)
Al_2O_3	6.47	8.22	7.30	8.44
B_2O_3	0.04	0.04	0.05	0.04
BaO	0.06	0.06	0.05	0.05
CaO	28.91	8.63	3.04	3.00
Cr_2O_3	0.01	0.00	0.02	0.01
Fe_2O_3	4.07	3.18	2.20	3.06
K_2O	1.33	2.11	2.01	2.06
Li_2O	0.25	0.09	0.05	0.04
MgO	4.23	3.64	1.38	1.59
MnO_2	0.33	0.11	0.12	0.11
Na_2O	0.79	1.10	1.15	0.85
NiO	0.01	0.01	0.00	0.00
P_2O_5	0.26	0.23	0.08	0.20
SiO_2	44.63	67.18	85.33	78.25
SrO	0.05	0.02	0.01	0.01
TiO_2	0.29	0.67	0.60	0.71
U_3O_8	0.74	0.22	NA	0.16
ZrO_2	0.01	0.02	0.00	0.01
Total	92.5	95.51	103.4	98.59

Radionucleides (ppm)	FE6	FE7	FE8	FE9
Tc-99	<0.1	<0.1	NA	NA
U-233*	<0.1	<0.1	NA	NA
U-234*	<0.1	<0.1	NA	NA
U-235*	39.4	11.5	NA	NA
U-236*	0.5	0.2	NA	NA
U-238	5400	2090	NA	NA

Heavy Metals (ppm)	FE6	FE7	FE8	FE9
Pb	92	47	NA	NA
Hg	<2	<2	NA	NA
Ba	690	520	NA	NA
Cr	72	48	NA	NA

*Analyzed in semiquantitative mode.
NA = Not Analyzed.
Note: For the samples that contain "+" see Table 3.2 for explanation.

Table 3.4 (continued)

Oxide (wt. %)	FE10 (Inorganic)	FE11 (Organic)	FE12 (Organic)	
Al_2O_3	9.16	10.98	10.37	10.33
B_2O_3	0.32	0.10	0.05	0.04
BaO	0.06	0.07	NA	NA
CaO	6.45	12.19	8.67	8.60
Cr_2O_3	0.04	0.02	NA	NA
Fe_2O_3	3.40	6.51	5.16	5.11
K_2O	2.21	2.34	2.07	2.19
Li_2O	0.14	0.09	0.08	0.07
MgO	3.22	3.60	3.21	3.19
MnO_2	0.16	0.29	0.20	0.20
Na_2O	1.34	0.94	0.97	0.95
NiO	0.04	0.16	NA	NA
P_2O_5	0.38	0.66	0.52	0.50
SiO_2	76.01	59.73	61.95	61.22
SrO	0.02	0.02	NA	NA
TiO_2	0.67	0.62	0.60	0.60
U_3O_8	0.24	1.0	NA	NA
ZrO_2	0.03	0.02	NA	NA
Total	103.60	99.34	93.85	93

Radionucleides (ppm)	FE10	FE11	FE12
Tc-99	NA	<0.1	NA
U-233[*]	NA	0.3	NA
U-234[*]	NA	<0.1	NA
U-235[*]	NA	66.7	NA
U-236[*]	NA	1.2	NA
U-238	NA	8160	NA

Heavy Metals (ppm)	FE10	FE11	FE12
Pb	NA	32	NA
Hg	NA	<2	NA
Ba	NA	661	NA
Cr	NA	78	NA

[*] Analyzed in semiquantitative mode.
NA = Not Analyzed.
Note: For the samples that contain "+" see Table 3.2 for explanation.

Table 3.4 (continued)

Oxide (wt.%)	FE13 (Inorganic)			FE22+ (Inorganic)	FE24+ (Organic)		
Al_2O_3	13.92	13.94	13.51	9.30	10.4	10.09	10.50
B_2O_3	0.06	0.06	0.06	0.50	0.60	0.58	0.53
BaO	NA	NA	NA	0.07	0.06	0.06	0.06
CaO	4.56	4.60	4.45	9.59	9.04	8.97	9.07
Cr_2O_3	NA	NA	NA	0.00	NA	NA	NA
Fe_2O_3	5.85	5.86	5.79	3.99	7.11	7.03	6.91
K_2O	2.88	2.71	2.25	2.10	2.53	2.55	2.49
Li_2O	0.05	0.05	0.05	0.19	0.15	0.15	0.14
MgO	2.97	2.88	2.70	3.54	3.0	3.03	2.98
MnO_2	0.07	0.07	0.02	0.16	0.14	0.13	0.12
Na_2O	0.74	0.74	0.67	1.41	1.12	1.11	1.10
NiO	NA	NA	NA	0.02	NA	NA	NA
P_2O_5	0.36	0.38	0.31	0.41	0.59	0.62	0.59
SiO_2	68.05	67.43	68.13	63.93	58.51	58.01	58.07
SrO	NA	NA	NA	0.03	0.02	0.02	0.02
TiO_2	0.89	0.90	0.81	0.58	0.58	0.58	0.60
U_3O_8	NA	NA	NA	0.2	NA	NA	NA
ZrO_2	NA	NA	NA	0.06	0.02	0.02	0.02
Total	100.4	99.62	98.75	96.08	93.87	92.95	93.20

Radionucleides (ppm)	FE13	FE22	FE24
Tc-99	NA	<0.1	NA
U-233*	NA	0.7	NA
U-234*	NA	<0.1	NA
U-235*	NA	7.8	NA
U-236*	NA	0.4	NA
U-238	NA	1250	NA

Heavy Metals (ppm)	FE13	FE22	FE24
Pb	NA	61	NA
Hg	NA	<2	NA
Ba	NA	486	NA
Cr	NA	127	NA

*Analyzed in semiquantitative mode.
NA = Not Analyzed.
Note: For the samples that contain "+" see Table 3.2 for explanation.

Table 3.4 (continued)

Oxide (wt.%)	FE26+ (Inorganic)		FE27+ (Inorganic)			FE30+ (Organic)		
Al_2O_3	8.92	9.04	8.73	8.62	8.73	4.58	4.51	4.49
B_2O_3	0.12	0.10	0.68	0.66	0.71	0.07	0.07	0.08
BaO	NA	NA	0.13	0.12	0.12	NA	NA	NA
CaO	9.95	9.88	10.56	10.06	10.43	48.76	48.43	49.79
Cr_2O_3	NA	NA	0.01	NA	NA	NA	NA	NA
Fe_2O_3	3.57	3.49	3.76	3.78	3.80	2.79	2.73	2.80
K_2O	2.1	2.09	2.04	1.98	2.07	1.09	1.08	1.11
Li_2O	0.06	0.06	0.08	0.08	0.08	0.37	0.37	0.38
MgO	3.47	3.41	3.88	3.89	3.94	12.75	12.75	12.64
MnO_2	0.14	0.13	0.15	0.14	0.14	0.26	0.25	0.26
Na_2O	1.25	1.26	1.60	1.56	1.61	0.49	0.47	0.49
NiO	NA	0.01	0.02	NA	NA	0.02	0.03	0.06
P_2O_5	0.42	0.42	0.42	0.40	0.42	0.37	0.37	0.36
SiO_2	63.77	61.98	60.55	58.34	60.16	26.28	26.27	26.45
SrO	0.03	0.03	0.03	0.03	0.03	0.06	0.06	0.06
TiO_2	0.57	0.55	0.62	0.60	0.62	0.25	0.25	0.25
U_3O_8	NA	0.16	0.24	NA	NA	0.28	0.25	0.27
ZrO_2	0.02	0.02	0.03	0.03	0.03	0.01	0.01	0.01
Total	94.39	92.63	93.50	90.29	92.86	98.43	97.90	99.50

Radionucleides (ppm)	FE26	FE27+	FE30+
Tc-99	<0.1	<0.1	<0.1
U-233*	<0.1	<0.1	<0.1
U-234*	<0.1	<0.1	<0.1
U-235*	13	13	12
U-236*	<0.2	<0.2	<0.2
U-238	1640	1770	1640

Heavy Metals (ppm)	FE26	FE27+	FE30+
Pb	68	100	57
Hg	<2	<2	<2
Ba	430	1110	190
Cr	54	125	49

*Analyzed in semiquantitative mode.
NA = Not Analyzed.
Note: For the samples that contain "+" see Table 3.2 for explanation.

Table 3.4 (continued)

Oxide (wt.%)	FE34+ (Inorganic)	FE38+ (Organic)		FE42+ (Organic)		
Al_2O_3	9.53	8.47	8.45	7.42	7.44	7.63
B_2O_3	0.37	0.03	0.04	0.35	0.36	0.36
BaO	0.08	NA	NA	0.04	0.04	0.04
CaO	10.50	13.71	13.69	27.03	26.68	26.93
Cr_2O_3	0.02	NA	NA	NA	NA	NA
Fe_2O_3	3.97	3.72	3.77	4.76	4.70	4.70
K_2O	2.17	2.19	2.34	1.83	1.78	1.80
Li_2O	0.09	0.11	0.11	0.23	0.23	0.21
MgO	3.67	4.65	4.71	8.31	8.20	8.20
MnO_2	0.14	0.16	0.17	0.12	0.12	0.11
Na_2O	1.36	1.09	1.06	0.74	0.75	0.78
NiO	0.02	0.07	0.06	NA	NA	NA
P_2O_5	0.40	0.50	0.51	0.40	0.38	0.47
SiO_2	60.67	59.76	58.57	44.98	44.28	44.36
SrO	0.03	0.03	0.03	0.03	0.03	0.04
TiO_2	0.62	0.44	0.43	0.32	0.31	0.29
U_3O_8	0.26	0.34	0.31	NA	NA	NA
ZrO_2	0.03	0.02	0.02	0.02	0.01	0.01
Total	93.89	95.29	94.27	96.58	95.19	95.93

Radionucleides (ppm)	FE34+	FE38+	FE42+
Tc-99	<0.1	<0.1	NA
U-233*	<0.1	<0.1	NA
U-234*	<0.1	<0.1	NA
U-235*	13	10	NA
U-236*	0.8	0.7	NA
U-238	1410	2030	NA

Heavy Metals (ppm)	FE34+	FE38+	FE42+
Pb	120	49	NA
Hg	<2	<2	NA
Ba	530	470	NA
Cr	91	50	NA

*Analyzed in semiquantitative mode.
NA = Not Analyzed.
Note: For the samples that contain "+" see Table 3.2 for explanation.

Table 3.5
Physical Characterization and Carbon Content of Lockheed Soil Wash Fractions

	FE6 Organic	FE7 Inorganic	FE8 Mixed	FE9 Mixed	FE10 Inorganic	FE11 Organic	FE12 Organic	FE13 Inorganic
Specific Gravity at 20°C (gcm^{-3})								
As Received	2.09	2.36	2.35	2.33	2.47	1.86	1.7	2.13
Dried at 110°C/18 hours	2.12	2.42	2.39	2.34	2.55	2.03	2.37	2.45
Weight Loss, %								
110° C	1.18	1.79	1.26	0.37	1.84	8.77	29.0	10.68
450° C	14.4	3.4	5.57	2.37	3.37	26.82	40.0	15.32
850° C	28.82	11.88	8.06	5.49	10.1	32.68	44.9	20.24
1150° C	29	12.08	9.4	5.65	10.28	33.03	45.2	20.64
Carbon Content, wt.% (as received basis)								
Total Carbon	10.2	3.3	3.0	1.2	2.5	9.4	7.3	3.7
Total Organic Carbon	9.5	1.3	1.8	0.8	1.0	9.0	5.0, 4.7*	1.2, 1.5*

* For FE12 and FE13, two separate samples of soil were tested to determine variation from sample to sample. The reproducibility for TC and TOC is ± 7% for a given sample, but from one 50 mg sample of FE13 to another 50 mg sample of FE13 it is larger (± 11%).

Table 3.5 (continued)

	FE22+ Inorganic	FE24+ Organic	FE26+ Inorganic	FE27+ Inorganic	FE30+ Organic	FE34+ Inorganic	FE38+ Organic	FE42+ Organic
Specific Gravity at 20°C (gcm^{-3})								
As Received	NA	NA	NA	1.60	NA	1.42	NA	NA
Dried at 110°C/18 hours	NA	NA	NA	2.76	NA	2.22	NA	NA
Weight Loss, %								
450° C	NA	NA	NA	34.0	NA	NA	NA	NA
1150° C	29.9	46.9	30.5	32.0	50.6	43.7	42.7	49.5
Carbon Content, wt.% (as received basis)								
Total Carbon	2.5	2.2	2.7	2.2	1.9	2.2	2.6	2.5
Total Organic Carbon	1.8	2.0	1.9	2.1	1.9	1.9	1.9	2.3

NA = Not Analyzed

Table 3.6
Physical Characterization and Carbon Content of Various Pit 5 Sludges

	FE1	FE14	FE15	FE16	FE51	FE52
Weight Loss, %						
450° C	70.6	90	78	73	89.6	91.2
1150° C	77.4	91.7	81.5	81.4	91.5	93.0
Specific Gravity at 20°C (gcm^{-3})						
As Received	1.3	NA	NA	NA	1.1	1.1
Dried at 110°C/18 hours	2.8	NA	NA	NA	NA	NA
Carbon Content, wt.% (as received basis)						
Total Carbon	2.0	NA	NA	NA	0.38	0.25
Total Organic Carbon	0.26	NA	NA	NA	0.28	0.12

NA = Not Analyzed

Table 3.7
Anion Characterization of Soil-Wash Fractions.
All samples were dried for 4 hours at 1150°C before analysis.

VSL ID	Wt% SO_4^{-2}	Wt% Chloride	Wt% Fluoride
FE6	0.54	< 0.2	NA
FE7	0.18	< 0.2	NA
FE8	0.36	< 0.2	NA
FE9	0.10	< 0.2	NA
FE10	0.10	< 0.2	NA
FE11	0.54	< 0.2	NA
FE22+	NA	NA	<1
FE26+	NA	NA	<1
FE27+	NA	NA	<1
FE34+	NA	NA	<1

NA = Not Analyzed

Table 3.8
Fluoride Content of Pit 5 Sludges from Direct Analysis and as Deduced from Analysis of Glass Melts.

Pit 5 Sample Name	Wt.% Fluoride (direct analysis) for samples dried at 450°C	Highest F Value (wt.%) for Samples Dried at 450°C	Corrected fluoride at 1150°C (wt.%)*	Corresponding MgF_2(wt.%)	MgF_2 obtained from analysis of glass melts** (wt.%)
FE14 (Dried 450°C/4 hours)	2.0, 2.1, 2.1	2.1	2.5	4.1	6.0
FE15 (Dried 450°C/4 hours)	7.6, 7.6, 6.0	7.6	9.1	14.8	14.8
FE16 (Dried 450°C/4 hours)	4.3, 3.9, 3.0	4.3	6.2	10.2	10.2
FE1 (Dried 450°C/4 hours)	19.3	19.3	25.1	41.2	38
FE51 (Dried 450°C/4 hours)	<1%	<1%	-	-	-
FE52 (Dried 450°C/4 hours)	<1%	<1%	-	-	-

*Corrected to fluoride value at 1150°C by dividing the weight percent of fluoride found for samples dried at 450°C by the relative amount of solid retained on heating from 450°C to 1150°C.
**At least two glass melts made from each sludge.

Table 3.9
Sulfate and Chloride Analysis of Various Pit 5 Sludges

Sample	Cl^- (wt.%)	SO_4^{2-} (wt.%)	SO_4^{2-} Converted to SO_3 (wt.%)
FE1 (dried at 450°C)	<0.2	3.6	3.0
FE1 (dried at 1150°C)	<0.2	2.6	2.2
FE14 (dried at 450°C)	<1	10.0	8.3
FE15 (dried at 1150°C)	<1	3.0	2.5
FE16 (dried at 450°C)	<1	4.5	3.8
FE51 (dried at 450°C)	<1	11	9.2
FE51 (dried at 1150°C)	<1	13.4	11.2
FE52 (dried at 450°C)	<1	11	9.2
FE52 (dried at 1150°C)	<1	12.8	10.7

Note: Rather than assume any specific speciation of SO_4^{2-}, we report the SO_4^{2-} as SO_3 which is both convenient and conventional for glass compositions.

Table 3.10
Radionuclides and Heavy Metals Content of
Soil Wash Fractions from Lockheed. All
Samples Dried at 1150°C for Four Hours before Analysis.

Radionuclides (ppm)	FE6 (Organic)	FE7 (Inorganic)	FE11 (Organic)	FE22+ (Inorganic)	FE26+ (Inorganic)	FE27+ (Inorganic)	FE30+ (Organic)	FE34+ (Inorganic)	FE38+ (Organic)
Tc-99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U-233*	<0.1	<0.1	0.3	0.7	<0.1	<0.1	<0.1	<0.1	<0.1
U-234*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U-235*	39.4	11.5	66.7	7.8	5	13	12	13	10
U-236*	0.5	0.2	1.2	0.4	<0.2	<0.2	<0.2	0.8	0.7
U-238	5400	2090	8160	1250	970	1770	1640	1410	2030
Heavy Metals (ppm)	FE6	FE7	FE11	FE22+	FE26+	FE27+	FE30+	FE34+	FE38+
Pb	92	47	32	61	68	100	57	120	49
Hg	<2	<2	<2	<2	<2	<2	<2	<2	<2
Ba	690	520	661	486	430	1110	190	530	470
Cr	72	48	78	127	54	125	49	91	50

*Analyzed in semiquantitative mode.

Figure 3.1
Weight loss vs. temperature of some Lockheed soil-wash fractions.

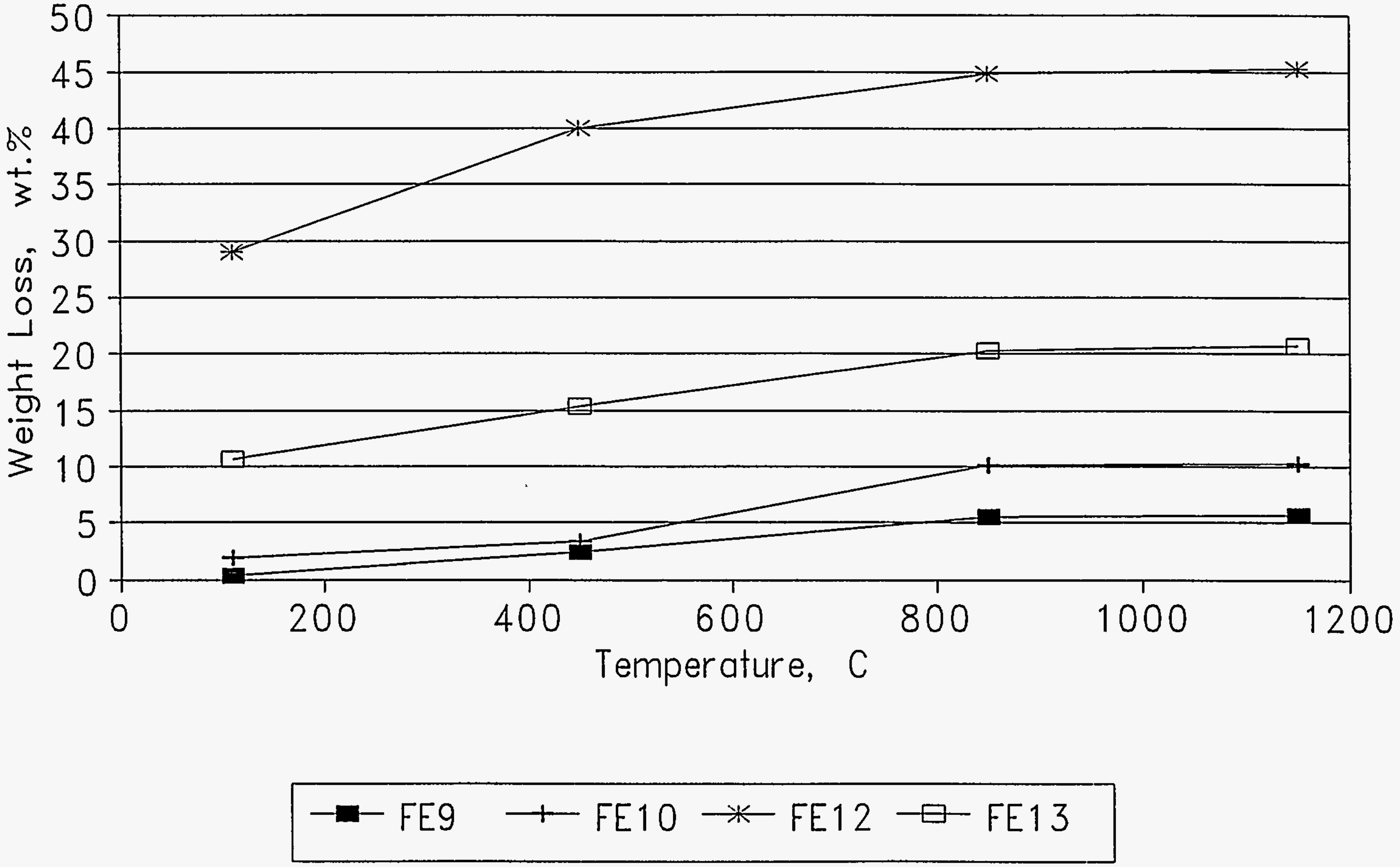


Figure 3.2
Weight loss vs. temperature of various Pit 5 sludges.

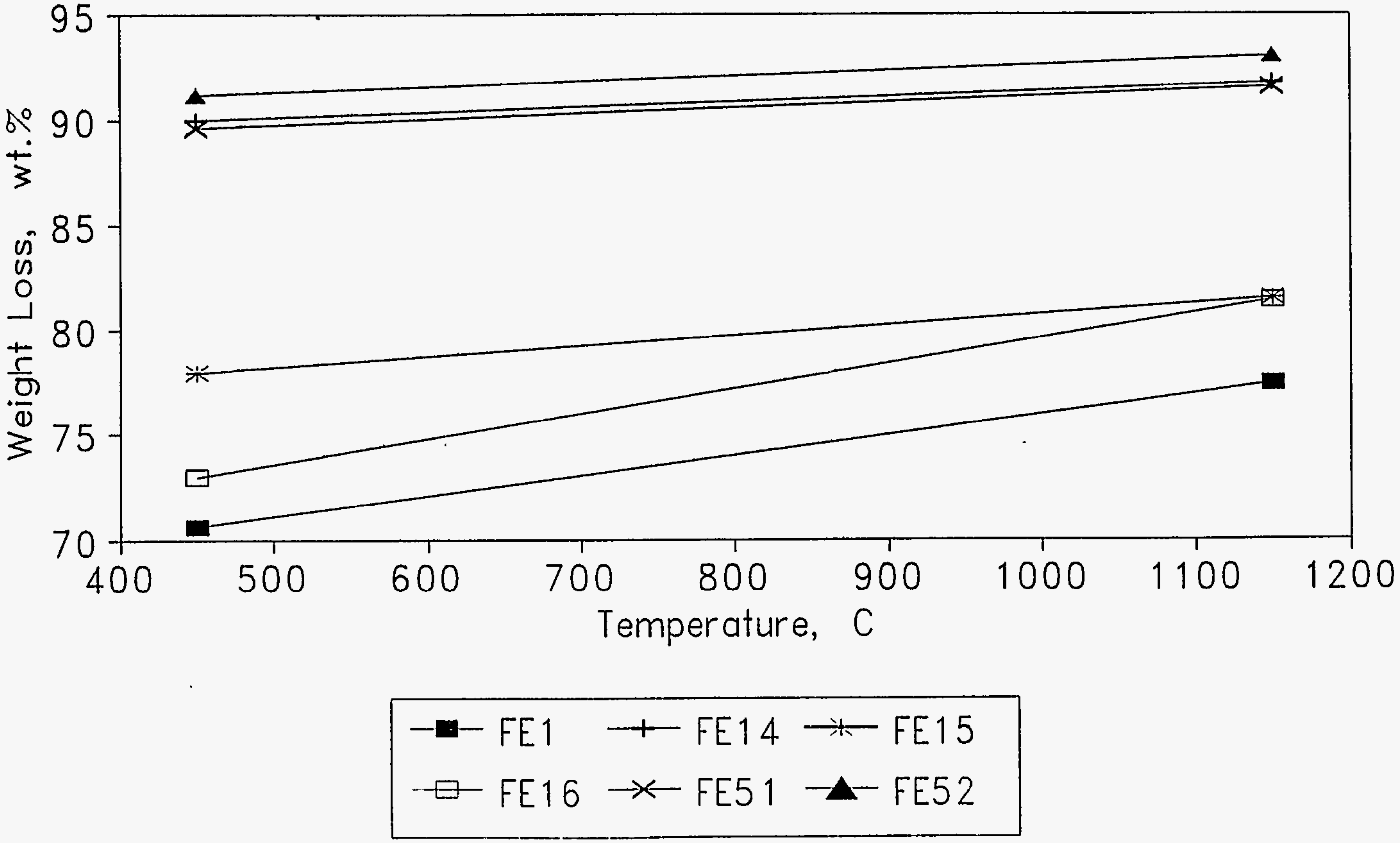
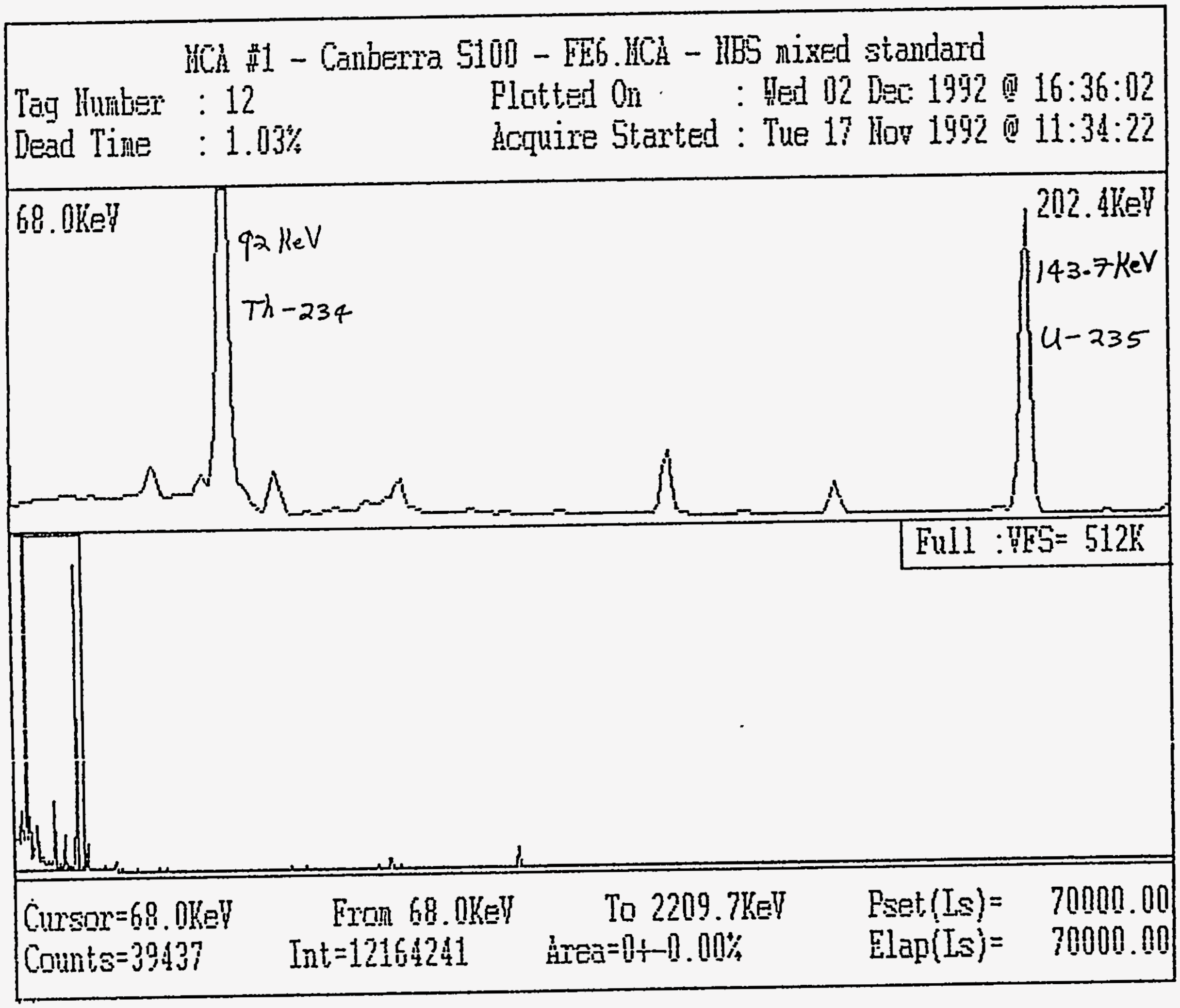


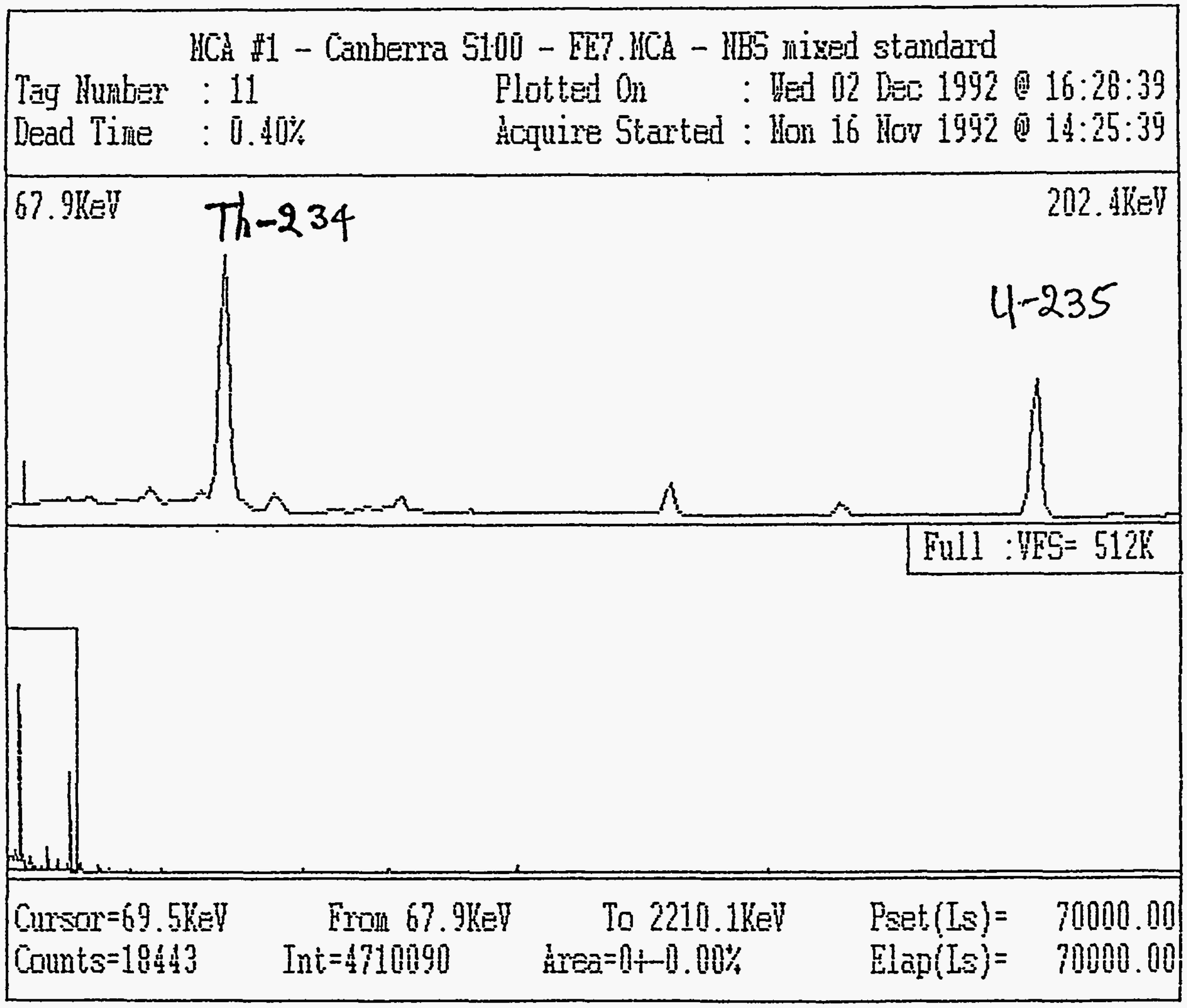
Figure 3.3
Gamma spectroscopy - FE6 soil wash fraction



```
              MCA #1 - Canberra S100 - FE6.MCA - NBS mixed standard
Tag Number  : 12                    Plotted On       : Wed 02 Dec 1992 @ 16:36:02
Dead Time   : 1.03%                 Acquire Started  : Tue 17 Nov 1992 @ 11:34:22
```

```
Cursor=68.0KeV      From 68.0KeV      To 2209.7KeV      Pset(Ls)=   70000.00
Counts=39437      Int=12164241      Area=0+-0.00%       Elap(Ls)=   70000.00
```

Figure 3.4
Gamma Spectroscopy - FE7 soil wash fraction

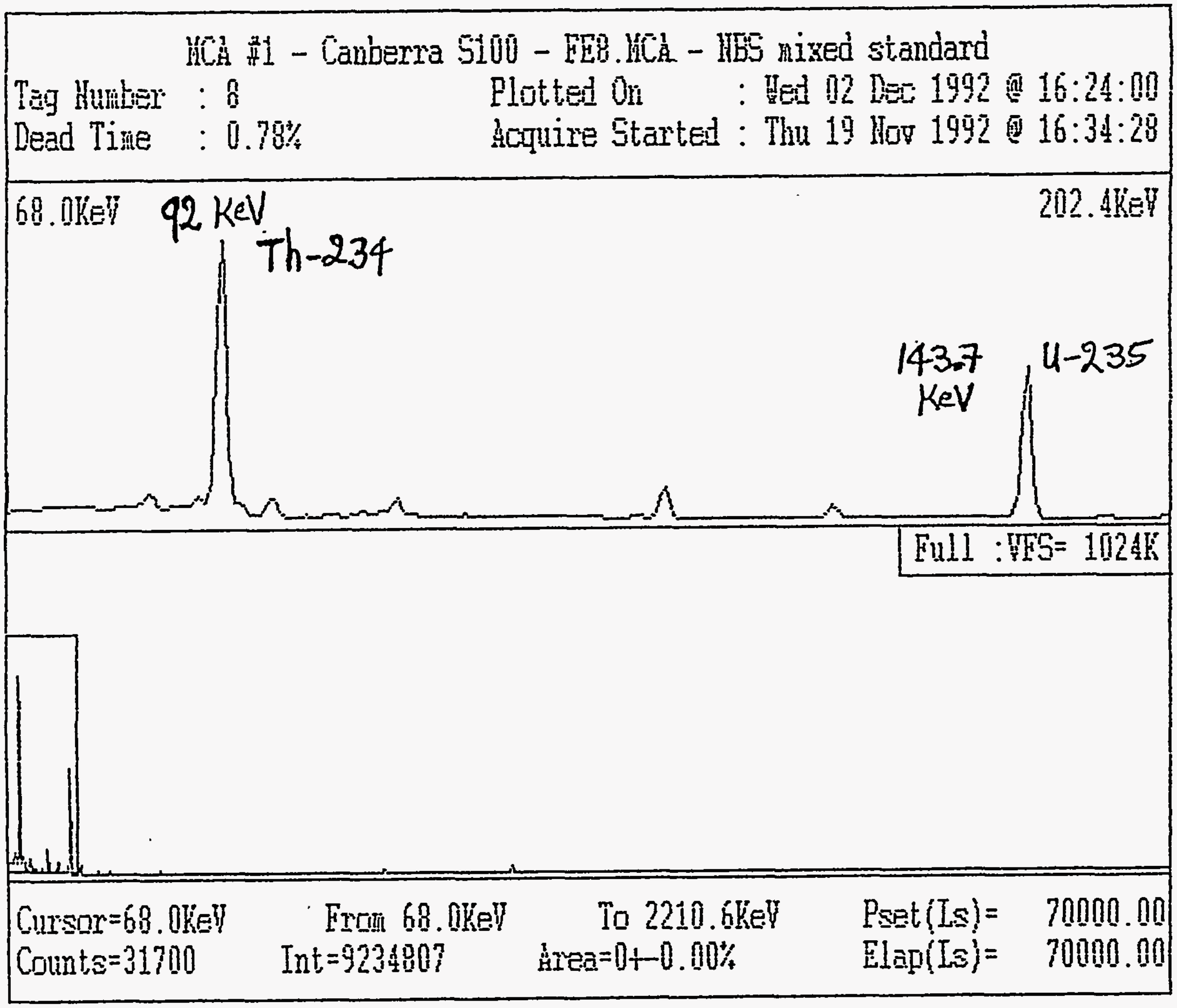


MCA #1 - Canberra S100 - FE7.MCA - NBS mixed standard

```
Tag Number  : 11              Plotted On       : Wed 02 Dec 1992 @ 16:28:39
Dead Time   : 0.40%           Acquire Started  : Mon 16 Nov 1992 @ 14:25:39
```

```
Cursor=69.5KeV      From 67.9KeV      To 2210.1KeV      Pset(Ls)=   70000.00
Counts=18443      Int=4710090      Area=0+-0.00%      Elap(Ls)=   70000.00
```

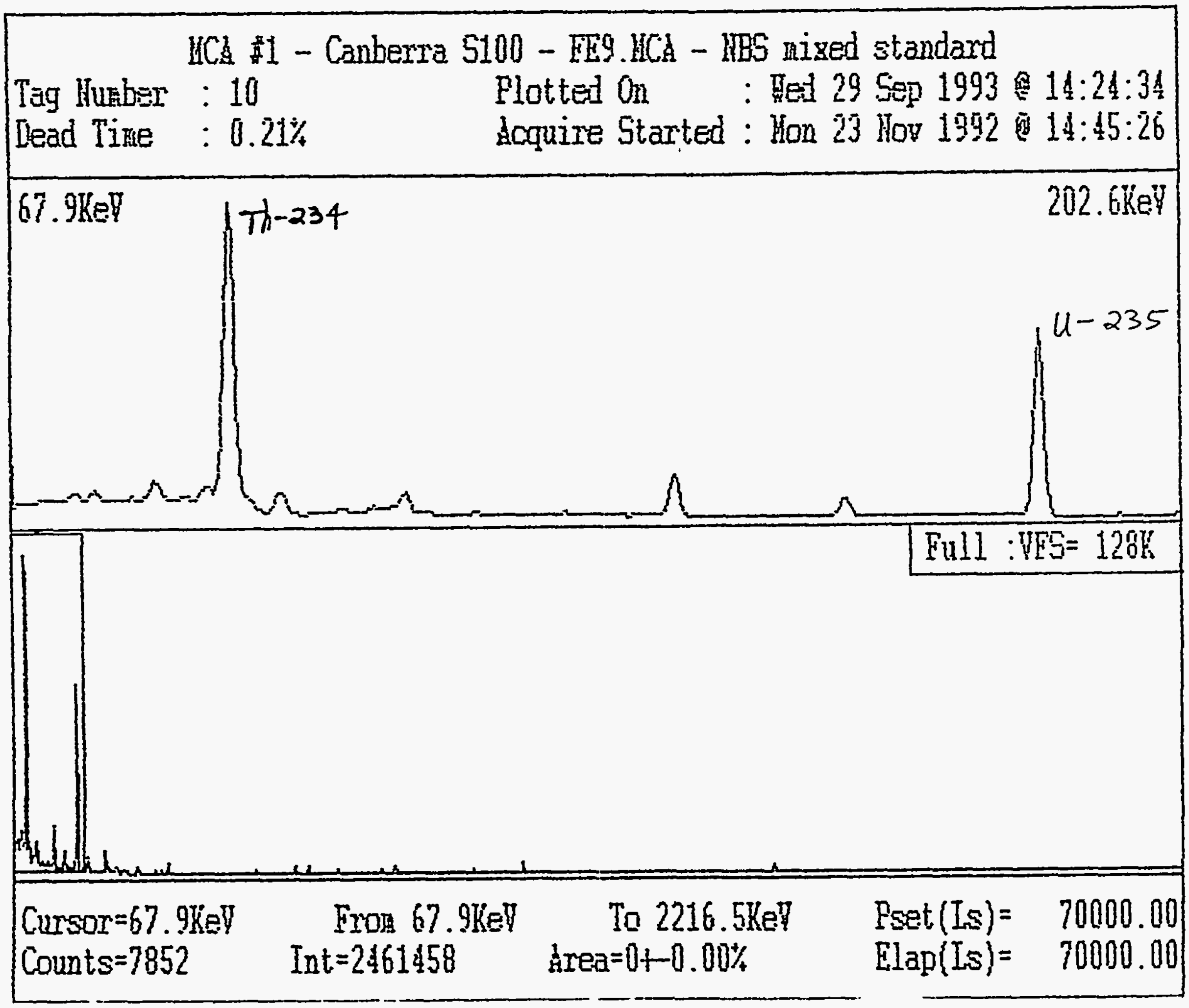
Figure 3.5
Gamma Spectroscopy - FE8 soil wash fraction



```
              MCA #1 - Canberra S100 - FE8.MCA - NBS mixed standard
Tag Number  : 8                 Plotted On       : Wed 02 Dec 1992 @ 16:24:00
Dead Time   : 0.78%             Acquire Started : Thu 19 Nov 1992 @ 16:34:28
```

```
Cursor=68.0KeV      From 68.0KeV       To 2210.6KeV       Pset(Ls)=   70000.00
Counts=31700      Int=9234807       Area=0+-0.00%         Elap(Ls)=   70000.00
```

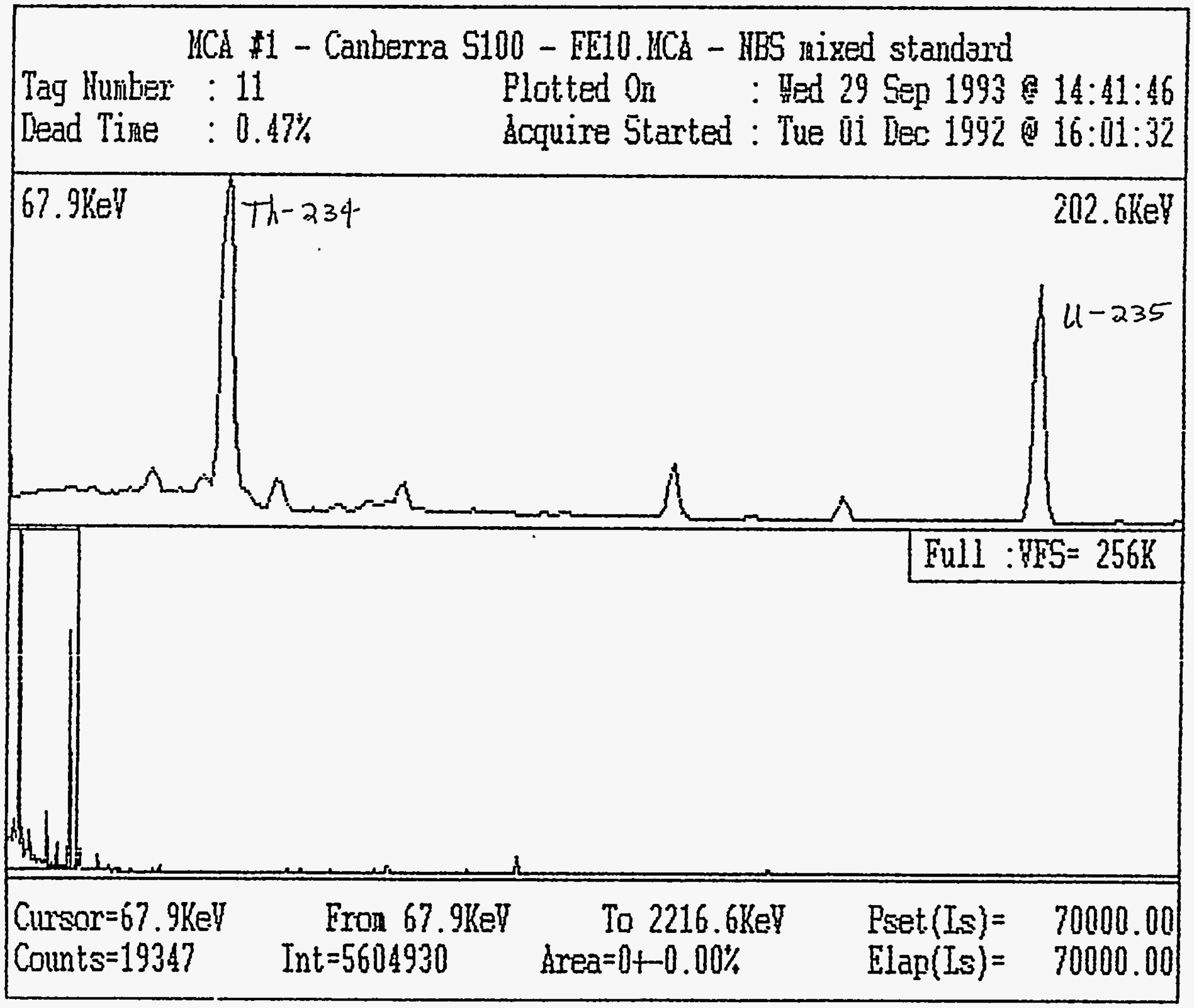
Figure 3.6
Gamma Spectroscopy - FE9 soil wash fraction



```
               MCA #1 - Canberra S100 - FE9.MCA - NBS mixed standard
Tag Number  : 10                   Plotted On      : Wed 29 Sep 1993 @ 14:24:34
Dead Time   : 0.21%                Acquire Started : Mon 23 Nov 1992 @ 14:45:26
```

```
Cursor=67.9KeV      From 67.9KeV      To 2216.5KeV      Pset(Ls)=   70000.00
Counts=7852       Int=2461458       Area=0+-0.00%       Elap(Ls)=   70000.00
```

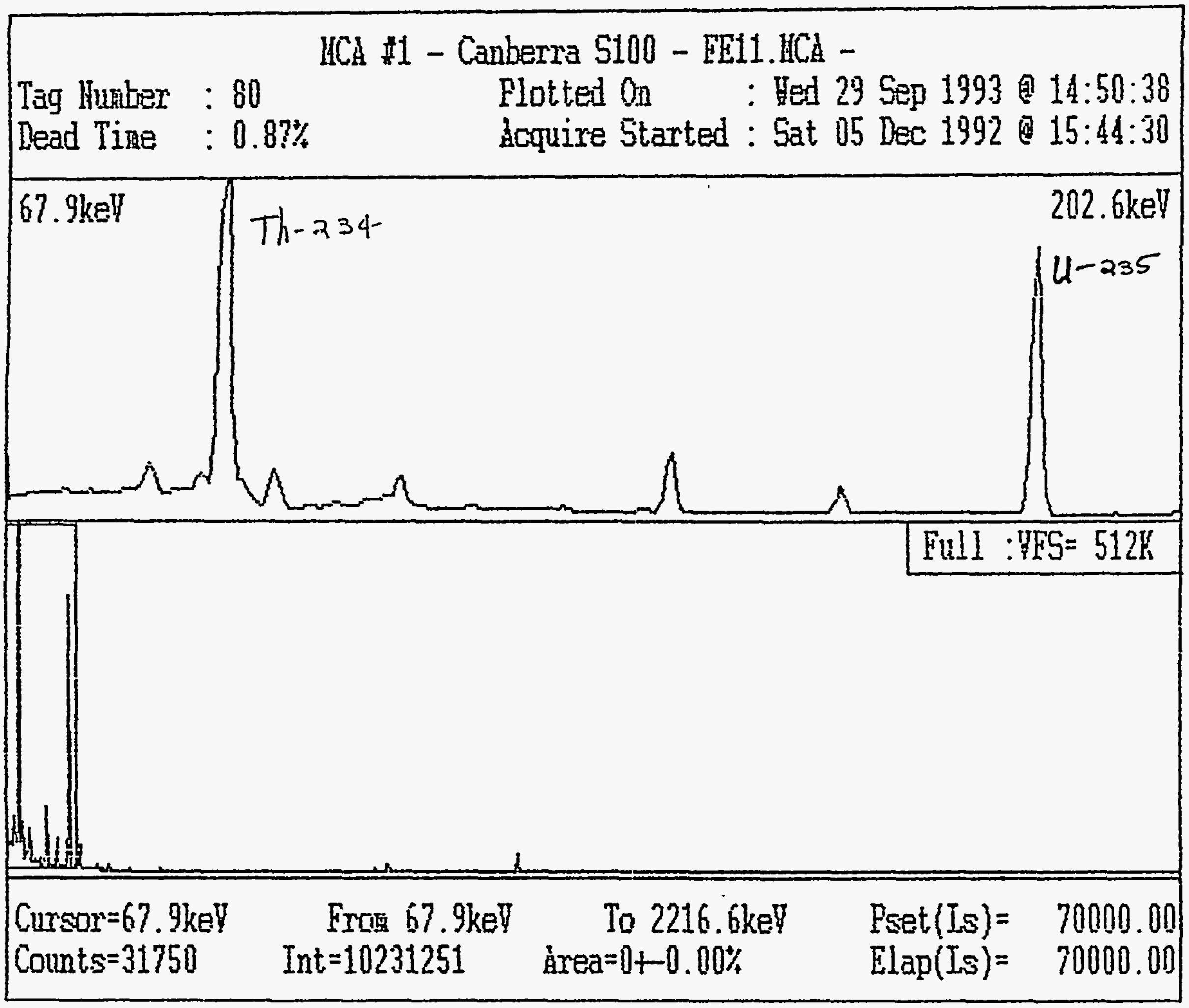
Figure 3.7
Gamma Spectroscopy - FE10 soil wash fraction



```
          MCA #1 - Canberra S100 - FE10.MCA - NBS mixed standard
Tag Number  : 11                  Plotted On       : Wed 29 Sep 1993 @ 14:41:46
Dead Time   : 0.47%               Acquire Started  : Tue 01 Dec 1992 @ 16:01:32
```

```
Cursor=67.9KeV      From 67.9KeV      To 2216.6KeV      Pset(Ls)=   70000.00
Counts=19347      Int=5604930      Area=0+-0.00%        Elap(Ls)=   70000.00
```

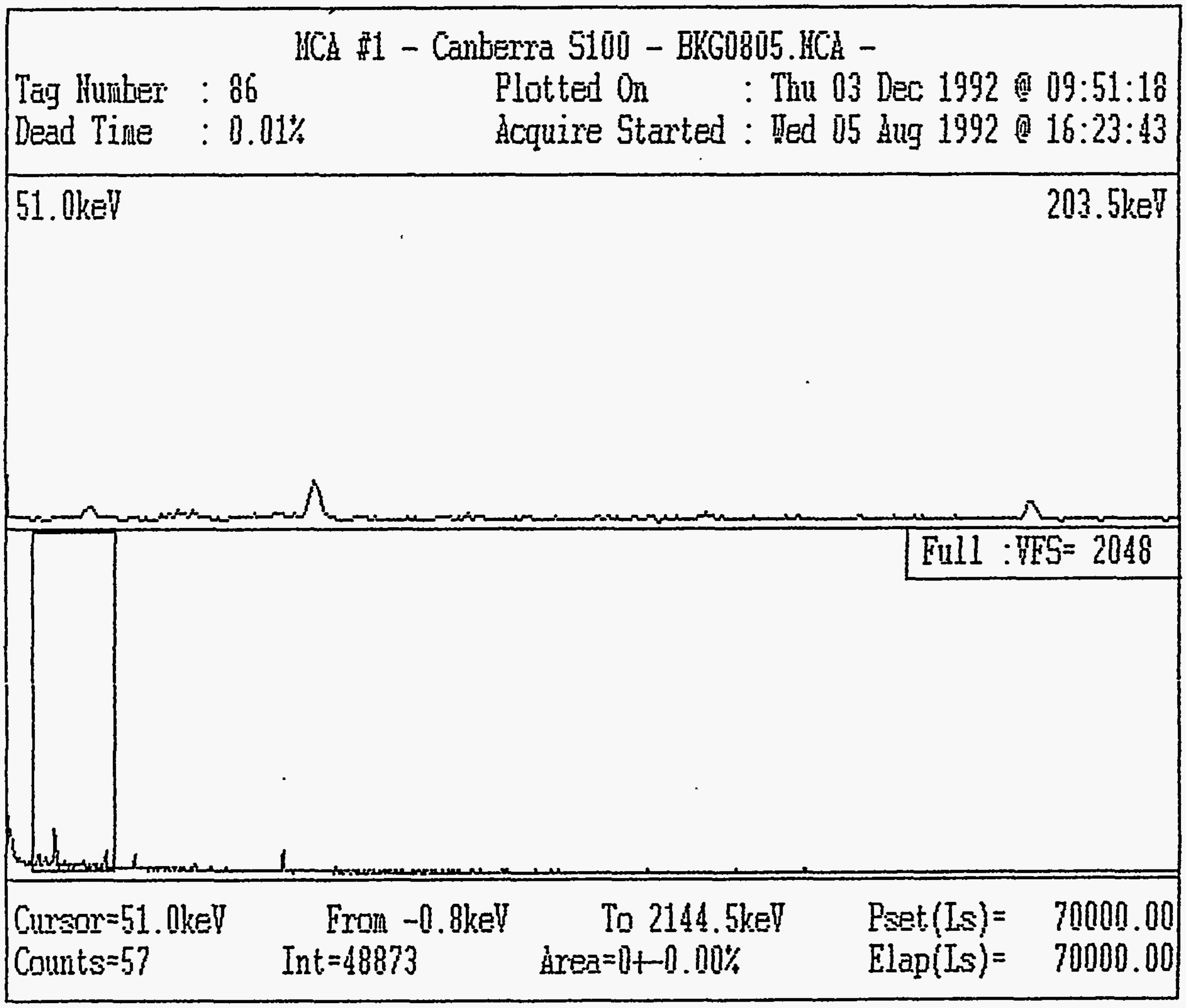
Figure 3.8
Gamma Spectroscopy - FE11 soil wash fraction



```
                  MCA #1 - Canberra S100 - FE11.MCA -
Tag Number  : 80             Plotted On       : Wed 29 Sep 1993 @ 14:50:38
Dead Time   : 0.87%          Acquire Started  : Sat 05 Dec 1992 @ 15:44:30
```

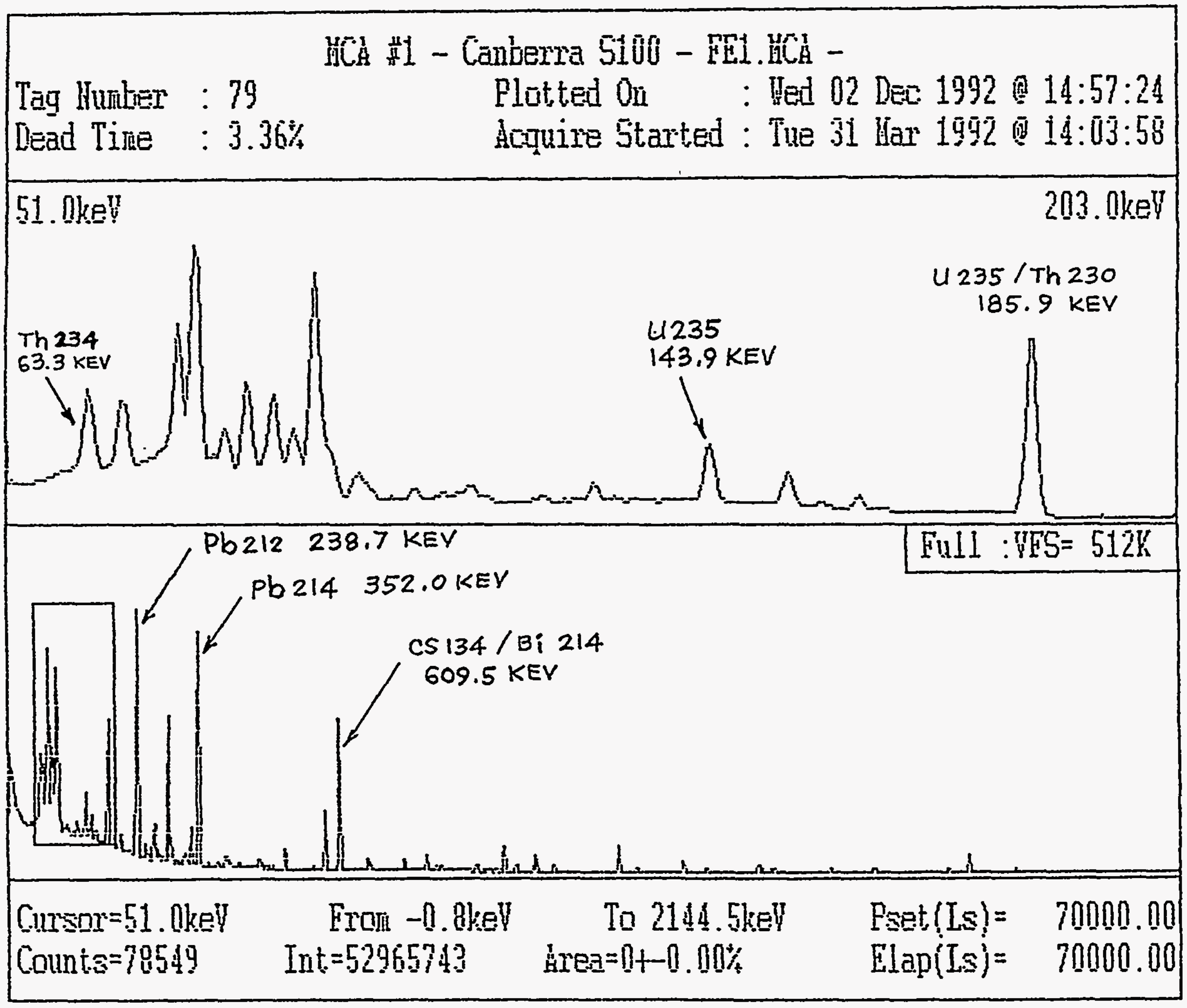
```
Cursor=67.9keV      From 67.9keV      To 2216.6keV     Pset(Ls)=   70000.00
Counts=31750     Int=10231251     Area=0+-0.00%        Elap(Ls)=   70000.00
```

Figure 3.9
Gamma Spectroscopy - background



```
                    MCA #1 - Canberra S100 - BKG0805.MCA -
Tag Number  : 86                Plotted On       : Thu 03 Dec 1992 @ 09:51:18
Dead Time   : 0.01%             Acquire Started  : Wed 05 Aug 1992 @ 16:23:43
51.0keV                                                              203.5keV
                                                           Full :VFS= 2048
Cursor=51.0keV        From -0.8keV        To 2144.5keV       Pset(Ls)=   70000.00
Counts=57           Int=48873          Area=0+-0.00%        Elap(Ls)=   70000.00
```

Figure 3.10
Gamma Spectroscopy - FE1 (Pit 5)



```
                    MCA #1 - Canberra S100 - FE1.MCA -
Tag Number  : 79              Plotted On       : Wed 02 Dec 1992 @ 14:57:24
Dead Time   : 3.36%           Acquire Started  : Tue 31 Mar 1992 @ 14:03:58
```

```
Cursor=51.0keV     From -0.8keV     To 2144.5keV     Pset(Ls)=   70000.00
Counts=78549     Int=52965743     Area=0+-0.00%      Elap(Ls)=   70000.00
```

Section 4.0
Glass Melting -- Crucible Melts

4.1 Introduction

A total of 31 crucible melts were made from six different 55-gallon drums of Pit 5 material and seven different soil-wash fractions. Some of the crucible melts were used to determine the composition of the various Pit 5 sludges, but most of the melts were made to ascertain the compositional range in which processable (for a definition of "processable" in this context, refer to Sections 2.0, 5.0, and 6.0), leach-resistant (for a definition of "leach resistant" in this context, refer to Sections 2.0 and 7.0) glasses can be made. We have made glasses from sludges containing various amounts of CaO, MgF_2, and SiO_2, but had difficulty making homogeneous glasses with high waste loadings from sludges containing ~10 wt.% sulfates. However, relatively few glasses were made from the high-sulfate sludges since those samples were received late in our study and available process knowledge from FEMP at the time suggested that the overall sulfate content in the pit should be low; further work on high-sulfate sludges will be completed in Phase II if the majority of Pit 5 sludge material is, in fact, found to contain large quantities of sulfate. We will discuss the as-melted glasses in this section, and then cover in later sections the viscosity, the conductivity, the phase stability, and the leach resistance of these glass melts.

4.2 Overview

The 31 crucible melts made in MAWS Phase I used Pit 5 sludge samples received over a 15-month period from Fernald. As discussed in the previous section, the Pit 5 materials varied greatly in composition from one 55-gallon drum to the next and this represents an important issued that must be addressed in Phase II (or, indeed, in any further treatability studies). The feasibility of processing Pit 5 material of FE1 and FE15 composition along with soil-wash concentrates was addressed in our Phase I studies since FE1 and FE15 were the first two 55-gallon drums to be analyzed and were also the pit waste streams used for the first 12 crucible melts. The later data obtained on samples with surprisingly high sulfate contents (and low fluoride contents) will support, and indeed, demonstrate the need for, further testing with such compositions.

For each crucible melt, the Pit 5 material was thoroughly mixed before sampling, as described in Section 3.3. The samples of Pit 5 material were then either (i) mixed with additives and vitrified or (ii) dried at 450°C for four hours, mixed with soil dried at 1150°C and additives, and the entire blend vitrified. The pre-drying procedure for the sludge was used in order to increase the mass of glass produced from each crucible loading since all six 55-gallon drums of Pit 5 had high water contents.

A series of 31 glass melts, 27 melts from sludges dried at 450°C and four melts from wet sludges, was made from blends of six different types of Pit 5 sludge, five different types of Lockheed soil-wash fractions, ion exchange media regeneration solution, and additives. These crucible melts demonstrate the lab-scale feasability of blending various waste streams to minimize additives and increase volume reduction, thereby minimizing treatment costs from the perspective of purchased chemicals, processing costs, and disposal costs. A summary of the 31 melts and the analyses completed on them is given in Table 4.1. The weight percent data quoted in Table 4.1 are based on dry weights unless noted; sludges were dried at 450°C for four hours while Lockheed soils were dried at 1150°C for four hours. The blends were usually melted at 1150°C for one hour with continuous stirring for the last 0.5 hour. The glass melts were then removed from the furnace and either air cooled followed by quenching in water (the outside of the crucible, not the glass, was exposed to water) in the case of Pt/Au crucibles, or by pouring into graphite molds if the melts were made in clay crucibles.

Note that in some instances the same blend was melted twice, as in the case of F5-50 and F5-50B. That was because the supply of F5-50 glass was exhausted and a second batch was prepared (F5-50B) in order to complete the required analysis. We consider F5-50 and F5-50B to be interchangeable since exactly the same recipe and melting procedure were used for each.

4.3 Results

The 31 crucible melts were produced from combinations of Pit 5 sludges and Lockheed soil-wash fractions or from glasses produced in the 100 kg/day melter runs with additives of various amounts of SiO_2, NaF, Na_2O, and B_2O_3. The 100 kg/day melter glass was used because it provided a convenient base glass in large supply for making specific composition variations and clear one-to-one comparisons of the effects. In addition, the only Pit 5 sludges available at that time (late in the project) were FE51 and FE52, both with >10 wt.% SO_3 which, on the basis of site process knowledge were believed to be unrepresentative of the overall contents of Pit 5. The large SO_3 content caused separation of the melt into two layers when high waste loadings were used; a glassy layer appeared on the bottom, and a sulfate-rich layer appeared on the top. The investigation of high-sulfate wastes may have to be extended if the FE51 and FE52 samples are, in fact, representative of a major fraction of the Pit 5 waste. Most of the crucible melts were used to investigate the effects of the variations in Mg, Si, Ca, and F on glass formation, as was done with the use of 100 kg/day melter glasses.

Table 4.2 presents the batch composition, the crucible type used, and the appearance-upon-cooling of the crucible-melt glasses. The objectives of the batch composition variations included: varying the source of the Pit 5 material; varying the soil wash fractions to ascertain whether the same batch composition could be used with different sources of the soil fines; varying sludge-to-soil ratio; and examining the effect of changing ratios such as Mg/F, Mg/Ca, and Mg/Si.

We began crucible melts for the MAWS program with F5-42 based on results from a previous study conducted at our lab. After reviewing the compositional analysis of Pit 5 (FE1) sludge and soil-wash fractions FE6 and FE7, we decided to melt a glass with 65 wt.% dried Pit 5; 18 wt.% dried FE6 and FE7 in a 1:3 weight ratio; and 5 wt.% SiO_2, 4 wt.% Na_2O, and 8 wt.% B_2O_3. This glass was predicted to be both processable and leach resistant based on information from our previous studies ("Vitrification Development Studies for OU1 Wastes", Final Report, PO 917844-00, April, 1993). Upon cooling, the blend produced a homogeneous dark brown glass. (We will see in the following sections that only slight modifications are needed in order to make F5-42 processable.) F5-43, F5-44, F5-45, F5-46, and F5-47 were melted to determine how high in SiO_2 loading these blends could be taken before encountering solubility problems. We were interested in high SiO_2 loadings to prepare for a case when there are greater amounts of contaminated soil to be disposed of than Pit 5 material. For F5-43, F5-44, F5-45, and F5-46, the undissolved portions all were rich in silicon. This indicates that for MgF_2 content between 15-20 wt.%, CaO content of 20-24 wt.%, and B_2O_3 content of 9-12 wt.%, greater than about 30 wt.% SiO_2 cannot be dissolved at 1150°C. This places an upper limit on the amount of silicon-rich waste stream which can be blended with pit material of FE1 composition. We saw in Section 3.0 that FE15 Pit 5 material contained much less MgF_2 and more Al_2O_3, MgO, SiO_2, and Fe_2O_3 than FE1 Pit 5 material. Because of these changes in sludge composition, the batch recipe for F5-44 can be made into a homogeneous glass melt at 1150°C if FE15 Pit 5 material is used. This is confirmed by the F5-44B crucible melt, in which 35 wt.% SiO_2 could be incorporated into the glass matrix at 1150°C because the MgF_2 content was reduced from 17 wt.% to 7 wt.% (see Table 4.5) for the resulting glass composition.

The crucible melt, F5-48, was used to determine the lower limit in SiO_2. For that melt, no SiO_2 additives were used and only 19.8 wt.% soil-wash fractions. This produced a nice looking glass, but as discussed in Section 5.0, the viscosity and conductivity of F5-48 at 1150°C would make this glass difficult to process in the current Duramelter vitrification system. In addition, Section 6.0 shows that F5-48 has a liquidus temperature of 1050°C, which is on the borderline of our processing requirements. This type of information is necessary in order to determine a "workable" compositional range.

Crucible melts from F5-49 to F5-59 were used to experiment with FE14, FE15, FE16, FE51, and FE52 Pit 5 sludges. Since these sludges were each different in composition, and so drastically different from FE1 Pit 5 sludge, the main concern was the possibility of sludge loading with these new sludges. From crucible studies, we found that ~60 wt.% of FE15 Pit 5 sludge (dried basis) could be incorporated at 1150°C to form a homogeneous glass. However, for the high-sulfur sludges (~10 wt.% SO_3) such as FE52, even a 45 wt.% sludge loading caused solubility problems. These initial studies on FE51 and FE52 suggest that, if the remaining Pit 5 sludges are similar to FE51 and FE52, further compositional studies are needed in MAWS Phase II. The crucible melts made directly from wet sludge (F5-54B and F5-55B) will be discussed in Section 4.5.

As shipments of sludge were received (over a considerable period of time due to shipping delays), it became clear how much the Pit 5 sludge composition varied from one 55-gallon drum to the next. Consequently, we decided to use the same base glass produced from one of the 100 kg/day melter runs and vary the amounts of MgF_2, CaO, MgO, SiO_2, and NaF in order to determine the effects of large variations in Mg, F, Ca, and Si previously seen in the Pit 5 sludges and Lockheed soil fractions. These experiments are crucible melts F5-60 to F5-68. We added various amounts of SiO_2, CaO, MgF_2, and MgO to determine the effects of changing these major waste components on a base glass. From these crucible melts, we determined that no more than 20 wt.% MgF_2 can be added if we are to dissolve about 30 wt.% SiO_2 into the glass matrix and greater than 25 wt.% CaO will cause insolubility problems.

An additional additive was used for the F5-68 melt. In this melt, 90 ml of ULT122 ion exchange resin stripping solution was added to the 100 kg/day glass, which contained soil fractions and Pit 5 materials, and the blend vitrified. This melt demonstrates an additional step in the MAWS program since we combined sludge, soil, and the elluent from stripping the ion exchange material used in the treatment of soil washing process waters to produce one glass product, minimize additives and stabilize what would otherwise become a secondary waste stream. This demonstrates, on a lab-scale, the fulfillment of key MAWS concepts such as blending waste streams and integrating treatment subsystems.

We had determined from earlier FEMP studies that at least 6 wt.% B_2O_3 additive was needed in order to produce "good" glasses. (A good glass in this context is defined as one which has processable viscosity, conductivity, and liquidus temperature, and passes the TCLP test.) Adding more B_2O_3 increased the solubility of the wastes since B_2O_3 acts as a flux, but increasing the B_2O_3 content also has detrimental effects including higher cost and reduced leach resistance. The B_2O_3 variation in this study was from 7 wt.% to 11 wt.% on a dried basis. From earlier studies it was found that the amount of Na_2O needed on a dried basis is at least 4 wt.% to produce a processable glass. Thus, the amount of Na_2O added was kept in the range of 4 to 5 wt.% on a dried basis, except for F5-63, where greater than 8 wt.% Na_2O (converting NaF to Na_2O) was added to determine effects of high sodium content. As discussed in later sections, loss of fluoride from the melters during vitrification leads to NaF in the feed batch as a result of the off-gas recycle stream.

The crucible types used for the glass melts are also listed in Table 4.2. Because Pt/Au crucibles are the most unreactive, they are the preferred crucible type to use. For the first 15 crucible melts, only Pt/Au crucibles were used. When wet sludge was used, clay crucibles were employed due to the possible presence of carbon in the wet sludge which could reduce iron in the melt and eventually destroy the Pt/Au by forming Pt/Fe alloys. We had discovered from earlier work with Fernald Pit 5 material that some of the silicon and aluminum in the clay crucibles reacts with the glass; hence, our preference for using Pt/Au crucibles. However, the amount of Al_2O_3 and SiO_2 added to the glass matrix from the clay is less than the uncertainty in the composition of the sludge starting material. For example, clay crucibles add on the order of 0-1 wt.% of Al_2O_3 and 1-3 wt.% of SiO_2 to the glass matrix, while the uncertainty in using one 100 g sample of sludge to the next is slightly larger. Furthermore, the composition of the final glasses was determined by chemical analysis.

The appearance-upon-cooling indicates whether there are potential insolubility problems and potential phase separation problems. For example, from Table 4.2 we see that F5-43, F5-44, and F5-45 all had some undissolved materials remaining after vitrification, suggesting that these blends may have solubility problems at 1150°C. When there are two distinct and physically separate phases produced from the melts, such as in F5-43, we attempt to separate the two and analyze each separately. If physical measurements are made, we attempt to use only the glassy phase. Some of the glasses are described as phase-separated, indicated by the opaque greenish color which had been shown previously to be due to microscopic amorphous phase separation (<0.2 micron globules). This microscopic phase separation can be suppressed by cooling the glass at a faster rate and is, therefore, not a significant factor in determining what may be a viable glass composition.

Most of our crucible melts were made from sludges dried at 450°C and soil dried at 1150°C; the waste loadings listed in Table 4.2 refer to a dry, rather than as-received, basis. Table 4.3 shows the batch recipes for the crucible melts both on a dry and a wet basis. These melts achieved Pit 5 waste loadings (on a wet basis) ranging from 60 to 96 wt.% and soil wash fractions (on a wet basis) ranging from 0 to 36 wt.%.

4.4 Compositional Analysis of Crucible Melts

The MAWS crucible melts contain considerable amounts of species that are not determined by DCP-ES. Hence, the traditional dissolution and analysis by DCP-ES and the subsequent conversion of elements to oxides produces a misleading analysis. The species of concern for Pit 5 materials are fluorides and sulfates. Because the Pit 5 materials containing large amounts of sulfates (FE14, FE51, and FE52) did not produce homogeneous glasses, we did not analyze for sulfates in these glasses. We did, however, analyze for fluoride in the majority of MAWS crucible melts. Table 4.4 shows the calculated and analyzed fluoride content of the crucible melts. In general, the calculated and analyzed fluoride contents are in agreement; there is 0-11 relative % fluoride loss during vitrification for blends containing less than 9 wt.% fluoride, but the fluoride loss increases to almost 30 relative % for blends containing 10-17 wt.% fluoride. These studies indicate that fluoride loss at 1150°C is a consideration that must be carefully addressed in any continuous melter system. In Sections 9.0 and 10.0 we will see how this problem can be resolved by capturing the fluoride in the off-gas system as NaF and recycling it to the feed batch.

The results from the analyzed fluoride content combined with DCP-ES analysis are described in Table 4.5. In this table, we present the calculated and analyzed compositions of the crucible melts. Note that the calculated columns all add up to 98-101 wt.% except for the melts containing high sulfates (for example, F5-54A) and the glasses made from 100 kg/day melter glasses. The 100 kg/day melter glasses had not been analyzed for sulfates and other elements which are present in small amounts, but which together total 3-4 wt.%; thus we expect about 96 wt.% recovery for these glasses. Note also that some analyses were performed in either duplicates or triplicates; these data indicate that more than one 100 mg sample was dissolved by total acid dissolution and analyzed by DCP-ES. The fluoride analyses, which were performed as sets of triplicates, were averaged and the average used to determine the amount of MgF_2. As mentioned previously, the form of the fluoride in the sludge is not known but assumed to be predominantly MgF_2 because of the history of the pits. There are always more moles of Mg in each sample than there are of F, so the excess Mg is reported as MgO. The multiple dissolutions and analyses show that the reproducibility of the overall glass analyses is good.

The analyzed and calculated columns of Table 4.5 are generally in good agreement except for some of the heterogeneous glasses; not all heterogeneous glasses show poor agreement because some only have a small amount of undissolved material or macroscopic phase separation. For example, the F5-44 melt produced mainly a glassy phase with some undissolved materials. Both the glassy phase and the undissolved material (named F5-44W for the white portion of F5-44) were analyzed. The analyzed composition of the glassy part of F5-44 agreed well with the target composition, except for the loss of some fluoride. In comparison, the white portion of F5-44 melt (F5-44W), is much richer in SiO_2 and poorer in B_2O_3 than the targeted glass. Note that the column for F5-44W only adds up to 91.14 wt.%. Most of the remaining 8.86 wt.% is most likely fluoride. The glasses for which fluoride analysis has been completed generally add up to 95 wt.% or greater (unless there is sulfate in the glass) while the glasses which had been expected to contain fluoride, but for which fluoride was not analyzed, show totals of less than 95 wt.%.

There were five glass melts in which a greenish cake layered the top of the crucible melts: F5-54A, F5-57A, F5-57B, F5-58A, and F5-58B. These melts were made from blends using Pit 5 sludge containing high sulfur. The greenish cake materials, F5-57A-Gr, F5-54A-Gr and F5-58A-Gr, were analyzed by DCP-ES. Table 4.5 shows that these layers are basically the same; composed mainly of sulfur, sodium, and calcium, with some boron, potassium, magnesium, and silicon. The cations only account for 39-44 wt.% of the sample; the other 56-57 wt.% is most likely due to SO_3. We examined one of the greenish cakes, F5-57A-Gr (the greenish part of F5-57A), under SEM/EDS and found it contains large amounts of sulfur along with noticeable amounts of calcium, barium, sodium, and silicon. The EDS spectrum of F5-57A-Gr is shown in Figure 4.1. The problem of phase separation forming a sulfur-rich layer will have to be investigated further if the 55-gallon drums of FE-14, FE-51, and FE-52 Pit 5 materials are typical of the overall composition of Pit 5 sludge. The solubility of sulfur in borosilicate glasses have been extensively studied at VSL using Weldon Spring wastes; however, further studies are needed in order to maximize sludge loading for the production of a homogeneous leach-resistant glass optimized for the wastes at Fernald.

4.5 Vitrifying Wet Sludge to Determine Sludge Composition

From the experience of many crucible melts, we have seen that vitrifying ~200 g of dried sludge then analyzing the resulting glass gave a representative analysis of the sludge, while analyzing 100 mg sub-samples of dried sludge did not generate reproducible analyses from one subsample to the next (i.e. 47 melts made from FE1 Pit 5 sludge gave consistently the same FE1 Pit 5 sludge composition. Seven of those glass compositions are reported in this section while the remaining melts were reported elsewhere ("Vitrification Studies for OU1 Wastes", Final Report, PO917844-00, April, 1993)). This suggests that if we dissolve 200 g portions of dried sludge then analyze the resulting solution, we would produce a representative analysis of the sludge. However, as noted above, of the order of 400 l of radioactive solution would also be produced each time we dissolved 200 g of sludge. To avoid the creation of so much sidestream waste, the analysis of glasses made from the sludges seems more appropriate. It is very time consuming to dry the sludge at 450°C for 4 hours, mix with additives, vitrify, crush, dissolve, and analyze. In order to minimize the time required for sludge analysis (which is particularly important for process control in the demonstration continuous melter runs), we experimented with vitrifying wet sludges directly. Table 4.6 summarizes the calculated and analyzed compositions of the products from two of these experiments. The boron in the final glass is 19-23 relative % lower than the targeted values and the aluminum is 24-37 relative % higher than the targeted values, but all other elements present at greater than 1 wt.% in the glass have less than 10 relative % error. The aluminum discrepancy may be due to leaching from the clay crucibles, while the boron discrepancy may be due to weighing errors (we used 2.1 g of boron for some 300-400 g of sludge due to the high water content of the sludge). These results suggest the viability of using wet sludge vitrification as a reliable and relatively rapid method for determining sludge composition, but clearly further tests are necessary to confirm this. These tests should be performed early in Phase II in order to ensure a more rapid turnaround time for sludge analysis since this is crucial for the process control in prolonged 300 kg/day melter runs on site at Fernald.

4.6 Summary and Discussion

In this section, we examine a number of crucible melts made from six different 55-gallon drums of Pit 5 material. The results show that (1) greater than 60 wt.% Pit 5 sludge loadings, corresponding to 80^+ wt.% Pit 5 loadings on an as-received basis, can be used to produce homogeneous glass melts at 1150°C if Pit 5 has a composition similar to either of the 55-gallon drums of FE1 or FE15. (2) The high SO_3 content (~ 10 wt.%) of FE14, FE51, and FE52 presented solubility problems at high sludge loadings. These solubility problems should be resolved in MAWS Phase II if the majority of Pit 5 material is similar to FE14, FE51, or FE52. (3) A "workable" compositional range, consisting of glass compositions which have acceptable values of key process parameters (as discussed in Sections 5.0 and 6.0) and are leach resistant (as discussed in Section 7.0) is presented in Table 4.7. This "workable" compositional range includes the compositions of crucible melts F5-44B, F5-47, F5-49, F5-52, F5-60, F5-66, and F5-68, and should be used following the guidelines specified in the footnote of Table 4.7. These glasses are produced from a feed which is composed of in excess of 80 wt.% waste on a dry basis (and considerably higher on an "as-received" basis), fulfilling one of the major MAWS objectives of maximizing waste streams and minimizing additives.

From crucible melts, we have determined that a number of batch recipes can produce a homogeneous melt at 1150°C. These batch recipes are tolerant to some variations in Pit 5 material composition. For example, very similar batch compositions were used for F5-42 and F5-52 melts, but one melt used FE1 while the other used FE15 sludge and both produced homogeneous glasses. However, the drastic variation in sulfur content from FE15 to FE51, for example, does not allow for similar batch recipes to be used, as shown by crucible melts F5-52 and F5-57A (where soil and SiO_2 were interchanged since FE11 soil is predominantly SiO_2).

Given this situation, it is certainly of interest, and probably of importance, to study sulfur solubility for glasses made from FE51-like sludge in order to maximize waste loadings. However, the more important questions relate to the source of such large drum-to-drum variability in composition and the overall average composition of the material in Pit 5. For example, if the average composition of all of Pit 5 was found to be similar to FE1 or FE15, additional compositional studies would not be needed. Furthermore, variations on the 55-gallon scale may be irrelevant for the control of a large-scale process in which the batch size will probably be many tens-of-thousands of gallons. Conversely, even on this scale the average composition of such a sample may change from sample-to-sample with the location of the dredging point in the pit. As a result, an essential next step in MAWS Phase II (and indeed, for any treatability study) is to obtain improved estimates of the overall average composition and variability of the Pit 5 material.

Table 4.1
Summary of MAWS Crucible Melts and Data Collected
(See notes for key)

Glass Name	Pit 5 (wt.%)							Soil Wash Fractions (wt.%)				Additives (wt.%)	DCP-ES Analysis	Fluoride Analysis	Vis & Con	TCLP	PCT	XTAL
	FE1	FE14	FE15	FE16	FE51	FE52	100 kg/day melter glass	FE6+FE7	FE8	FE11	FE38+							
F5-42	65							18				17	*		*		*	*
F5-43	45							42				13	*		*	*	*	*
F5-44	50							32				18	*	*	*		*	*
F5-44B			50					32				18	*	*				
F5-45	55							33				12	*		*	*	*	*
F5-46	45							39				16	*		*	*	*	
F5-47	44.2							38.3				17.5	*	*	*	*	*	*
F5-48	68.1							19.8				12.1	*		*			*
F5-49			60.8					24.5				14.8	*	*	*	*	*	*
F5-50 & F5-50B			62					18				20	*	*		*	*	
F5-51 & F5-51B					68.1				19.8			12.1	*	*	*	*	*	*
F5-52 & F5-52B					68.1					19.8		12.1	*	*	*	*	*	*
F5-54A		68.9										31.1	*		*	*	*	*
F5-54B		88.1**										11.9	*	*				
F5-55A				68.9								31.1	*	*				*
F5-55B				88.1**								11.9	*		*			

Note:The numbers for Pit 5, soil wash fractions and additives are on a dried basis in weight percent except for F5-54B, F5-55B, F5-57B, and F5-58B. Pit 5 materials were dried at 450°C for 4 hours and soil wash fractions were dried at 1150°C for 4 hours.
* = analysis completed
** = sludge used was wet (as received)
DCP-ES = glass composition analysis by dissolution followed by DCP-ES spectroscopy
Fluoride analysis = glass composition analysis by dissolution followed by selective electrode analysis of fluoride
Vis & Con = melt viscosity and electrical conductivity data
TCLP - toxicity characteristic leaching procedure completed on glass.
PCT = product consistency test completed on glass
XTAL = crystallization data

Table 4.1 (continued)

Glass Name	Pit 5 (wt.%)							Soil Wash Fractions (wt.%)				Additives (wt.%)	DCP-ES Analysis	Fluoride Analysis	Vis & Con	TCLP	PCT	XTAL
	FE1	FE14	FE15	FE16	FE51	FE52	100 kg/day melter glass	FE6+FE7	FE8	FE11	FE38+							
F5-56				39							50	11		*	*	*	*	*
F5-57A					68.9							31.1	*		*	*	*	*
F5-57B					95.6**							4.4						
F5-58A						68.9						31.1				*	*	
F5-58B						96**						4						
F5-59					45				33			22	*		*	*	*	*
F5-60							90					10	*	*	*	*	*	*
F5-61							80					20	*	*	*	*	*	*
F5-62							94					6	*	*	*	*	*	*
F5-63							80					20	*	*	*	*	*	*
F5-64A							75					25	*	*	*		*	*
F5-65							84					16	*	*	*	*	*	*
F5-66							80					20		*	*	*	*	*
F5-67							75					25		*		*	*	*
F5-68							83					17	*	*	*			*

Note: The numbers for Pit 5, soil wash fractions and additives are on a dried basis in weight percent except for F5-54B, F5-55B, F5-57B, and F5-58B. Pit 5 materials were dried at 450°C for 4 hours and soil wash fractions were dried at 1150°C for 4 hours.

* = analysis completed
** = sludge used was wet (as received)
DCP-ES = glass composition analysis by dissolution followed by DCP-ES spectroscopy
Fluoride analysis = glass composition analysis by dissolution followed by selective electrode analysis of fluoride
Vis & Con = melt viscosity and electrical conductivity data
TCLP = toxicity characteristic leaching procedure completed on glass.
PCT = product consistency test completed on glass
XTAL = crystallization data

Table 4.2

Batch Composition, Crucible Type, and Appearance Upon Cooling of MAWS Crucible Melts F5-42 through F5-68.

Component (wt.%)	F5-42	F5-43	F5-44	F5-44B	F5-45	F5-46	F5-47	F5-48
Pit 5*	65 (FE1)	45 (FE1)	50 (FE1)	50 (FE15)	55 (FE1)	45 (FE1)	44.2 (FE1)	68.1 (FE1)
Soil-Wash Fractions**	18 (FE6 + FE7)	42 (FE6+FE7)	32 (FE6+FE7)	32 (FE6 +FE7)	33 (FE6+FE7)	39 (FE6+FE7)	38.3 (FE6+FE7)	19.8 (FE6+FE7)
100U-2-56B(a)	0	0	0	0	0	0	0	0
SiO_2	5	0	5	5	0	0	0	0
NaF	0	0	0	0	0	0	6.7	0
Na_2O	4	5	5	5	4	5	0	4.4
B_2O_3	8	8	8	8	8	11	10.8	7.7
CaO	0	0	0	0	0	0	0	0
MgF_2	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
Crucible Type	Pt/Au	Pt/Au	Pt/Au	Pt/Au	Pt/Au	Pt/Au	Pt/Au	Pt/Au
Appearance upon cooling	dark brown glass	phase separated green/black glass with undissolved chemicals	phase separated green/black glass with undissolved chemicals	brown glass	green/black phase separated glass undissolved chemicals	brown glass undissolved chemicals	pale green glass	smooth brown glass

* All Pit 5 dried at 450°C for 4 hours, except where indicated.

** Lockheed soil-wash fractions dried at 1150°C for 4 hours.

(a) Glass produced from 100 kg/day melter runs and used to prepare subsequent composition variations as crucible melts.

Table 4.2 continued

Component wt%	F5-49	F5-50 & F5-50B	F5-51 & F5-51B	F5-52 & F5-52B	F5-54A	F5-54B	F5-55A	F5-55B	F5-56
Pit 5*	60.8 (FE15)	62 (FE15)	68.1 (FE15)	68.1 (FE15)	68.9 (FE14)	88.1 (FE14,wet)***	68.9 (FE16)	88.1 (FE16, wet)***	39 (FE16)
Soil-Wash Fractions**	24.5 (FE6+FE7)	18 (FE6+FE7)	19.8 (FE8)	19.8 (FE11)	0	0	0	0	50 (FE38,40,50)
100U-56B(a)	0	0	0	0	0	0	0	0	0
SiO_2	2	9	0	0	18.9	7.2	18.9	7.2	0
NaF	5.9	0	0	0	0	0	0	0	0
Na_2O	0	4	4.4	4.4	4.4	1.7	4.4	1.7	4
B_2O_3	6.9	7	7.7	7.7	7.8	3.0	7.8	3.0	7
CaO	0	0	0	0	0	0	0	0	0
MgF_2	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
Crucible	Pt/Au	Pt/Au	Pt/Au	Pt/Au	Pt/Au	clay	Pt/Au	clay	clay
Appearance Upon Cooling	homogeneous brown glass	black with small phase-separated regions	brown homogeneous glass	brown homogeneous glass	phase separated/3 layers black/brown/green	black glass	black/brown homogeneous glass	black glass	black homogeneous glass

* All Pit 5 dried at 450°C for 4 hours, except where indicated.
** Lockheed soil-wash fractions dried at 1150°C for 4 hours.
*** Wet = as-received.
(a) Glass produced from 100 kg/day melter runs are used to prepare subsequent composition variations as crucible melts.

Table 4.2 continued

Component (wt%)	F5-57A	F5-57B	F5-58A	F5-58B	F5-59	F5-60	F5-61	F5-62
Pit 5*	68.9 (FE51)	95.6 (FE51,wet)***	68.9 (FE52)	96 (FE52,wet)***	45 (FE52)	0	0	0
Soil-wash Fractions**	0	0	0	0	33 (FE8)	0	0	0
100U-2-56B(a)	0	0	0	0	0	90	80	94
SiO_2	18.9	2.7	18.9	2.3	0	0	0	0
NaF	0	0	0	0	5	0	0	0
Na_2O	4.4	0.5	4.4	0.5	0	0	0	0
B_2O_3	7.8	1.1	7.8	1.0	12	0	0	0
CaO	0	0	0	0	0	0	0	6
MgF_2	0	0	0	0	5	10	20	0
MgO	0	0	0	0	0	0	0	0
Crucible	Pt/Au	clay	clay	clay	clay	clay	clay	clay
Appearance Upon Cooling	brown phase separated glass w/ yellow green layer on top	Brown glass; yellow green top layer	Brown glass w/yellow- green material on top	Yellow green top on brown glass	Undissolved chemicals in black glass	Dark brown homogeneous glass	brown glass, with green streaks on surface	Dark brown; green streaks on surface

* All Pit 5 dried at 450°C for 4 hours, except where indicated.
** Lockheed soil-wash fractions dried at 1150°C for 4 hours.
*** Wet = as-received
(a) Glass produced from 100 kg/day melter runs and used to prepare subsequent composition variations as crucible melts.

Table 4.2 continued

Component (wt.%)	F5-63	F5-64A	F5-65	F5-66	F5-67	F5-68***
Pit 5	0	0	0	0	0	0
Soil-wash Fractions	0	0	0	0	0	0
100U-2-56B(a)	80	75	84	80	75	83****
SiO_2	0	15	10	5	5	8
NaF	5	0	0	0	0	0
Na_2O	0	0	0	0	0	0
B_2O_3	0	0	0	0	0	0
CaO	0	0	6	10	0	4
MgF_2	15	10	0	0	20	5
MgO	0	0	0	5	0	0
Crucible Type	clay	clay	clay	clay	clay	clay
Appearance Upon Cooling	brown glass with streaks on surface	green phase separated/ glass mixing problem	brown glass with undissolved chunks	homogeneous glass	brown glass w/crystals	black homogeneous glass

* All Pit 5 dried at 450°C for 4 hours, except where indicated.
** Lockheed soil-wash fractions dried at 1150°C for 4 hours.
*** With 90 ml of effluent from stripping ion exchange material.
**** Used 100U-2-56C glass instead of 100U-2-56B glass. The two should be very similar since they were drained from the melter 1.3 hours apart.
(a) Glass produced from 100 kg/day melter runs and used to prepare subsequent composition variations as crucible melts.

Table 4.3
Compositions of Crucible-Melt Blends.
Weight Percent on Dry and Wet Basis.

Component (wt%)	F5-42**		F5-43		F5-44		F5-45		F5-46		F5-47		F5-48	
	dry*	wet+	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet
Pit 5	65	85	45	70.3	50	74.8	55	78.1	45	70.6	44.2	70.0	68.1	86.7
Soil Wash Fractions	18	8.4	42	23.5	32	17.1	33	16.7	39	21.9	38.3	21.7	19.8	8.8
SiO_2	5	2	0	0	5	2.2	0	0	0	0	0	0	0	0
NaF	0	0	0	0	0	0	0	0	0	0	6.7	3.1	0	0
Na_2O	4	1.6	5	2.3	5	2.2	4	1.7	5	2.4	0	0	4.4	1.6
B_2O_3	8	3.1	8	3.8	8	3.6	8	3.4	11	5.2	10.8	5.1	7.7	2.9

Component (wt.%)	F5-49***		F5-50***		F5-51***		F5-52***	
	dry*	wet+	dry	wet	dry	wet	dry	wet
Pit 5	60.8	86.3	62	87.2	68.1	90.1	68.1	88.1
Soil Wash Fractions	24.5	9.1	18	6.6	19.8	6.4	19.8	8.4
SiO_2	2	0.6	9	2.8	0	0	0	0
NaF	5.9	1.8	0	0	0	0	0	0
Na_2O	0	0	4	1.2	4.4	1.3	4.4	1.3
B_2O_3	6.9	2.2	7	2.2	7.7	2.2	7.7	2.2

* Pit 5 sludge was dried for 4 hours at 450°C. Soil-wash fractions were dried at 1150°C for 4 hours, and mixed in a ratio of 3:1 for inorganic:organic fractions.
** Glasses F5-42 through F5-48 were made from FE1 Pit 5 sludge
*** FE15 Sludge was used to melt these glasses.
\+ Pit 5 sludge and soil-wash fractions "as-received" (i.e. without drying).
<u>Note:</u> Na_2O and B_2O_3 are actually added as sodium carbonate and boric acid, respectively.

Table 4.3 (continued)

Component (wt.%)	F5-54A		F5-55A		F5-56		F5-57A		F5-58A		F5-59	
	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet
Pit 5	62[1]	95.7	62[2]	89.1	39[2]	59.5	62'	95.5	62''	96.2	45''	89.7
Soil Wash Fractions	0	0	0	0	50[5]	36.0	0	0	0	0	33[6]	6.4
SiO_2	17	2.6	17	6.6	0	0	17	2.7	17	2.3	0	0
NaF	0	0	0	0	0	0	0	0	0	0	5	0.9
Na_2O	4	0.6	4	1.6	4	1.6	4	0.6	4	0.5	0	0
B_2O_3	7	1.1	7	2.7	7	2.9	7	1.1	7	1.0	12	2.1
CaO	0	0	0	0	0	0	0	0	0	0	0	0
MgF_2	0	0	0	0	0	0	0	0	0	0	5	0.9

Component (wt.%)	F5-60'''	F5-61	F5-62	F5-63	F5-64	F5-65	F5-66	F5-67	F5-68''''
Pit 5	0	0	0	0	0	0	0	0	0
Soil Wash Fractions	0	0	0	0	0	0	0	0	0
100U-2-56B	90	80	94	80	75	84	80	75	83
SiO_2	0	0	0	0	15	10	5	5	8
NaF	0	0	0	5	0	0	0	0	0
Na_2O	0	0	0	0	0	0	0	0	0
B_2O_3	0	0	0	0	0	0	0	0	0
CaO	0	0	6	0	0	6	10	0	4
MgF_2	10	20	0	15	10	0	0	20	5
MgO	0	0	0	0	0	0	5	0	0

* Pit 5 sludge was dried for 4 hours at 450°C. Soil-wash fractions were dried at 1150°C for 4 hours, and mixed in a ratio of 3:1 for inorganic:organic fractions.
\+ Pit 5 sludge and soil-wash fractions "as-received" (i.e. without drying).
# FE51 sludge was used to melt this glass;
FE52 sludge was used to melt this glass
*** FE15 Sludge was used to melt this glass;
[1] FE14 sludge was used to melt this glass.
[2] FE16 sludge was used to melt this glass;
[3] FE8 soil was used to melt this glass.
[4] FE11 soil was used to melt this glass;
[5] FE38+ soil was used to melt this glass.
[6] FE8 soil was used to melt this glass;
<u>Note:</u> Na_2O and B_2O_3 are actually added as sodium carbonate and boric acid, respectively.
Glass 100U-2-56B was used as the starting material for glasses F5-60 through F5-67
Glass 100U-2-56C was used as the starting material for this glass.

Table 4.4
Fluoride Analysis for Crucible Melt Glasses

Glass	Wt.% Fluoride (calc.)	Wt.% Fluoride (analy.)	% loss during vitrification
F5-44	10.7	7.8	27
F5-44B	4.1	4.48	0
F4-47	12.6	11.22	11
F5-49	8.0	7.57	5
F5-50	5.2	5.10	2
F5-51	5.8	5.81	0
F5-52	5.8	5.47	6
F5-54B	2.4	2.19	9
F5-55A	3.8	3.23, 3.13	16
F5-56	2.5	<2	--
F5-60	12.0	10.44*	13
F5-61	17.4	15.41*	11
F5-62	6.1	6.21*	0
F5-63	16.6	14.6*	12
F5-64	11.0	9.23*	16
F5-65	5.5	5.58*	0
F5-66	5.2	5.36*	0
F5-67	17.1	13.97*	18
F5-68	8.5	8.26*	3

*Average of three different analyses.

Table 4.5
Calculated and Analyzed Compositions of Crucible-Melt Glasses
(DCP-ES and Fluoride Analysis). Weight Percent.

Oxide	F5-42		F5-43			F5-44		
Wt.%	calc	anal	calc	anal	F5-43W anal*	calc	anal	F5-44W anal*
Al_2O_3	2.92	3.19	4.62	4.24	5.58	3.84	3.99	4.77
B_2O_3	9.36	9.12	8.91	8.79	6.15	9.02	8.97	6.76
BaO	1.13	1.20	0.76	0.78	0.55	0.85	1.03	0.63
CaO	24.95	22.27	21.2	18.10	14.56	21.47	17.62	15.43
Cr_2O_3	0.05	0.02	0.03	0.03	0.01	0.04	0.03	0.02
Fe_2O_3	2.62	2.85	2.91	3.34	3.18	2.68	3.34	3.08
K_2O	0.59	0.58	1.05	1.03	1.43	0.85	0.98	1.17
Li_2O	0.23	0.13	0.18	0.22	0.11	0.19	0.21	0.14
MgO	0.85	19.0	1.88	12.88	9.81	1.45	5.77	10.77
MgF_2	23.63	NA	15.6	NA	NA	17.49	12.84	NA
MnO_2	0.11	0.09	0.13	0.14	0.11	0.11	0.14	0.10
Na_2O	5.45	5.12	6.42	5.71	4.77	6.42	6.11	4.87
NiO	0.05	0.02	0.03	0.03	0.02	0.04	0.04	0.03
P_2O_5	0.20	0.25	0.21	0.32	0.21	0.20	0.34	0.30
SiO_2	27.70	26.68	35.7	33.99	44.47	35.10	34.87	42.28
SrO	0.04	0.04	0.04	0.04	0.03	0.04	0.04	0.03
TiO_2	0.11	0.20	0.25	0.33	0.42	0.19	0.30	0.35
U_3O_8	0.51	0.41	0.36	0.35	0.32	0.40	0.44	0.31
ZrO_2	0.21	0.15	0.17	0.14	0.09	0.17	0.15	0.10
Total	100.71	91.32	100.45	90.46	91.82	100.55	97.21	91.14

* The white portions of the F5-43 and F5-44 glasses contain some white undissolved material, shown here to be rich in silica.

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.
b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5. Continued

Oxide	F5-44B			F5-45		F5-46	
	calc	anal(1)	anal(2)	calc	anal	calc	anal
Al_2O_3	5.15	4.92	4.70	4.07	4.02	4.35	6.93
B_2O_3	8.72	8.95	8.98	9.13	9.24	12.2	8.45
BaO	0.87	0.82	0.78	0.95	1.02	0.76	0.81
CaO	21.91	20.99	20.16	23.55	20.56	20.8	21.37
Cr_2O_3	--	NA	NA	0.04	NA	0.03	0.03
Fe_2O_3	4.00	3.32	3.16	2.89	3.32	2.79	2.76
K_2O	0.81	0.84	0.88	0.89	0.92	0.98	0.91
Li_2O	0.17	0.11	0.13	0.12	0.13	0.12	0.14
MgO	6.19	4.05	3.86	1.51	15.98	1.74	12.80
MgF_2	6.76	7.38	7.38	19.48	NA	15.6	NA
MnO_2	0.08	0.12	0.12	0.12	0.11	0.12	0.11
Na_2O	6.27	6.71	6.44	5.42	5.12	6.39	5.17
NaF	0.0	0.0	0.0	0.0	NA	0.0	NA
NiO	0.05	NA	0.03	0.04	0.04	0.03	0.04
P_2O_5	1.8	0.52	0.52	0.21	0.36	0.20	0.31
SiO_2	35.37	35.04	34.91	31.20	29.07	33.6	32.7
SrO	0.02	0.04	0.04	0.04	0.04	0.04	0.04
TiO_2	0.28	0.23	0.31	0.20	0.28	0.23	0.30
U_3O_8	1.0	NA	NA	0.44	NA	0.36	0.46
ZrO_2	0.17	0.15	0.16	0.19	0.13	0.17	0.12
Total	100.07	93.99	92.56	100.49	90.34	100.51	93.45

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5. Continued

Oxide	F5-47				F5-48
	calc	anal(1)	anal(2)	anal(3)	calc
Al_2O_3	4.26	6.7	5.85	5.78	3.17
B_2O_3	12.00	11.8	11.95	12.00	9.09
BaO	0.75	0.8	0.86	0.82	1.20
CaO	20.34	19.4	18.14	18.42	26.51
Cr_2O_3	0.03	0.4	NA	NA	0.04
Fe_2O_3	2.73	4.3	2.96	2.95	2.80
K_2O	0.96	0.8	0.75	0.77	0.64
Li_2O	0.18	0.1	0.11	0.13	0.22
MgO	1.71	2.51	1.09	1.45	0.94
MgF_2	15.24	18.39	18.39	18.39	24.96
MnO_2	0.12	0.3	0.09	0.10	0.10
Na_2O	0.81	6.0	5.47	5.51	6.02
NaF	7.43	0.0	0.0	0.0	0.0
NiO	0.03	0.03	NA	0.03	0.04
P_2O_5	0.20	0.3	0.33	0.33	0.19
SiO_2	32.91	29.3	29.89	29.88	23.80
SrO	0.04	0.04	0.05	0.04	0.05
TiO_2	0.23	0.3	0.26	0.36	0.13
U_3O_8	0.35	0.3	NA	NA	0.50
ZrO_2	0.16	0.1	0.10	0.11	0.20
Total	100.48	101.87	96.29	97.07	100.6

-- Could not be calculated due to lack of starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-49				F5-50	
	calc	anal(1)	anal(2)	anal(3)	calc	anal
Al_2O_3	5.06	4.84	4.81	4.71	4.54	4.23
B_2O_3	7.65	7.99	7.87	8.01	7.79	7.95
BaO	1.07	0.98	0.94	0.96	1.09	0.95
CaO	24.78	23.94	23.89	24.13	24.21	23.77
Cr_2O_3	--	NA	NA	0.18	--	NA
Fe_2O_3	4.37	4.32	4.30	4.38	4.19	3.98
K_2O	0.68	0.79	0.79	0.91	0.54	0.61
Li_2O	0.17	0.19	0.19	0.27	0.17	0.15
MgO	7.02	2.3	2.2	2.41	6.87	4.7
MgF_2	8.36	12.5	12.5	12.46	8.56	8.4
MnO_2	0.10	0.15	0.15	0.16	0.07	0.08
Na_2O	0.86	5.95	5.91	6.11	5.24	5.85
NaF	6.53	0.0	0.0	NA	0.0	0.0
NiO	0.5	NA	NA	0.12	0.5	NA
P_2O_5	1.8	0.55	0.55	0.54	1.8	0.56
SiO_2	28.9	30.45	30.87	30.96	32.24	34.05
SrO	0.04	0.05	0.05	0.05	0.04	0.04
TiO_2	0.25	0.22	0.21	0.30	0.22	0.22
U_3O_8	1.2	NA	NA	0.69	1.2	NA
ZrO_2	--	0.18	0.18	0.18	--	0.16
Total	99.34	95.40	95.41	97.53	99.27	95.7

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-51		F5-52	
	calc	anal	calc	anal
Al_2O_3	4.79	5.55	5.67	5.36
B_2O_3	8.66	9.38	8.67	9.24
BaO	1.21	1.08	1.22	1.07
CaO	24.27	26.14	26.35	27.70
Cr_2O_3	--	NA	-	NA
Fe_2O_3	4.33	4.65	5.31	5.00
K_2O	0.58	0.75	0.67	0.73
Li_2O	0.2	0.14	0.2	0.14
MgO	7.04	5.02	7.55	5.79
MgF_2	9.50	9.50	9.50	9.02
MnO_2	0.10	0.10	0.10	0.12
Na_2O	5.83	7.07	5.79	6.82
NaF	0.0	0.0	0.0	0.0
NiO	0.5	NA	0.5	NA
P_2O_5	1.8	0.64	1.8	0.59
SiO_2	28.61	26.17	23.64	23.05
SrO	0.04	0.05	0.04	0.05
TiO_2	0.25	0.28	0.26	0.24
U_3O_8	0.8	NA	1.0	NA
ZrO_2	--	0.19	--	0.18
Total	98.51	96.7	98.27	95.11

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.
b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-54A-Bl**				F5-54A-Gr**	
	calc	anal(1)	anal(2)	anal(3)	anal(1)	anal(2)
Al_2O_3	2.27	2.07	2.04	2.04	0.10	0.09
B_2O_3	10.75	10.32	10.26	10.26	0.70	0.71
BaO	1.21	NA	NA	NA	NA	NA
CaO	28.50	27.91	27.91	28.05	8.27	8.16
Cr_2O_3	--	NA	NA	NA	NA	NA
Fe_2O_3	3.24	3.26	3.21	3.18	0.00	0.01
K_2O	0.65	0.12	0.13	0.12	1.68	1.60
Li_2O	0.11	0.21	0.20	0.21	0.06	0.06
MgO	6.48	12.38	12.36	12.03	0.32	0.36
MgF_2	3.89	NA	NA	NA	NA	NA
MnO_2	0.07	0.12	0.12	0.12	0.00	0.00
Na_2O	5.68	5.78	5.60	5.63	27.81	26.82
NaF	0.0	NA	NA	NA	NA	NA
NiO	0.6	NA	NA	NA	NA	NA
P_2O_5	0.42	0.57	0.58	0.55	0.13	0.16
SiO_2	30.46	28.05	28.53	28.34	0.44	0.67
SrO	0.03	NA	NA	NA	NA	NA
TiO_2	0.19	0.10	0.10	0.10	0.00	0.00
U_3O_8	0.3	NA	NA	NA	NA	NA
ZrO_2	--	NA	NA	NA	NA	NA
Total	94.74	90.87	91.04	90.62	39.5	38.6

**F5-54A, F5-57A, and F5-58A all had a green top layer and a glassy black bottom layer; hence the suffix Bl for black and Gr for green. The two layers were analyzed separately.

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-54B				F5-55A				F5-55B			
	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)
Al_2O_3	1.33	1.79	1.74	1.82	2.60	2.59	2.48	2.59	2.49	3.85	3.61	3.96
B_2O_3	16.66	12.77	12.70	12.94	9.89	9.84	9.37	9.84	10.46	8.49	8.27	8.50
BaO	0.71	NA	NA	NA	0.60	NA	NA	NA	0.58	NA	NA	NA
CaO	16.73	18.59	17.98	18.29	32.46	32.44	31.85	32.44	31.10	31.02	30.59	30.55
Cr_2O_3	--	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA
Fe_2O_3	1.90	0.53	0.61	0.64	2.42	2.43	2.21	2.43	2.32	2.17	2.06	2.21
K_2O	0.38	0.34	0.34	0.33	0.15	0.15	0.15	0.15	0.14	0.19	0.19	0.19
Li_2O	0.08	NA	NA	NA	0.14	NA	NA	NA	0.14	NA	NA	NA
MgO	3.80	4.13	4.13	4.17	3.26	3.80	3.40	3.80	3.13	6.76	6.63	6.82
MgF_2	2.28	3.61	3.61	3.61	6.16	5.30	5.30	5.30	5.91	NA	NA	NA
MnO_2	0.05	0.08	0.08	NA	0.06	NA	NA	NA	0.06	NA	0.08	0.08
Na_2O	9.22	7.80	7.71	7.81	6.50	6.48	6.23	6.48	6.50	5.10	5.03	5.13
NaF	0.0	0.0	0.0	0.0	0.0	NA	0.0	0.0	0.0	NA	NA	NA
NiO	0.02	0.02	0.02	NA	0.0	NA	NA	NA	0.0	NA	0.03	0.04
P_2O_5	0.30	0.35	0.35	0.33	0.30	0.44	0.41	0.44	0.30	0.43	0.40	0.40
SiO_2	42.94	42.45	41.42	41.61	31.94	31.98	30.92	31.98	33.17	36.02	34.66	36.48
SrO	0.02	0.03	0.03	NA	0.02	NA	NA	NA	0.02	NA	0.05	0.05
TiO_2	0.11	0.12	0.12	0.12	0.12	0.13	0.13	0.13	0.12	0.20	0.21	0.20
U_3O_8	0.2	0.24	0.24	NA	0.8	NA	NA	NA	0.8	NA	0.67	0.66
ZrO_2	--	0.08	0.09	NA	--	NA	NA	NA	--	NA	0.21	0.21
Total	96.73	92.92	92.15	91.69	97.42	95.57	92.47	95.57	97.24	94.22	92.69	95.49

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-56	F5-57A-Bl**				F5-57A-Gr**	
	calc	calc	anal(1)	anal(2)	anal(3)	anal(1)	anal(2)
Al_2O_3	5.58	2.45	2.44	2.52	2.52	0.25	0.25
B_2O_3	10.53	9.14	8.60	8.79	8.81	1.23	1.22
BaO	0.40	0.0	NA	NA	NA	NA	NA
CaO	27.93	29.66	25.10	25.23	24.93	10.91	11.00
Cr_2O_3	–	–	NA	NA	NA	NA	NA
Fe_2O_3	3.31	4.58	3.81	3.89	3.90	0.25	0.26
K_2O	1.10	0.16	0.46	0.45	0.46	1.38	1.39
Li_2O	0.13	–	0.25	0.25	0.26	0.13	0.13
MgO	4.29	10.77	9.85	9.87	9.65	1.05	1.04
MgF_2	4.12	0.0	0.0	0.0	0.0	NA	NA
MnO_2	0.06	–	NA	NA	NA	NA	NA
Na_2O	7.07	5.98	7.08	7.21	7.24	25.43	25.98
NaF	0.0	0.0	0.0	0.0	0.0	NA	NA
NiO	0.0	–	NA	NA	NA	NA	NA
P_2O_5	0.3	–	0.59	0.59	0.59	0.18	0.21
SiO_2	32.41	27.50	26.16	26.15	25.87	2.19	2.23
SrO	0.04	–	NA	NA	NA	NA	NA
TiO_2	0.28	0.13	0.18	0.18	0.18	0.02	0.02
U_3O_8	0.7	0.3	0.33	0.34	0.33	0.07	0.08
ZrO_2	–	–	NA	NA	NA	NA	NA
Total	98.25	100	84.85	85.46	84.74	43.09	43.80

**F5-54A, F5-57A, and F5-58A all had a green top layer and a glassy black bottom layer; hence the suffix Bl for black and Gr for green. The two layers were analyzed separately.

– Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-58A-Bl**				F5-58A-Gr**		
	calc	anal(1)	anal(2)	anal(3)	anal(1)	anal(2)	anal(3)
Al_2O_3	1.85	2.03	2.02	2.06	NA	NA	NA
B_2O_3	9.28	9.26	9.28	9.24	0.58	0.58	0.56
BaO	0.0	NA	NA	NA	NA	NA	NA
CaO	30.17	26.01	26.13	26.28	10.10	10.23	9.84
Cr_2O_3	--	NA	NA	NA	NA	NA	NA
Fe_2O_3	3.0	2.85	2.85	2.84	NA	NA	NA
K_2O	0.19	0.31	0.31	0.30	2.26	2.16	2.09
Li_2O	--	0.21	0.21	0.21	0.10	0.09	0.09
MgO	11.25	10.85	10.91	10.84	0.56	0.55	0.54
MgF_2	0.0	0.0	0.0	0.0	NA	NA	NA
MnO_2	--	NA	NA	NA	NA	NA	NA
Na_2O	6.11	7.59	7.65	7.69	23.56	23.30	23.73
NaF	0.0	0.0	0.0	0.0	NA	NA	NA
NiO	--	NA	NA	NA	NA	NA	NA
P_2O_5	--	0.50	0.51	0.51	0.23	0.21	0.19
SiO_2	28.30	28.29	28.47	28.51	0.60	0.59	0.55
SrO	--	NA	NA	NA	NA	NA	NA
TiO_2	0.16	0.11	0.11	0.11	0.01	0.01	0.01
U_3O_8	0.24	0.21	0.21	0.21	0.07	0.05	0.05
ZrO_2	--	NA	NA	NA	NA	NA	NA
Total	90.55	88.23	88.66	88.80	38.06	37.76	37.65

**F5-54A, F5-57A, and F5-58A all had a green top layer and a glassy black bottom layer; hence the suffix Bl for black and Gr for green. The two layers were analyzed separately.

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-59		F5-60				F5-61			
	calc	anal	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)
Al_2O_3	3.72	4.73	5.13	5.35	5.11	5.37	4.56	4.82	4.88	4.94
B_2O_3	13.36	14.27	9.45	9.56	9.12	9.49	8.40	7.85	7.98	8.10
BaO	0.02	1.27	1.0	0.93	0.92	0.92	1.0	0.83	0.83	0.82
CaO	19.72	20.05	20.79	21.47	20.85	20.97	18.48	18.74	19.19	19.91
Cr_2O_3	--	NA	--	NA	NA	NA	--	NA	NA	NA
Fe_2O_3	2.63	3.24	2.61	2.89	2.74	2.81	2.32	2.36	2.40	2.45
K_2O	0.83	0.91	0.81	0.80	0.79	0.79	0.72	0.71	0.73	0.72
Li_2O	--	NA	0.16	NA	NA	NA	0.14	NA	NA	NA
MgO	7.45	12.13	3.51	5.59	5.17	5.40	3.12	4.12	4.36	4.02
MgF_2	5.49	NA	19.63	17.12	17.12	17.12	28.56	25.26	25.26	25.26
MnO_2	--	NA	0.06	NA	NA	NA	0.05	NA	NA	NA
Na_2O	1.00	5.24	5.94	5.97	5.68	5.93	5.28	5.24	5.32	5.34
NaF	5.49	NA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NiO	--	NA	0.0	NA	NA	NA	0.0	NA	NA	NA
P_2O_5	--	NA	0.42	NA	NA	NA	0.38	NA	NA	NA
SiO_2	33.88	29.87	25.74	27.84	27.35	27.70	22.88	24.47	24.60	25.93
SrO	--	NA	--	NA	NA	NA	--	NA	NA	NA
TiO_2	0.31	NA	0.27	NA	NA	NA	0.24	NA	NA	NA
U_3O_8	0.16	0.25	0.31	0.30	0.29	0.31	0.27	0.32	0.30	0.31
ZrO_2	--	NA	--	NA	NA	NA	--	NA	NA	NA
Total	94.06	91.96	95.83	97.82	95.15	96.82	96.40	94.73	95.84	97.81

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-62				F5-63				F5-64			
	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)
Al_2O_3	5.36	4.98	5.01	4.91	4.56	4.92	4.99	4.99	4.28	4.18	4.25	4.18
B_2O_3	9.87	9.84	9.73	9.47	8.40	8.56	8.55	8.50	7.88	8.17	8.31	8.35
BaO	1.0	0.96	0.96	0.96	1.0	0.81	0.80	0.77	1.0	0.70	0.67	0.67
CaO	27.71	28.29	28.53	27.91	18.48	17.54	17.54	17.38	17.33	16.82	16.37	16.56
Cr_2O_3	--	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA
Fe_2O_3	2.73	2.88	2.79	2.68	2.32	2.60	2.62	2.59	2.18	2.43	2.48	2.43
K_2O	0.85	0.80	0.80	0.79	0.72	0.71	0.70	0.68	0.68	0.62	0.61	0.61
Li_2O	0.16	NA	NA	NA	0.14	NA	NA	NA	0.14	NA	NA	NA
MgO	3.67	5.67	5.20	5.55	3.12	1.95	1.80	1.70	2.93	5.38	4.99	5.24
MgF_2	10.06	10.18	10.18	10.18	23.56	23.94	23.94	23.94	18.03	15.13	15.13	15.13
MnO_2	0.06	NA	NA	NA	0.05	NA	NA	NA	0.05	NA	NA	NA
Na_2O	6.20	6.21	6.12	6.01	5.28	8.22	8.21	8.21	4.95	4.95	5.08	4.96
NaF	0.0	0.0	0.0	0.0	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NiO	0.0	NA	NA	NA	0.0	NA	NA	NA	0.0	NA	NA	NA
P_2O_5	0.42	NA	NA	NA	0.38	NA	NA	NA	0.35	NA	NA	NA
SiO_2	26.88	29.07	28.14	29.12	22.88	24.55	24.52	23.56	36.45	37.95	37.24	38.02
SrO	--	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA
TiO_2	0.28	NA	NA	NA	0.24	NA	NA	NA	0.23	NA	NA	NA
U_3O_8	0.32	0.35	0.36	0.34	0.27	0.31	0.31	0.31	0.26	0.28	0.28	0.28
ZrO_2	--	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA
Total	95.57	99.23	97.91	97.90	96.40	94.12	93.98	92.63	96.74	96.61	95.42	96.44

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.
b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-65				F5-66	F5-67
	calc	anal(1)	anal(2)	anal(3)	calc	calc
Al_2O_3	4.79	4.62	4.70	4.77	4.56	4.28
B_2O_3	8.82	9.61	9.62	9.69	8.40	7.88
BaO	1.0	0.83	0.85	0.86	1.0	1.0
CaO	25.40	23.36	22.82	24.70	28.48	17.33
Cr_2O_3	–	–	–	–	-	
Fe_2O_3	2.44	3.28	3.31	3.30	2.32	2.18
K_2O	0.76	0.81	0.82	0.83	0.72	0.68
Li_2O	0.14	NA	NA	NA	0.14	0.14
MgO	3.28	4.29	4.21	4.75	8.12	2.93
MgF_2	8.99	9.15	9.15	9.15	8.56	28.03
MnO_2	0.05	NA	NA	NA	0.05	.05
Na_2O	5.54	5.61	5.75	5.82	5.28	4.95
NaF	0.0	0.0	0.0	0.0	0.0	0.0
NiO	0.0	NA	NA	NA	0.0	0.0
P_2O_5	0.38	NA	NA	NA	0.38	0.35
SiO_2	34.02	33.26	32.44	33.15	27.88	26.45
SrO	–	NA	NA	NA	NA	–
TiO_2	0.25	NA	NA	NA	0.24	0.23
U_3O_8	0.27	0.34	0.33	0.35	0.27	0.26
ZrO_2	–	NA	NA	NA	–	–
Total	96.13	95.16	94.00	97.36	96.40	96.74

– Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.5: Continued

Oxide	F5-68			
	calc	anal(1)	anal(2)	anal(3)
Al_2O_3	4.73	4.48	4.53	4.45
B_2O_3	8.72	9.08	9.06	9.08
BaO	1.0	0.80	0.81	0.80
CaO	23.17	21.99	22.82	23.0
Cr_2O_3	--	NA	NA	NS
Fe_2O_3	2.41	3.51	3.51	3.52
K_2O	0.75	0.76	0.76	0.77
Li_2O	0.14	0.17	0.17	0.17
MgO	3.24	3.80	3.31	3.62
MgF_2	13.88	13.54	13.54	13.54
MnO_2	0.05	NA	NA	NA
Na_2O	5.48	5.90	5.93	5.88
NaF	0.0	0.0	0.0	0.0
NiO	0.0	NA	NA	NA
P_2O_5	0.38	NA	NA	NA
SiO_2	31.74	31.62	32.70	32.93
SrO	--	NA	NA	NA
TiO_2	0.25	NA	NA	NA
U_3O_8	0.4	0.41	0.39	0.38
ZrO_2	--	NA	NA	NA
Total	96.21	96.06	97.53	98.14

-- Could not be calculated due to lack of information on starting material for those elements.

Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.

b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.6
Compositional Results of Using Wet Sludge for Vitrification

Oxide	F5-54B				F5-55B			
	calc	anal(1)	anal(2)	anal(3)	calc	anal(1)	anal(2)	anal(3)
Al_2O_3	1.33	1.79	1.74	1.82	2.49	3.85	3.61	3.96
B_2O_3	16.66	12.77	12.70	12.94	10.46	8.49	8.27	8.50
BaO	0.71	NA	NA	NA	0.58	NA	NA	NA
CaO	16.73	18.59	17.98	18.29	31.10	31.02	30.59	30.55
Cr_2O_3	–	NA	NA	NA	–	NA	NA	NA
Fe_2O_3	1.90	0.53	0.61	0.64	2.32	2.17	2.06	2.21
K_2O	0.38	0.34	0.34	0.33	0.14	0.19	0.19	0.19
Li_2O	0.08	NA	NA	NA	0.14	NA	NA	NA
MgO	3.80	4.13	4.13	4.17	3.13	6.76	6.63	6.82
MgF_2	2.28	3.61	3.61	3.61	5.91	NA	NA	NA
MnO_2	0.05	0.08	0.08	NA	0.06	NA	0.08	0.08
Na_2O	9.22	7.80	7.71	7.81	6.50	5.10	5.03	5.13
NaF	0.0	0.0	0.0	0.0	0.0	NA	NA	NA
NiO	0.02	0.02	0.02	NA	0.0	NA	0.03	0.04
P_2O_5	0.30	0.35	0.35	0.33	0.30	0.43	0.40	0.40
SiO_2	42.94	42.45	41.42	41.61	33.17	36.02	34.66	36.48
SrO	0.02	0.03	0.03	NA	0.02	NA	0.05	0.05
TiO_2	0.11	0.12	0.12	0.12	0.12	0.20	0.21	0.20
U_3O_8	0.2	0.24	0.24	NA	0.8	NA	0.67	0.66
ZrO_2	–	0.08	0.09	NA	–	NA	0.21	0.21
Total	96.73	92.92	92.15	91.69	97.24	94.22	92.69	95.49

– Could not be calculated due to lack of information on starting material for those elements.

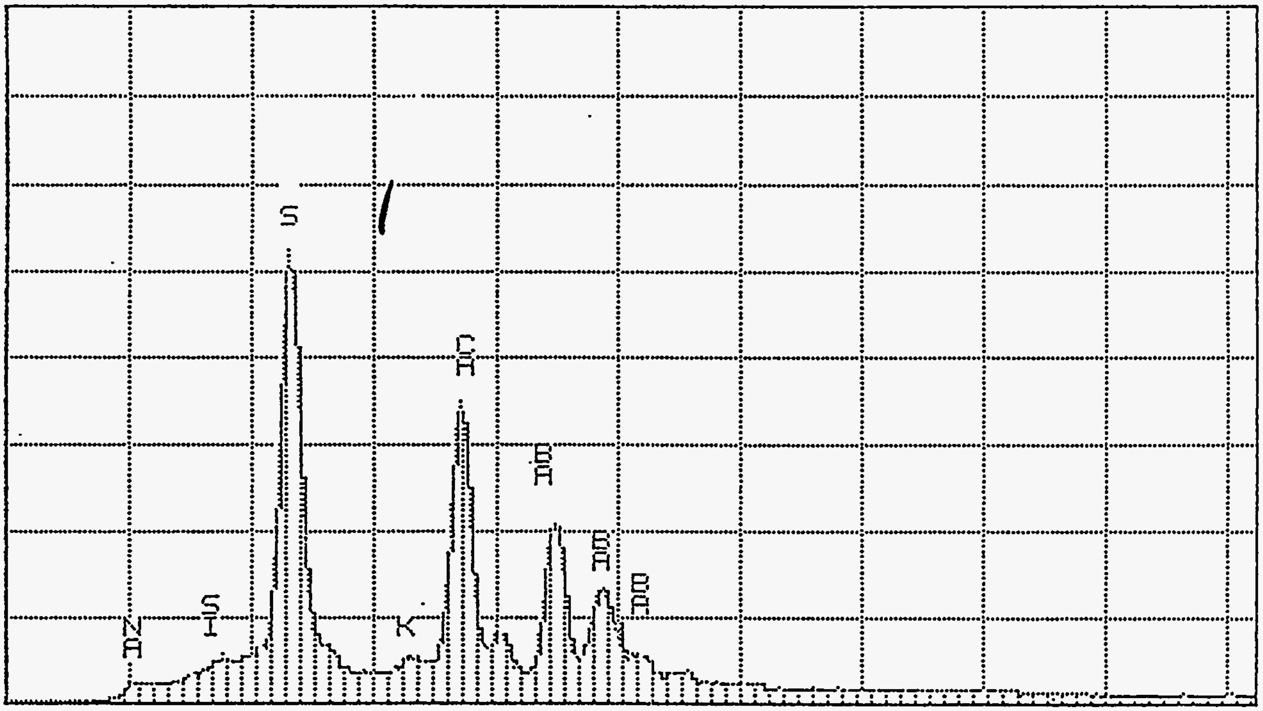
Note: a) Some of the glasses were not analyzed for fluoride - hence "NA" in MgF_2 row.
b) The average fluoride analysis was used to calculate the amount of MgF_2 and the remaining Mg detected by DCP-ES analysis was converted to MgO.

Table 4.7
Processable Composition for Vitrification of Pit 5
Waste Stream with Soil Fines

Al_2O_3	3.2-6.7
B_2O_3	8.0-12.0
BaO	0.8-1.2
CaO	18.1-27.7
Fe_2O_3	2.7-5.0
K_2O	0.6-0.9
MgO	1.1-8.6
MgF_2	7.4-18.4
Na_2O	5.1-6.8
P_2O_5	0.3-0.6
SiO_2	23.1-35.0

Note: All combinations are possible with the following guidelines. 1) High MgF_2 must be combined with low MgO content. 2) SiO_2 content should not exceed 30 wt.% unless MgF_2 content is below 15 wt.%, and 3) high CaO content should be accompanied by low SiO_2 and low MgF_2 contents.

Figure 4.1
EDS spectrum of the top layer (F5-57A-GR) of F5-57A glass melt.
The top layer is Ba-Ca-S rich due to the high sulfur content (11 wt.%) of the starting material (FE51 contained 11 wt.% SO_3).



Section 5.0
Viscosity and Conductivity

5.1 Introduction

Both viscosity and electrical conductivity data as functions of temperature are needed in order to assess the processability of prospective glass formulations. The melt viscosity has a major effect on processing rates and the melt electrical conductivity determines power dissipation in joule-heated melting systems.

Conductivity measurements were made following the method of Tickle (J.Phys. Chem. Glass 8-3 (1967) 101-112). In this method the complex impedance of the molten glass is measured as a function of frequency and temperature using a simple conductivity cell. The resistance is taken as the value obtained extrapolated to infinite frequency (to eliminate electrode polarization effects). The cell constant is calibrated using salt solutions of known conductivity. To confirm the method, the conductivity of NIST standard glass SRM711 is measured and compared to published values. Agreement is within 5% at all temperatures measured. The measurements are performed with a Hewlett Packard automatic impedance analyzer. This instrument uses internal routines to provide zeroing of the cell and compensation for lead impedance. By employing a dummy short of approximately equal length and wire size to that of the probe which is run parallel to the probe leads into the furnace, compensation accounts for the temperature dependence of the lead resistance. Alternately, temperature dependence of lead resistance is removed by measuring the sample impedance as a function of probe depth in the sample and determining the resistance from the difference of two measurements thus subtracting out the effects of the lead resistance.

Viscosity is measured using a rotating platinum/rhodium spindle and a Brookfield viscometer. The instrument is calibrated using NIST traceable viscosity fluid standards.

In this study, conductivity and viscosity were measured at typically four temperatures to span the range of likely processing parameters. While we were prepared to collect viscosity and conductivity data up to 1500°C, this did not prove necessary since the viscosities were already below 10 poise at 1150°C for all glasses except F5-56, and rapid fluoride loss occurs above 1150°C; thus higher processing temperatures would be impractical. The electrical conductivity data and the viscosity data were fitted to Vogel-Fulcher equations (Arrhenius equation with allowance for the rapid rise in viscosity on approach to the glass transition temperature)

$$\sigma = \exp\ (A_\sigma/T-T_o) + C_\sigma)$$

and

$$\eta = \exp(A_\eta/(T-T_o) + C_\eta).$$

The coefficients A_σ, C_σ, A_η, C_η, and T_o, were determined by least-squares regression of the data for each glass. For convenience, these equations were used to interpolate the viscosity and conductivity data to standard temperatures, which facilitates comparisons between glasses.

5.2 Results of Viscosity and Conductivity Measurements of Crucible Melts

Table 5.1 and 5.2 show the viscosity and conductivity measurements of 23 crucible-melt glasses interpolated to standard temperatures. Certain glasses began to crystallize during the viscosity and conductivity measurements. For conductivity measurements, the readings for such melts were usually stable enough to obtain a reading within the usual ±5% reproducibility. However, for viscosity measurements, the readings were out of the ±10% range that is typically possible for viscosity measurements. The entries marked "unstable" indicate readings that were unstable due to crystallization for those glass melts. The glasses which produced unstable viscosity readings at 1050°C had been found by heat treatments to have liquidus temperatures above 1050°C (see Section 6.2). Note that not all glasses which have liquidus temperatures above 1050°C produce unstable viscosity readings at 1050°C. This is because the rate of crystallization also plays a role; some glasses may have crystallization rates large enough to produce significant amounts of crystals which renders the viscosity measurement unstable at that temperature, while other glasses may have crystallization rates too small to produce significant amounts of crystals in the 30 minutes needed to measure viscosity at one temperature.

Viscosity and conductivity measurements were made in the processing temperature range of 1100-1050°C and idling temperature range of 950-1050°C. All of the glasses have viscosities in the range of 0.8 to 7.3 Poise at a temperature of 1150°C, with the exception of F5-56 (a glass that has ~2.5 wt.% fluoride, and is not processable due to a >1050°C liquidus temperature). In addition, all of the glasses have conductivities in the range of 0.10 to 0.67 S/cm at a temperature of 1150°C. Conventional high-level waste vitrification systems require a processing viscosity in the range of 20-80 poise and a processing conductivity in the range of 0.15 to 0.55 S/cm. The use of the Duramelter system, however, extends the processing viscosity and conductivity to about 2 Poise and 0.05 S/cm, respectively. This enables us to process these low-viscosity, high-waste loadings feeds, as shown in Figure 5.1.

In Section 4.0, certain compositional ranges for MAWS glasses were eliminated based on the appearance of the glass upon cooling. The crucible melts which produce homogeneous glasses are: F5-42, F5-44B, F5-47, F5-48, F5-49, F5-51, F5-52, F5-54B, F5-55A, F5-55B, F5-56, F5-60, F5-66, and F5-68 (F5-51B and F5-52B are not included since they are duplicate melts of F5-51 and F5-52, respectively). The other glass melts produced solubility problems typically in the form of undissolved SiO_2-rich portions, macroscopic phase separation, and crystallization. It is possible that these problems could also be due to insufficient stirring and slow cooling. However, we provided 0.5 hours of mechanical stirring and quite rapid cooling since the melt was either quenched in water or poured into graphite molds at room temperature. The effects of the cooling rate on microscopic phase separation, macroscopic phase separation, and crystallization will be discussed in Section 6.0. In this section, we see that of all the viable glasses seen in Section 4.0, the ones which can be eliminated due to viscosities outside our preferred processing range are F5-42 and F5-48. Note, however, that F5-42 and F5-48 have viscosities very close to 2 Poise at 1150°C.

Viscosity and conductivity measurements were made on glasses which produced heterogeneous melts as well as homogeneous melts. The reason for this was to obtain additional data to model the effect of the various components in the glass matrix on the viscosity and conductivity. As mentioned in Section 4.0, when using heterogeneous glass melts for measurements such as viscosity and conductivity, only the glassy component of the melt (and its analyzed composition) is used. This type of modelling allows us to predict many of the intermediate compositions obtained during turnover from one composition to the next in the melter runs.

5.3 Predicting Viscosity and Conductivity of Melter Glasses

In the previous subsection, we saw viscosity and conductivity measurements over a wide range of glass compositions. The results suggest that the compositional change during turnover from one target glass composition to the next will still produce a processable glass. In addition, the fluoride content in the glasses was varied sufficiently in order to account for possible effects of large fluoride loss during melter operations.

Many of the glasses that were drained from the melters had intermediate compositions between several crucible melts, but all melter glasses had viscosities and conductivities in the range of 3-7 Poise and 0.1-0.4 S/cm at 1100°C as had been predicted by the crucible melt studies. Tables 5.3 and 5.4 compare crucible melt compositions, viscosities, and conductivities to glasses from melter runs. From Table 5.3, we see that the main difference between the F5-60 crucible melt and the MIC3-62A (glass from 10 kg/day melter runs) is the lower fluoride content of MIC3-62A glass as shown by the MgO and MgF_2 contents of the glasses. The lower fluoride content of MIC3-62A glass produces a higher viscosity glass with lower conductivity, as shown in Tables 5.3(b) and 5.3(c).

A pair of glasses which have closer compositions is F5-68 and 100U-2-48A (a glass from the 100 kg/day melter). Here, the fluoride contents of the crucible melt and the melter glass are considerably closer, and the viscosity and conductivity measurements of 100U-2-48A are within 20 relative % of those of F5-68.

The majority of the crucible melts have viscosity and conductivities within the processable range of the Duramelter. For these high-waste loading formulations and the extended processing range of the Duramelter systems, the limiting parameters are not viscosity and conductivity, but rather liquidus temperature, as we shall see in the next section.

Finally, the coefficients for Vogel-Fulcher fits to the viscosity and conductivity data for each glass are summarized in Table 5.5. Note that since the measurement range is far above the glass transition temperature, the values of T_0 have little physical significance beyond providing a slight improvement in fit.

5.4 Summary and Discussion

We have seen in this section that of the 14 crucible melt glasses shown to be homogeneous melts in Section 4.0, only two have viscosities and conductivities that fall outside our preferred processing range. We will see in the next section that a number of the 12 remaining melts will be eliminated based on their liquidus temperatures.

All of the glasses made from Pit 5 sludge have low viscosity due to the high flux content of the Pit 5 sludges. It is likely that lower viscosity melts produce a more corrosive environment within the melter, but these lower viscosities are a natural consequence of the high fluoride content. The corrosiveness associated with both fluoride and low viscosity melts can only be judged with time. Materials screening and selection studies performed for the design of the Duramelters for Fernald operations showed very encouraging results with the materials selected. Furthermore, at the time of writing, several melters have been exposed to these melts for over a year with no adverse effects. The extent to which low viscosity fluoride melts cause increased corrosion of the melter will be pursued further in MAWS Phase II, however.

The viscosity and conductivity measurements of crucible melts were used to predict the conductivity and viscosity of melter glasses. We compared the viscosity and conductivity of two crucible melts to two melter glasses and found that if the compositions are within about 20 relative % of each other, so too will be their viscosities and conductivities.

Table 5.1
Viscosity of Crucible Melt Glasses (Poise) Interpolated to Standard Temperatures

Temp (°C)	F5-42	F5-43	F5-44	F5-45	F5-46	F5-47	F5-48
950	NA	NA	NA	NA	NA	NA	NA
1000	3.53	15.41	9.91	7.07	13.61	10.41	4.21
1050	2.07	8.34	6.10	3.79	8.38	6.20	1.22
1100	1.27	5.21	3.90	2.40	6.10	4.22	1.02
1150	0.82	3.60	2.59	1.70	4.87	3.13	0.95
1200	NA	NA	NA	NA	NA	NA	NA

Temp(°C)	F5-49	F5-51B	F5-52B	F5-54A	F5-55A	F5-56	F5-57A
950	24.3	NA	NA	NA	196.7	NA	NA
1000	12.1	15.0	15.1	Unstable	53.2	NA	Unstable
1050	6.9	8.5	7.3	Unstable	22.1	119.4	Unstable
1100	4.4	5.4	4.1	Unstable	11.7	35.8	Unstable
1150	3.0	3.7	2.6	6.3	7.3	19.6	6.5
1200	NA	2.7	1.8	3.7	5.0	13.7	4.6

Temp (°C)	F5-59	F5-60	F5-61	F5-62	F5-63	F5-64A	F5-65	F5-66	F5-68
950	43.6	14.6	NA	24.1	NA	NA	NA	43.8	48.0
1000	19.5	7.7	Unstable	13.1	Unstable	36.0	62.6	19.0	19.9
1050	10.7	4.3	Unstable	7.4	2.4	18.5	20.0	9.9	10.3
1100	6.8	2.5	1.9	4.4	1.7	10.8	10.2	5.8	6.1
1150	4.7	1.5	1.2	2.7	1.2	7.0	6.5	3.8	4.0
1200	3.5	0.9	0.9	1.7	1.0	4.8	4.8	2.6	2.8

NA = Not Analyzed

Table 5.2
Conductivity of Crucible Melt Glasses (S/cm) Interpolated to Standard Temperatures

Temp (°C)	F5-42	F5-43	F5-44	F5-45	F5-46	F5-47	F5-48
950	NA	NA	NA	NA	NA	NA	NA
1000	0.21	0.08	0.10	0.11	0.03	0.10	0.26
1050	0.30	0.13	0.16	0.15	0.06	0.14	0.35
1100	0.40	0.17	0.23	0.22	0.09	0.18	0.46
1150	0.52	0.20	0.29	0.31	0.10	0.21	0.60

Temp (°C)	F5-49	F5-51B	F5-52B	F5-54A	F5-55A	F5-56	F5-57
950	0.04	NA	NA	NA	NA	NA	NA
1000	0.08	0.12	0.05	NA	0.05	0.01	0.01
1050	0.12	0.17	0.10	0.05	0.09	0.02	0.05
1100	0.18	0.22	0.16	0.12	0.14	0.03	0.09
1150	0.24	0.28	0.22	0.19	0.20	0.05	0.13
1200	NA	0.34	0.28	0.24	0.28	0.08	0.16

Temp(°C)	F5-59	F5-60	F5-61	F5-62	F5-63	F5-64A	F5-65	F5-66	F5-68
950	NA	NA	NA	NA	NA	NA	NA	NA	NA
1000	0.06	0.19	0.32	0.08	0.30	0.08	0.05	0.06	0.07
1050	0.09	0.27	0.39	0.13	0.42	0.12	0.07	0.11	0.11
1100	0.13	0.37	0.47	0.19	0.54	0.16	0.11	0.16	0.16
1150	0.18	0.50	0.57	0.27	0.67	0.19	0.16	0.23	0.24
1200	0.24	0.66	0.67	0.38	0.79	0.22	0.23	0.31	0.33

NA = Not Analyzed

Table 5.3
Comparison of Viscosity and Conductivity of Melter Glasses and Crucible Melts: F5-60 and MIC3-62A

(a) Comparison of the Major Components (analyzed composition)

Components (wt.%)	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	MgO	MgF_2	Na_2O	SiO_2
F5-60	5.4	9.6	21.5	2.9	0.8	5.6	17.1	6.0	27.8
MIC3-62A	4.9	10.4	21.3	5.2	1.0	8.0	10.0	6.3	29.0

(b) Comparison of Viscosity Measurements Interpolated to Standard Temperatures

	Viscosity (Poise)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
F5-60	14.6	7.7	4.3	2.5	1.5
MIC3-62A	18.8	7.8	4.3	2.8	2.0

(c) Comparison of Conductivity Measurements Interpolated to Standard Temperature

	Conductivity (S/cm)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
F5-60	NA	0.19	0.27	0.37	0.50
MIC3-62A	0.07	0.10	0.15	0.22	0.30

The lower fluoride content of MIC3-62A produces higher viscosity and lower conductivity than F5-60 glass.
NA = Not Analyzed

Table 5.4
Comparison of Viscosity and Conductivity of Melter Glasses and Crucible Melts: F5-68 and 100U-2-48A

(a) Comparison of the Major Components (analyzed composition)

Components (wt.%)	Al_2O_3	B_2O_3	CaO	Fe_2O_3	K_2O	MgO	MgF_2	Na_2O	SiO_2
F5-68	4.5	9.1	22.0	3.5	0.8	3.8	13.5	5.9	31.6
100U-2-48A	5.3	10.8	25.7	3.5	1.0	4.8	9.7	5.6	30.5

(b) Comparison of Viscosity Measurements Interpolated to Standard Temperatures

	Viscosity (Poise)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
F5-68	48.0	19.9	10.3	6.1	4.0
100U-2-48A	51.4	21.5	11.0	6.5	4.2

(c) Comparison of Conductivity Measurements Interpolated to Standard Temperatures

	Conductivity (S/cm)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
F5-68	NA	0.07	0.11	0.16	0.23
100U-2-48A	NA	0.06	0.09	0.13	0.19

NA = Not Analyzed

Table 5.5
Fitting Coefficients for Viscosity (in Poise) and Conductivity (in S/cm) using the Vogel-Fulcher Equation
(note: T_0 is in °C and SD is the standard deviation of $\log \eta$ or $\log \sigma$).

Glass	Viscosity				Conductivity			
	A	C	T_0	SD	A	C	T_0	SD
F5-42	11212.3	-9.952	0	0.14	-6765.4	5.227	0	0.03
F5-43	1505.1	-1.882	674	0.01	-202.4	-0.829	883	0.01
F5-44	12893.9	-9.147	-127	0.01	-742.2	0.570	739	0.01
F5-45	1112.0	-2.088	725	0.06	-12826.0	7.835	-273	0.04
F5-46	442.4	0.283	810	0.02	-120.1	-1.743	930	0.07
F5-47	1009.6	-1.162	712	0.02	-700.4	-0.025	690	0.05
F5-48	28.1	-0.218	983	0.06	-9965.9	6.487	-273	0.02
F5-49	2395.1	-2.953	560	0.05	-1920.5	1.845	563	0.02
F5-51B	2270.9	-2.649	576	0.06	-1859.8	1.574	496	0.05
F5-52B	2194.1	-3.298	635	0.05	-476.8	0.056	844	0.08
F5-54A	22561.6	-14.018	-273	0.15	-236.2	-0.469	956	0.01
F5-55A	1378.2	-1.409	744	0.06	-2690.3	2.738	531	0.03
F5-56	335.8	1.189	951	0.07	-1579.8	0.923	738	0.07
F5-57	309.5	0.227	961	0.02	-270.6	-0.856	925	0.06
F5-59	1518.8	-1.591	667	0.01	-12485.7	7.031	-273	0.13
F5-60	19850.8	-13.545	-273	0.15	-11725.5	7.539	-273	0.03
F5-61	19135.5	-12.461	-273	0.05	-6353.7	5.312	-189	0.01
F5-62	1121.2	-2.764	770	0.09	-6996.7	4.347	-273	0.02
F5-63	2512.7	-3.874	506	0.02	-877.9	1.409	665	0.02
F5-64A	2462.5	-2.496	595	0.01	-391.5	-0.483	812	0.01
F5-65	637.9	-0.293	856	0.04	-15303.6	8.933	-273	0.02
F5-66	2504.7	-3.119	587	0.03	-2419.5	2.511	542	0.05
F5-68	2006.6	-2.520	636	0.03	-14139.2	8.485	-273	0.06
MIC2-138A	187.0	0.545	931	0.01	-3185.1	3.315	446	0.02
MIC2-142A	8220.0	-6.850	120	0.01	-4609.8	4.082	306	0.02
MIC3-36A	6733.7	-6.798	301	0.14	-3656.5	2.418	264	0.13
MIC3-42A	2071.9	-2.687	604	0.01	-927.1	0.875	722	0.01
MIC3-58A	921.2	-1.262	738	0.04	-6100.8	4.846	157	0.01
MIC3-62A	947.3	-1.623	742	0.06	-8142.0	5.883	0	0.05
100-2-44B	3240.0	-3.683	528	0.01	-626.8	-0.104	797	0.06
100U-2-48A	2220.2	-2.728	617	0.01	-7924.7	5.787	86	0.01
100U-2-52D	1306.4	-1.682	698	0.01	-1392.0	1.278	642	0.01
100U-2-56B	5113.9	-5.702	382	0.11	-12221.0	7.356	-273	0.07

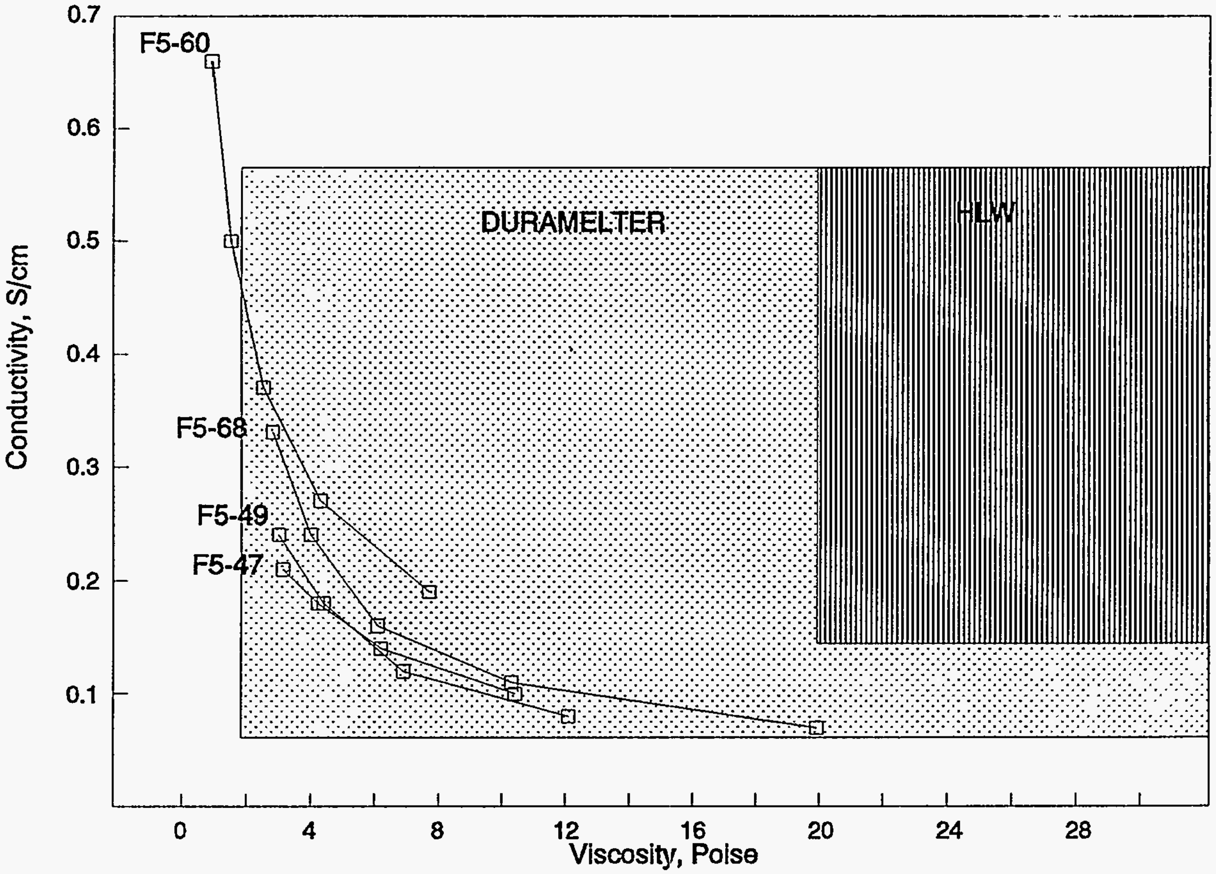


Figure 5.1
Glass Conductivity-Viscosity Behavior of Some MAWS Glasses in Relation to Melter Processing Constraints

Section 6.0
Phase Stability

6.1 Introduction

The stability of the vitreous phase with respect to crystallization impacts both the production process and leach resistance. Crystal formation during vitrification can cause melter clogging since the crystals formed may tend to sediment to the top or bottom of the melt and collect over long periods of time. Crystallinity in the final waste form (e.g. due to slow cooling from the melt temperature) may affect the leach resistance, either due to perturbation of the composition of the remaining glass phase or due to the formation of a crystalline phase that is more soluble than the glass. In Section 4.0, we discussed compositional ranges which produced macroscopic solubility problems and macroscopic phase separation. In this section, we will discuss microscopic phase separation (<1 micron) and crystallization.

6.2 Results of Heat Treatments

The MAWS glasses were first heat treated at 1050°C for two hours. The temperature was selected based on the minimum reasonable margin between the typical processing temperature for joule-heated melting (1150°C) and the glass liquidus temperature (maximum temperature at which crystals will form from the melt). The two hour time period was found experimentally for these low viscosity glasses (i.e. less than 25 poise at 1050°C) to be sufficiently long enough to achieve reasonable equilibrium of the melt with respect to crystal formation while minimizing the effects of fluoride loss. A two-hour heat treatment, therefore, should provide a meaningful estimate of the liquidus temperature.

Table 6.1 summarizes two-hour heat treatment results for 23 MAWS glasses. All of the heat treatments were accompanied by a one-hour pre-melt at 1100°C to melt any pre-existing nuclei or crystals. From the data in Table 6.1, one can determine which glasses have liquidus temperatures above 1050°C and which ones have liquidus temperatures below 1050°C. As discussed above, we imposed the selection criterion for joule-heated melter processing of a liquidus temperature of 1050°C or below. We see from Table 6.1 that 13 of the MAWS glasses tested have liquidus temperatures below 1050°C. Of these 13 glasses, only seven of them are on the list of processable glasses based on criteria from Sections 4.0 and 5.0. Based on the requirements for a homogeneous glass melt at 1150°C with viscosity in the range of 2-80 Poise and conductivity in the range of 0.1-0.6 S/cm at 1100-1150°C, the crucible melts F5-44, F5-47, F4-49, F4-52, F5-60, F5-66, and F5-68 are viable glass compositions. We will see in the next section that all of these seven glasses also meet the criteria of chemical durability as determined by the TCLP test and compare favorably to the high-level nuclear waste standard glass

(Savannah River Laboratory - Environmental Assessment (SRL-EA) glass) in the PCT test.

Even though visual observation after heat treatments provides information on whether a glass has a liquidus temperature below or above a certain temperature, it is informative to observe these glasses using SEM/EDS to obtain microscopic information about the crystals. The major crystals identified for some of the MAWS melts after heat treatment at 1050°C for two hours are listed in Table 6.2 (three of the 14 glasses were heat treated for 20 hours instead of 2 hours). The crystals identified are forsterite ($2[MgO] \cdot SiO_2$), diopsidic augite ($MgO \cdot CaO \cdot 2[SiO_2]$), and fluorophlogopite ($K_2Mg_6[Si_6Al_2O_{20}]F_4$). The SEM/EDS observations are consistent with the existence of these crystals. In addition, X-ray crystallography was used on some of the heat treated samples to confirm the existence of these major crystals. Determination of the chemical composition of the crystalline phases that form upon heat treatment is essential in order to determine how the glass formulation should be modified to prevent crystal formation (i.e. how to reduce the liquidus temperature).

Two of the glasses which had been examined by SEM/EDS after heat treatment at 1050°C for 20 hours were heat treated at 1000°C for 20 hours and then examined using SEM/EDS. The crystals identified after heat treatment at 1000°C for 20 hours are listed in Table 6.3. Two new crystals, pargasite ($[Ca, Na]_{2\text{-}3}\,[Mg, Fe^{2+}, Fe^{3+}, Al]_5\,[Al, Si]_8\,O_{22}\,[OH, F]_2$) and iron oxide ($Fe_2O_3$) were observed, and the total volume percent crystals increases for the lower temperature heat treatment, as expected.

In addition to SEM/EDS observations after heat treatments, the fluoride content in some of the glasses was measured after heat treatment to determine the approximate fluoride loss. The data, shown in Table 6.4, suggest that about 10% of the fluoride has been lost due to heat treatment at 1050°C. This is only slightly greater than the overall uncertainty in the fluoride analysis itself.

Although there are only 13 viable glasses after examination of homogeneity, viscosity, and conductivity, we examined 10 additional glasses which were not viable glass compositions for the reasons discussed in Sections 4.0 and 5.0. These measurements were made in order to accumulate a data base which will correlate composition to crystallization. For a glass such as F5-57A-B1, we examined only the glassy part of the melt and found that the glassy component produces crystallization problems as demonstrated by a liquidus temperature above 1050°C. By examining the crystalline phases which appear upon heat treatment at 1050°C (i.e. diopsidic augite), we can model which crystals are produced by certain compositions at that temperature. From these models, a composition can be tailored in order not to produce such crystals at the desired temperature. Preliminary results using a probability function to express the likelihood of certain crystal formations have shown this type of modelling to be quite successful. The formation of fluorophlogopite can now be predicted over a certain compositional range. By accumulating a larger data base, we hope to identify the major crystallization problems for a wide range of glass compositions and thereby guide subsequent glass design activities and reduce the number of experiments that are required.

6.3 Microscopic Phase Separation

A number of MAWS glasses, including F5-43, F5-44, F5-45, and F5-47, produced opaque glasses, usually green in color. Examination of these glasses under SEM/EDS shows the presence of liquid-liquid phase separation in the form of small globules, usually less than 0.2 microns in diameter. An example of liquid-liquid phase separation is found in F5-47 which is a pale green glass. Examination of this glass using SEM/EDS shows <0.2 micron globules indicative of liquid-liquid phase separation, as shown in Figure 6.1. These globules become considerably larger (i.e. 4 micron diameter) as the CaO content decreases to <5 wt.% and the MgF_2 and SiO_2 contents increase to 25 wt.% and 40 wt.%, respectively.

We have examined phase separation in a glass with 10 wt.% B_2O_3, 22 wt.% CaO, 5 wt.% Na_2O, and 2 wt.% Fe_2O_3 while varying Al_2O_3, MgF_2 and SiO_2. We chose these components because they represent >95 wt.% of the components in MAWS glasses (the elements Al, B, Ca, Na, Fe, Mg, Si, O, and F constitute 95^+ wt.% of the MAWS glasses), and the amounts of B, Ca, Na, and Fe are within the viable glass composition range for MAWS glasses. A number of surrogate crucible melts were made in which the Al_2O_3, MgF_2, and SiO_2 contents were varied and the resulting glasses were heat treated at various temperatures to determine the temperature at which liquid-liquid phase separation occurs. The surrogate glasses produced for this study are presented in Table 6.5 and the resulting pseudo-3-component phase diagram (three components are varied while four components are held constant) is presented in Figure 6.2. For a typical MAWS surrogate glass composition of CM45, liquid-liquid phase separation occurs at about 860°C. Thus, liquid-liquid phase will not present a problem in the melter since the melter temperatures are typically greater than 1050°C. In addition, we have determined that if the cooling rate is fast, such as in "gem" production (~ 1-2 cm diameter glass hemispheres produced from the Duramelter at Fernald), liquid-liquid phase separation will not be present in the cooled glass.

6.4 Summary and Discussion

In this section, we have seen that, based on a melter-imposed constraint of a liquidus temperature below 1050°C, the 12 viable crucible melts from Sections 4.0 and 5.0 have been reduced to seven viable glass melts. These seven viable glass melts span the compositional range presented in Table 4.7 which is reprinted for convenience as Table 6.6.

In addition, we have shown that two-hour heat treatments after a one-hour premelt at

1100°C are sufficient to obtain approximate liquidus temperatures for MAWS glasses. Some of the glasses were heat treated for longer periods (20 hours) to determine the effect of long melter idling on the fluoride content of the melt and consequently on the liquidus temperature. These 20-hour heat treatment present large losses in fluoride (~ 30 relative %) and subsequently do not provide a correct estimate of the liquidus temperature of the starting glass composition. On the other hand, two-hour heat treatments show about a 10 relative % loss in fluoride, within our fluoride analysis error of ± 10 relative %. This 10 relative % error in correlation of fluoride content to liquidus temperature should not present a problem since the processable compositional range is itself subject to an analytical uncertainty of ± 10 relative % for all components in the glass.

Both phase separation and crystallization need to be considered when formulating processable glasses. This section represents a part of our database on correlations between melt composition, crystal type formation, and liquid-liquid phase separation. By understanding quantitatively the effect of composition on phenomena such as phase separation and crystallization, one can ultimately predict a processable glass composition and reduce the number of experiments necessary to apply the MAWS concepts of minimizing additives and blending waste streams.

Table 6.1
Results of 2-Hour Heat Treatments at 1050°C for Crucible Melt Glasses

Glass Name	Appearance
F5-42	Clear
F5-43	Clear
F5-44	Clear
F5-45	Extensive crystallization
F5-47	Clear
F5-48	Some crystals near Pt-crucible-to-glass interface
F5-49	Clear
F5-51B	<5% crystals
F5-52	Clear
F5-54A	~10-20% crystals
F5-55A*	~1% crystals
F5-56	~10% crystals
F5-57A-Bl	~50% crystals
F5-59	Clear
F5-60	Clear
F5-61	~5% crystals
F5-62	Clear
F5-63	Clear
F5-64A	Clear
F5-65	~10% crystals
F5-66	Clear
F5-67	Extensive crystallization
F5-68	Clear

*Heat treated for 11 hours instead of two hours.

Table 6.2
SEM/EDS Observations After Heat Treatment at 1050°C for 2 Hours

Glass Name	Volume % of:					
	Forsterite	Diopsidic augite	Fluorophlogopite	Spinel	Unidentified Crystal	Total Volume of Crystals
F5-42*	trace					0
F5-43*		10	trace			10
F5-44*		10	trace			10
F5-57BI		10			40**	50
F5-59						0
F5-60						0
F5-61						0
F5-62			3			3
F5-63						0
F5-64A						0
F5-65		8				8
F5-66						0
F5-67	2		20	trace	35***	57
F5-68						0

* These results are for 20 hour heat treatments.

** Crystal containing Mg, Si, Ca, and Fe.

*** Two types of crystals: One type containing Mg, Al, Si, K, and Fe and the other type containing Mg, Al, Ca, Cr, and Fe.

Table 6.3
SEM Observations after 1000°C Heat Treatment for 20 Hours

Glass Name	Volume % of:				
	Forsterite	Diopsidic Augite	Pargasite	Iron Oxide	Total Volume Percent
F5-42	10		trace		10
F5-43		<1	15	trace	15

Table 6.4
Effect of Heat Treatments on Fluoride Content

Glass	wt.% Fluoride	Fluoride Loss
F5-47 before heat treatment	11.22	
F5-47 after 1100°C/1 hour and 1050°C / 2 hours	10.35	7.8%, relative
F5-55A before heat treatment	3.23, 3.13	
F5-55A after 1100°C/1 hour and 1050°C / 11 hours	2.78, 2.85	11.5%, relative

Note: Multiple entries indicate replicate analyses.

Table 6.5
Target Compositions of Surrogate Glasses

wt%	CM44	CM45	CM46	CM47	CM48	CM49	CM50	CM51	CM52	CM53
Al_2O_3	10.00	6.00	10.00	6.00	10.00	6.00	10.00	6.00	18.30	0.00
MgF_2	20.40	22.00	15.30	16.50	10.20	11.00	25.50	27.50	12.20	42.70
SiO_2	30.60	33.00	35.70	38.50	40.80	44.00	25.50	27.50	30.50	18.30
CaO	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
Na_2O	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Fe_2O_3	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
B_2O_3	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00

Table 6.6

Processable Composition Range for Vitrification of Pit 5 Waste Stream with Soil Wash Fractions

Al_2O_3	3.2-6.7
B_2O_3	8.0-12.0
BaO	0.8-1.2
CaO	18.1-27.7
Fe_2O_3	2.7-5.0
K_2O	0.6-0.9
MgO	1.1-8.6
MgF_2	7.4-18.4
Na_2O	5.1-6.8
P_2O_5	0.3-0.6
SiO_2	23.1-35.0

Note: All combinations are possible with the following guidelines.
1) High MgF_2 must be combined with low MgO content.
2) SiO_2 content should not exceed 30 wt.% unless MgF_2 content is below 15 wt.%.
3) High CaO content should be accompanied by low SiO_2 and low MgF_2 contents.

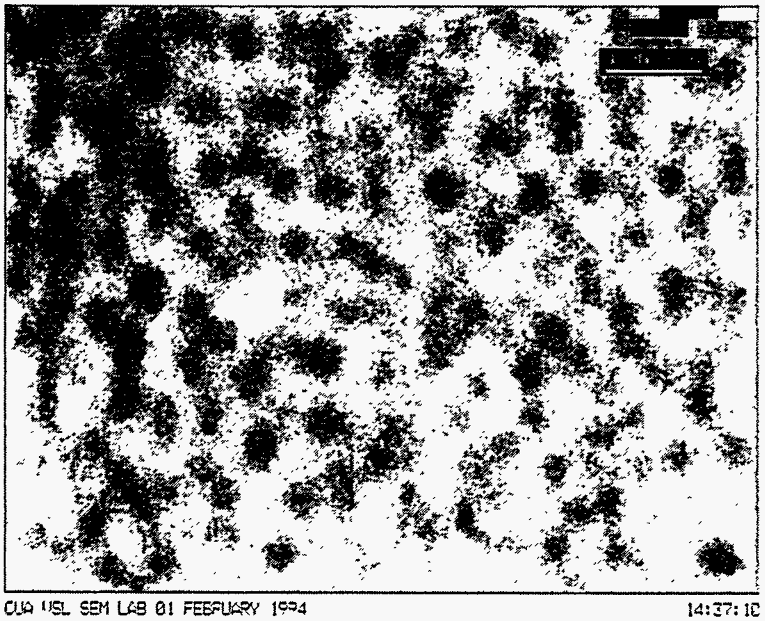


Figure 6.1.
SEM photograph of F5-47 glass. The <0.2 micron globules are indicative of liquid-liquid phase separation.

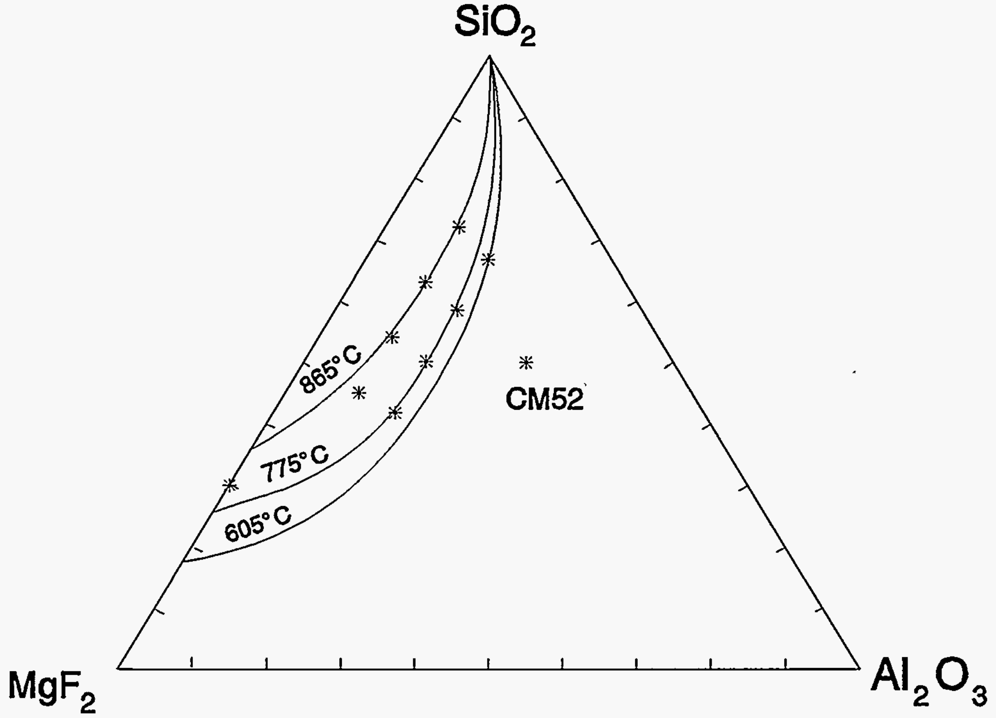


Figure 6.2. Estimated immiscibility isotherms in SiO_2-MgF_2-Al_2O_3 pseudo-ternary plane.

Section 7.0
Leach Testing

7.1 Introduction

In Sections 4.0, 5.0, and 6.0, we have seen that of the 31 MAWS crucible melts, seven have processable compositions as defined in Sections 4.0, 5.0, and 6.0. Having addressed the requirements for processability, we turn next to those for product performance. Generally, the most important requirement from a product performance perspective is that the waste form be highly resistant to leaching of the contaminants of concern, since a major objective of the remediation process is to effectively isolate those contaminants and prevent their release into the environment. As with other properties, glass leach resistance is strongly dependent on composition. However, it differs significantly from other properties, such as the viscosity, in that it is rather more subjectively defined. The observed rate of reaction of glass with water is highly dependent on the conditions that are imposed. Important factors include the temperature, the composition of the leachant (e.g. pure water, a natural groundwater, a pH-buffered solution, etc.) the time elapsed since the start of the reaction (initial rates are typically greater than later rates), and the ratio of the surface area of the glass to the volume of leachant. Standardized leach test methods have been developed which attempt to fix these factors at well-defined values so that meaningful comparisons between glasses can be made. The more relevant question is, however, "How will the waste form perform in the environment?", and in that respect data from some leach test procedures may be more relevant than others. In fact, efforts have been made to perform tests under the conditions expected to obtain in a given disposal site and to even perform tests in an actual location - so called *in situ* tests. Other tests have grown out of the need to regulate waste and waste forms based on leachability, such as the EPA Toxicity Characteristic Leaching Procedure (TCLP).

It is important to appreciate the critical dependence of the leachability measurement on the imposed test conditions. For example, if leachant pH is considered, the TCLP test is conducted under slightly acidic conditions and, therefore, by that measure, a glass formulation that shows good acidic leach resistance is favored. This may be of little relevance in terms of actual performance if the disposal conditions are likely to be alkaline. Unfortunately, disposal conditions are often unknown or poorly defined during the waste form development phase, and that is indeed the case at FEMP. We have, therefore, used a combination of both the TCLP and the PCT procedures since these evaluate leachability under two quite different sets of conditions and there is a large amount of existing data from these tests permits comparative evaluations to be made.

7.2 Results of TCLP Tests

Twenty-two MAWS glasses were subjected to the EPA TCLP leaching procedure for inorganics. This procedure involves reducing the particle size such that the sample passes through a 3/8" sieve followed by leaching the glass in a sodium acetate buffer solution for 18 hours at 22°C. The leachate solutions were analyzed for the eight listed metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se) by DCP, with sample spiking as required in the EPA TCLP test procedure. These results are listed in Table 7.1a along with the EPA regulatory limits. All of the glasses passed the TCLP test, except F5-46 for Se, and F5-57A, F5-58A, F5-59, and F5-61 all for Hg. Although four of the 22 crucible melts tested failed the TCLP test, all of the processable MAWS glasses (F5-47, F5-49, F5-52B, F5-60, F5-66, and F5-68) passed the TCLP test by a wide margin. Some of the concentrations in the leachates are so low that they are within the uncertainty of the DCP Emission Spectroscopy analysis. For example, the measured amounts of Cd and Hg in the leachates of MAWS glasses are within their DCP uncertainties of 0.05 and 0.10 ppm, respectively. The Cd and Hg leachate concentrations for some of the glasses were therefore also analyzed by ICPMS since that technique has a detection limit that is several orders of magnitude lower than that of the DCP.

In addition to examining the heavy metals, radionuclides in the leachates were also analyzed by ICPMS. These results are given in Table 7.1b. All of the leachates contained less than 0.2 ppb of Tc-99, while the amount of Th-232 and U-238 varied greatly from sample to sample. Further studies are needed in order to fully understand the reasons for these large variations in uranium and thorium concentrations in the leachates. Of the nine MAWS glass leachates tested, only two of them are leachates from processable glasses. Nevertheless, we are interested in the release of radionuclides from glasses in general as part of our attempt to understand how glass composition determines a number of physical and chemical properties. Although the U-238 release appears to be quite high for one of the processable glasses (1960 ppb in the leachate), it is still well below disposal limits: the 1960 ppb corresponds to 0.7 pCi/ml and the Nuclear Regulatory Commission (NRC) 10-CFR-20 regulation states that water below 3 pCi/ml is acceptable for direct release to sewers. Table 7.1c presents preliminary leachate action levels for FEMP based on a risk level of 10^{-5} and based on ARARs, as well as the NRC 10-CFR-20 limits for releases to sewers for comparison with the TCLP results presented in Table 7.1b. These data further confirm the ability of MAWS glasses to meet the TCLP leach resistance requirements.

7.3 Results of PCT Tests

While all of the processable glasses pass the EPA TCLP test, for the reasons stated in the introduction, that test is not necessarily a good measure of long-term glass durability. The main reasons for this are that (i) the TCLP test is conducted under acidic conditions which may not be representative of the conditions prevailing in an actual storage area; (ii) the test is conducted at room temperature and for only one day; and (iii) the ratio of glass surface area to solution volume (S/V) is very small (~20 m^{-1}). The PCT test is performed at 90°C for at least seven days with S/V=2000 m^{-1} (10 g of 75-150 μm powder) in water. Under these conditions, the leachant pH rises due to leaching of alkalies from the glass. These high-pH conditions increase the silicic acid saturation concentration and promote one of the major dissolution mechanisms for a glass matrix. For these reasons the more aggressive PCT test has been adopted as the benchmark test for distinguishing differences in the leach resistance of high-level nuclear waste glasses. A large database on the PCT performance of high-level nuclear waste glasses has now been accumulated and therefore collection of such data for MAWS glasses permits a direct comparative evaluation of the glass durability.

The results of the PCT tests after seven days at 90°C are presented in Table 7.2. The 24 glasses were tested in six sets, each of which included a standard glass (West Valley Reference 5). The glasses in each test set were tested in triplicate (i.e. three leach tests per glass) with two blanks (vessels with water but no glass) per test set. The blanks were tested for cations and fluoride and all were found to be below the detection limits. This confirms the absence of any contamination from either the deionized water used for the leach tests or from the leach vessels. The data on the standard glass are shown in Table 7.3 to give an indication of the reproducibility of the test results. There were seven test sets in all for the MAWS glasses with the F50F test set exclusively for 10 kg/day melter glasses. Only six Reference 5 results are reported here since F50K was sampled after 11 days rather than after seven days. Half of the Reference 5 boron data from the six MAWS test sets fall outside the standard deviation of Reference 5 data collected over four years in our laboratory for West Valley test sets. This is shown in Figure 7.1, where three of the six MAWS test sets have boron leachate concentrations for the Reference 5 standard glass which fall outside of the 18.45±3.33 ppm data collected over four years. We believe that this large deviation from the average West Valley test is due to small amounts of MAWS glass contamination into West Valley Reference 5 samples. This was confirmed by both SEM/EDS analysis of the Reference 5 glass powders used for these tests and fluoride analysis of the leachates (West Valley Reference 5 glass contains no fluoride and therefore the presence of fluoride in the leachate is a good indication of contamination). The contamination of the glass powders was estimated by SEM/EDS analysis to average about three particles in 1000 (i.e. about 99.97% purity; quite acceptable for most purposes). A number of MAWS glasses (such as F5-68) leach about 300 ppm B per 10 g sample, while Reference 5 leaches only about 20 ppm per 10 g sample. A small contamination of a glass like F5-68 could therefore significantly increase the leachate concentrations for the Reference 5 glass. Similar arguments are consistent with the data for sodium and potassium, however, the situation is more complex for elements other than boron due to the formation of secondary phases. Furthermore, it is conceivable that the addition of species such as fluorine to the leachate may accelerate the overall glass reaction rate; some evidence for this is afforded by the lithium and phosphorus concentrations which are increased even though their leachate concentrations are lower for the MAWS glasses than for Reference 5.

Note that if the reference glass was similar in composition to the sample glasses, this small contamination would have no measurable effect. Unfortunately, there is no reference glass (for which a large accepted body of PCT data exists) similar to the fluoride-containing MAWS glasses and we were forced to use a standard glass of radically different composition from our test glasses. Note also that contamination of Reference 5 glass into the MAWS glass samples will have little effect: a 1% contamination of a glass that leaches 20 ppm B for 10 g of glass (Reference 5) into a glass which leaches 20-500 ppm B under the same conditions will have negligible effect. We have implemented corrective actions for this contamination problem by using a separate grinder and sieves for the preparation of PCT tests on Fernald fluoride glasses and standard borosilicate waste glasses such as Reference 5.

Experience from the high-level waste vitrification program has shown that the boron concentration usually provides the best upper bound on overall glass leach rates since it does not form secondary phases which precipitate from solution; next best are usually lithium and sodium. Consequently, the high-level waste Waste Acceptance Product Specifications require reporting only these three elemental concentrations in the PCT leachate. Since there are very small amounts of lithium in the MAWS glasses (<0.3 wt.%), and since silicon is a major matrix component, we have focused on boron, sodium, and silicon for comparative purposes. The leachate concentrations are plotted as the normalized leachate concentrations (i.e. solution concentration normalized to that in the glass (Jantzen and Bibler, 1989)) for the 24 MAWS glasses in Figures 7.2a to 7.2d. We see in Figures 7.2a to 7.2d that all of these glasses compare favorably with the high-level nuclear waste standard glass after 7-days of leaching. In particular, F5-44, F5-47, F5-49, F5-52, F5-60, F5-66, and F5-68 glasses have normalized leachate concentrations for B, Na, and Si below that of the SRL-EA glasses.

After 28 days of leaching, several glasses have higher normalized Na concentrations than SRL-EA, including two of the processable glasses (F5-60 and F5-68), as shown in Figure 7.3a to 7.3d. After 56 days of leaching, the processable glasses continue to do well, as shown in Figure 7.4. The normalized concentrations of the processable glasses are below that of the SRL-EA glass for silicon, boron, and sodium except for the sodium for F5-68.

Figure 7.5 shows the normalized B leaching rate (since, for the reasons presented above, boron generally gives the best measure of the amount of glass reacted) for five of the processable glasses along with the SRL-EA glass. The long-time leach rates for the MAWS glasses are consistently low and fall well below that of the SRL-EA glass. All of the PCT tests are continuing to longer times (up to two years is planned) in order to examine the long-term durability of these glasses.

In addition to the cation release of the glasses, a number of the leachates were analyzed for fluoride. Table 7.4 shows the fluoride release of some of the processable MAWS glasses after 7, 28, and 120 days of leaching. The amount of fluoride in the leachate did not exceed 130 ppm, even after 120 days of leaching.

7.4 Discussion and Conclusions

We have seen that all of the processable glasses are also leach resistant as defined by the TCLP test. In the PCT test, the processable MAWS glasses compared well to the high-level nuclear waste standard SRL-EA, and the leach rates of these MAWS glasses decrease with time. A number of other glasses were also leach tested to obtain a database which we hope will permit correlation of properties such as leach resistance, conductivity, viscosity, and liquidus temperature to the glass composition. Table 7.5 summarizes the effects of the major constituents in Fernald glasses on the glass properties of concern. It should be emphasized that these general effects depend on the specific detailed glass composition as well as how the composition change is made (i.e., what other components are also varied).

The release of radionuclides and fluoride have also been measured for a number of MAWS glasses. TCLP radionuclide releases are below the preliminary leachate action level developed for FEMP and the NRC 10-CFR-20 maximum permissible concentration for release to sewers.

Table 7.1a
TCLP Results of MAWS Crucible Melts

	Elements (ppm)							
Glass Name	As	Se	Cd	Hg	Ag	Pb	Cr	Ba
F5-43	1.30	0.57	0.03	0.09	0.00	1.89	0.28	5.49
F5-45	2.33	0.61	0.02	0.19	0.01	1.66	0.38	6.87
F5-46	0.81	1.04	0.00	0.05	0.01	1.55	0.37	6.57
F5-47	0.44	0.36	0.03	0.08	0.04	0.90	0.05	9.18
F5-49	0.68	0.46	0.01	0.08	0.01	1.86	0.14	4.94
F5-50	0.70	0.76	0.01	0.16	0.01	1.78	0.23	3.53
F5-51B	0.93	0.66	0.01	0.03	0.02	1.82	0.14	3.97
F5-52B	0.54	0.48	0	0.06	0.01	1.95	0.17	10.8
F5-54A	1.68	0.66	0.01	0.14	0.02	1.91	0.15	2.60
F5-56	0.64	0.44	0.02	0.01	0.01	0.41	0.04	1.94
F5-57A	2.82	0.89	0.04	0.23	0.00	1.88	0.06	4.78
F5-58A	1.95	0.59	0.00	0.28	0.00	1.51	0.07	2.90
F5-59	2.22	0.58	0.01	0.34	0.01	1.37	0.14	11.0
F5-60	0.41	0.46	0.05	0.09	0.01	1.34	0.15	3.22
F5-61	1.03	0.47	0.03	0.21	0.02	1.63	0.13	10.9
F5-62	0.39	0.56	0.06	0.11	0.02	1.24	0.04	4.95
F5-63	0.56	0.30	0.07	0.10	0.02	1.36	0.18	2.94
F5-64A	0.78	0.20	0.04	0.08	0.02	1.52	0.53	4.80
F5-65	0.71	0.46	0.03	0.10	0.01	1.50	0.71	15.3
F5-66	0.60	0.55	0.03	0.07	0.01	1.52	0.20	11.1
F5-67	0.56	0.47	0.05	0.09	0.02	1.14	0.18	4.83
F5-68	1.02	0.14	0.03	0.06	0.02	1.72	0.48	10.14
EPA Limit	5	1	1	0.2	5	5	5	100

Table 7.1b
TCLP Leach Data for MAWS Glasses - Radionuclide Concentrations (ppb)

Radionuclides (ppb)	F5-58A	F5-59	F5-60	F5-61	F5-62	F5-63	F5-65	F5-66	F5-67
Tc-99	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Th-232	1.2	59	2.1	0.11	16.9	1.2	516	76	<0.1
U-238*	66	1950	1960	1140	56	1200	2900	570	2000

*Analyzed semi-quantitatively (uncertainty is about ±30%)

Table 7.1c
Preliminary Leachate Action Levels for FEMP and NRC 10-CFR-20 Limits for Releases to Sewers

Radionuclide	FEMP Leachate Action Levels				NRC 10-CFR-20 Maximum Permissible Levels for Releases to Sewers	
	Risk-Based (10^{-5})		ARAR-Based			
	pCi/l	ppb	pCi/l	ppb	pCi/l	ppb
Tc-99	16000	0.94	91400	5.38	600,000	35
Th-232	1300	11800	200	1820	300	2720
U-238	1000	2970	700	2080	3000	8980

Table 7.2
PCT Results of MAWS Glasses (ppm)
(7 days, 90°C, 100-200 mesh)

Test Name	F50E	F50E	F50E	F50G	F50G	F50G	F50G
Elements	F5-42	F5-43	F5-44	F5-45	F5-46	F5-47	F5-49
B	235	277	324	285	425	491	22.8
Si	2.24	20.7	12.64	5.02	9.41	10.96	24.6
Na	449	541	634	481	620	514	45.4
pH	9.76	9.70	9.72	9.73	9.55	9.15	10.4
Al	0.19	0.31	0.25	0.21	0.21	0.35	0.94
Ba	0.61	1.07	0.59	0.67	0.84	0.46	2.96
Ca	36.9	35.7	28.2	40.9	52.4	21.7	76.9
Cr	0.18	0.00	0.20	0.08	0.03	0.02	0.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	50.6	86.3	76.2	81.8	87.8	44.4	7.91
Li	1.18	0.43	0.39	0.44	0.50	0.95	0.30
Mg	0.21	0.22	0.16	0.20	0.21	0.38	0.04
Mn	0.03	0.10	0.10	0.03	0.04	0.02	0.00
Ni	0.04	0.05	0.10	0.00	0.01	0.04	0.01
P	0.00	0.11	0.19	0.18	0.20	1.52	0.74
Sr	0.29	0.21	0.15	0.30	0.32	0.19	0.28
Ti	0.00	0.04	0.04	0.00	0.00	0.02	0.00
U	0.02	0.23	0.64	0.17	0.22	1.11	0.50
Zr	0.00	0.02	0.00	0.00	0.00	0.04	0.03

[*] Eleven day results instead of seven day results

Note: These values are the average of triplicate samples.

Table 7.2 (continued)

Test Name	F50G	F50H	F50H	F50K	F50J	F50K	F50K
Elements	F5-50B	F5-51A	F5-52A	F5-54A*	F5-56	F5-57A*	F5-58A*
B	18.0	54.0	55.9	63.9	7.93	79.8	66.5
Si	28.8	5.62	3.27	3.17	19.2	3.32	3.16
Na	35.8	105	112	117	2.07	152	123
pH	10.7	11.3	11.5	11.6	10.9	11.51	11.68
Al	0.94	1.95	2.15	0.52	2.32	0.82	0.55
Ba	2.63	7.69	11.3	7.04	1.71	0.68	5.16
Ca	69.8	107	125	134	48.6	192	123
Cr	0.00	0.15	0.12	0.00	0.09	0.00	0.00
Fe	0.00	0.00	0.00	0.00	0.06	0.00	0.03
K	5.10	14.6	13.5	3.27	2.61	5.99	4.22
Li	0.27	0.50	0.56	0.83	0.36	1.12	0.77
Mg	0.03	0.01	0.00	0.00	0.03	0.00	0.01
Mn	0.01	0.01	0.00	0.00	0.04	0.00	0.00
Ni	0.00	0.08	0.00	0.00	0.16	0.00	0.00
P	0.79	0.59	0.02	0.05	0.98	0.00	0.00
Sr	0.24	0.55	0.74	0.50	0.07	0.65	0.49
Ti	0.00	0.04	0.00	0.00	0.07	0.00	0.00
U	0.46	1.02	0.28	0.29	1.03	0.05	0.16
Zr	0.03	0.02	0.00	0.01	0.11	0.00	0.00

*Eleven day results instead of seven day results

Note: These values are the average of triplicate samples.

Table 7.2 (continued)

Test Name	F50J	F50J	F50J	F50J	F50J	F50K	F50K	F50K	F50K	F40A
Elements	F5-59	F5-60	F5-61	F5-62	F5-63	F5-64A*	F5-65*	F5-66*	F5-67*	F5-68
B	365	315	107	226	333	284	31.3	106	244	284
Si	9.48	4.37	4.93	5.14	7.29	13.86	15.40	3.96	4.85	11.1
Na	379	526	182	333	794	412	44.5	192	365	484
pH	9.58	9.87	11.46	9.22	9.68	9.37	11.02	11.60	9.19	10.04
Al	1.01	0.41	1.72	0.20	0.61	0.08	1.11	1.02	0.02	0.64
Ba	1.12	0.82	6.67	0.49	0.54	0.66	3.73	6.84	0.52	1.30
Ca	180	33.2	131	5.64	2.83	23.1	93.6	135	6.16	54.8
Cr	0.18	0.51	0.11	0.21	0.18	0.28	0.20	0.14	0.04	0.49
Fe	0.00	0.02	0.04	0.06	0.08	0.07	0.15	0.11	0.00	0.00
K	84.6	79.0	25.9	37.9	63.5	39.3	6.01	28.7	33.6	70.0
Li	1.63	0.81	0.92	0.64	1.61	0.54	0.61	1.14	0.62	0.56
Mg	0.12	0.15	0.04	1.37	0.37	0.24	0.00	0.04	1.20	0.03
Mn	0.03	0.02	0.01	0.04	0.06	0.00	0.00	0.00	0.00	0.05
Ni	0.15	0.18	0.11	0.19	0.05	0.00	0.04	0.00	0.00	0.15
P	0.77	1.32	0.50	1.09	0.36	0.30	0.62	0.18	0.00	1.02
Sr	0.62	0.23	0.59	0.02	0.02	0.12	0.20	0.69	0.01	0.31
Ti	0.04	0.09	0.02	0.08	0.01	0.00	0.07	0.07	0.00	0.07
U	1.58	1.74	0.67	1.10	0.00	0.95	1.46	1.52	0.24	1.93
Zr	0.04	0.05	0.02	0.04	0.00	0.05	0.07	0.07	0.02	0.10

*Eleven day results instead of seven day results

Note: These values are the average of triplicate samples.

Table 7.3
PCT Results (7 days, 90°C) on the Reference 5
Standard Glass Tested in Parallel with the MAWS Glasses.
(ppm)

Test Name	F50E			F50G			F50J		
Replicate Number	1	2	3	1	2	3	1	2	3
B	31.5	26.7	26.2	15.6	15.7	15.7	21.0	18.3	18.2
Si	52.5	50.7	50.4	46.9	48.6	48.1	54.0	52.6	54.3
Na	54.0	46.7	46.0	32.5	33.1	33.0	35.9	33.5	33.7
pH	9.97	9.95	9.95	10.09	10.05	10.03	9.95	10.05	10.08
Al	4.80	5.75	5.91	6.29	6.55	6.58	6.7	7.0	7.1
Ba	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Ca	0.22	0.04	0.11	0.11	0.11	0.00	0.00	0.00	0.02
Cr	0.16	0.39	0.25	0.00	0.00	0.00	0.01	0.11	0.00
Fe	0.00	0.00	0.00	0.12	0.16	0.18	0.44	0.48	0.44
K	13.5	12.0	11.7	8.92	8.82	8.57	10.0	9.6	9.4
Li	9.29	8.19	7.99	5.72	5.82	5.92	6.1	5.8	5.8
Mg	0.02	0.21	0.09	0.07	0.10	0.10	0.15	0.19	0.15
Mn	0.00	0.05	0.05	0.00	0.00	0.00	0.01	0.16	0.09
Ni	0.00	0.11	0.14	0.00	0.00	0.00	0.07	0.21	0.10
P	5.98	4.92	5.96	2.22	3.49	3.92	4.95	4.90	4.71
Sr	0.09	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.00
U	0.49	0.77	0.46	0.53	0.13	0.42	0.00	0.00	0.00
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 7.3 (continued)

Test Name	F50H			F50J			F40A		
Replicate Number	1	2	3	1	2	3	1	2	3
B	34.5	32.4	34.4	21.0	18.3	18.2	34.0	31.0	30.4
Si	57.5	57.3	58.5	54.0	52.6	54.3	50.1	49.7	49.2
Na	64.1	60.3	64.9	35.9	33.5	33.7	50.2	47.2	47.7
pH	10.21	10.16	10.14	9.95	10.05	10.08	9.77	9.75	9.76
Al	3.08	3.34	3.09	6.71	7.04	7.14	3.9	4.1	4.3
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02
Ca	0.11	0.05	0.11	0.00	0.00	0.02	0.08	0.00	0.00
Cr	0.12	0.00	0.00	0.01	0.11	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.44	0.48	0.44	0.04	0.01	0.00
K	16.9	15.8	17.2	9.95	9.56	9.43	12.8	11.9	12.3
Li	9.89	9.38	9.86	6.05	5.75	5.77	8.0	7.7	7.5
Mg	0.00	0.02	0.00	0.15	0.19	0.15	0.01	0.03	0.02
Mn	0.03	0.02	0.00	0.01	0.16	0.09	0.04	0.15	0.10
Ni	0.05	0.00	0.00	0.07	0.21	0.10	0.06	0.15	0.00
P	1.35	2.09	2.28	4.95	4.90	4.71	7.1	6.4	4.4
Sr	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.03	0.00	0.01	0.02	0.04	0.00	0.03	0.13	0.00
U	0.44	0.47	0.53	0.00	0.00	0.00	1.8	2.3	0.2
Zr	0.00	0.01	0.00	0.00	0.00	0.00	0.1	0.1	0.0

Table 7.4
Fluoride Contents of PCT Leachates

Glass	F Content in Leachate (ppm)
F5-60 (7-Days)	104.1
F5-66 (7-Days)	33.0
F5-60 (28-Days)	122.7
F5-68 (28-Days)	129.7
F5-47 (120-Days)	120.2
F5-49 (120-Days)	60.7

Note: All data are average of triplicate leach tests.

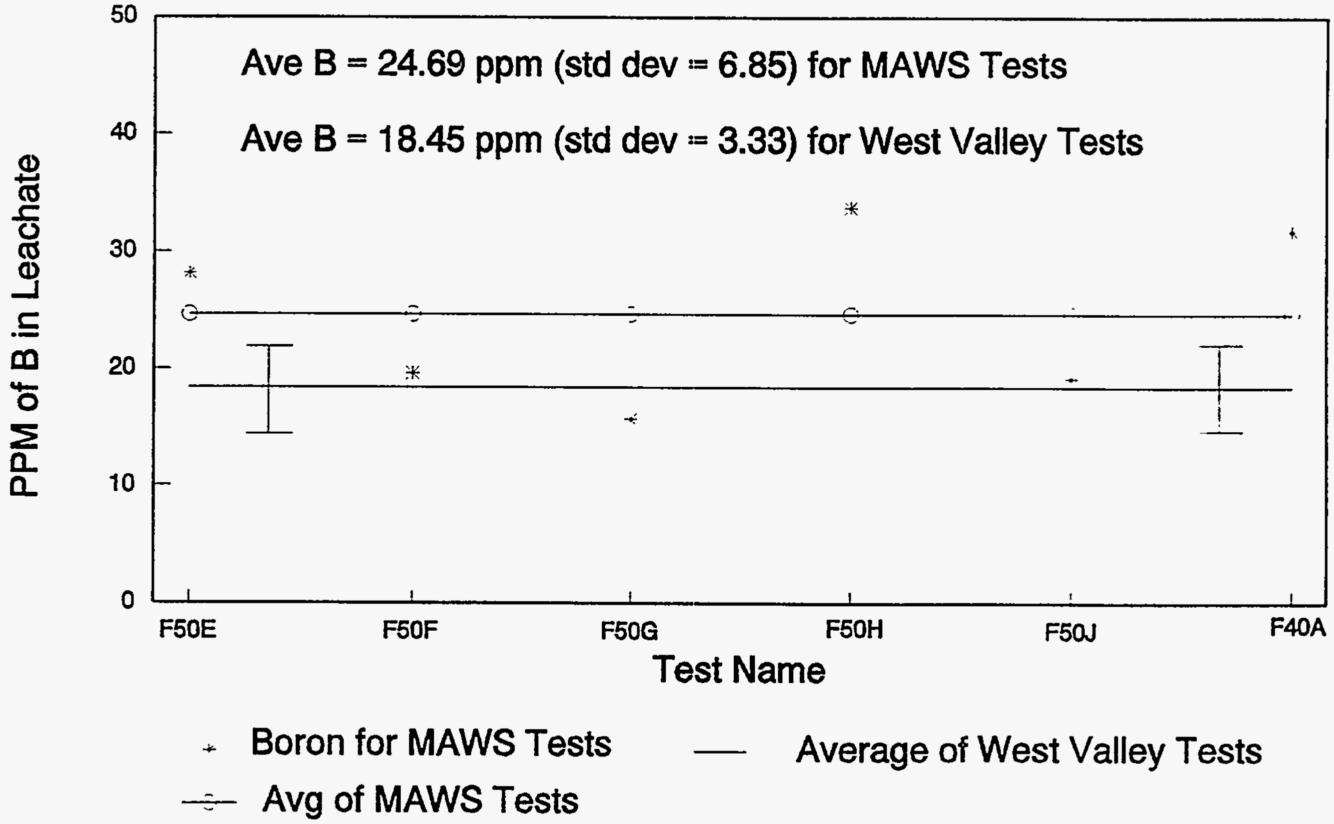


Figure 7.1
PCT boron concentrations after 7-days for the West Valley Reference 5 standard glass.
The figure compares the VSL 4 yr historical average and standard deviation
with those for the MAWS glass PCT tests.

Figure 7.2a
Results from PCT tests on MAWS crucible melts compared to SRL-EA after 7 days

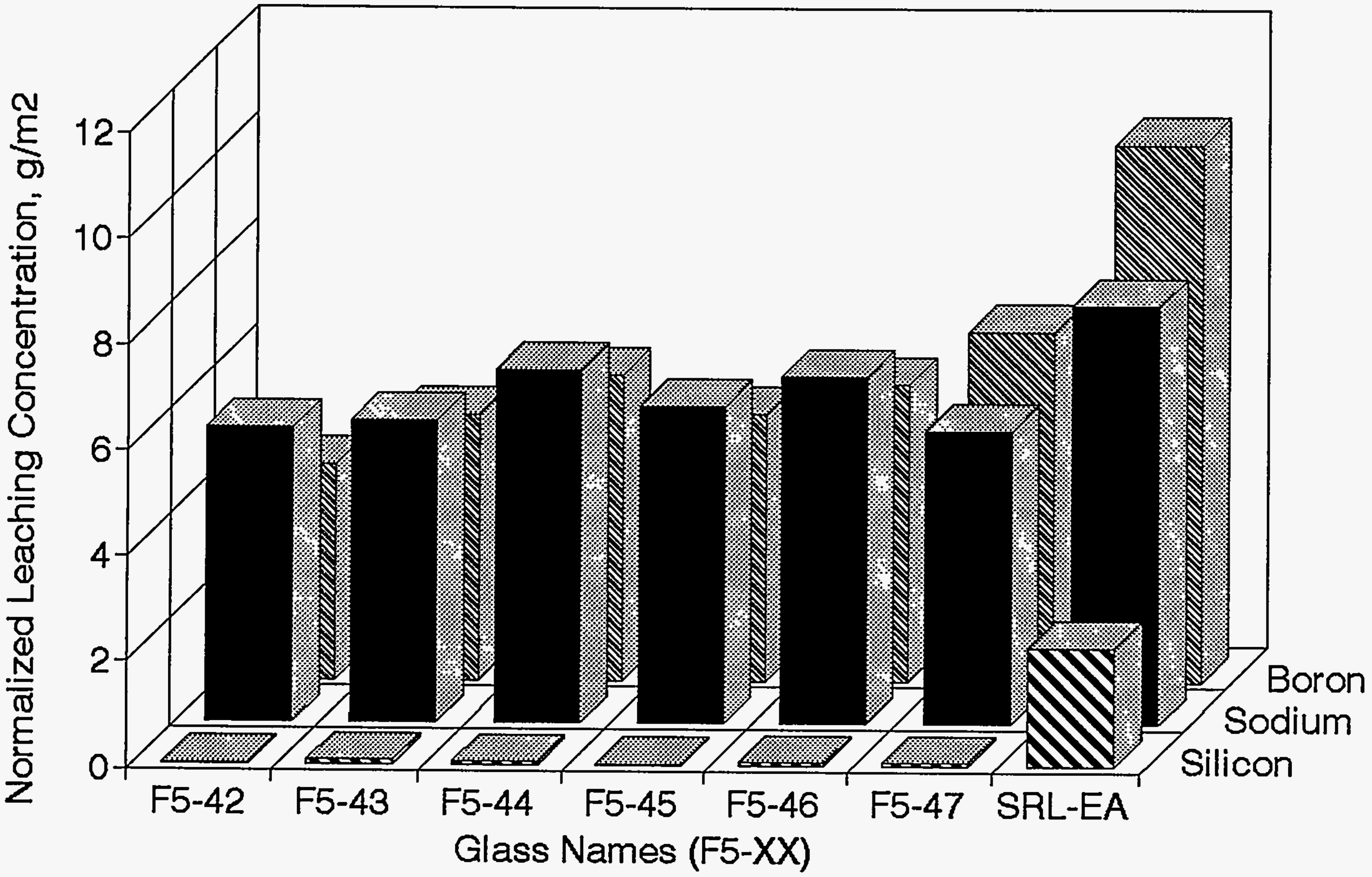


Figure 7.2b

Results from PCT tests on MAWS crucible melts compared to SRL-EA after 7 days

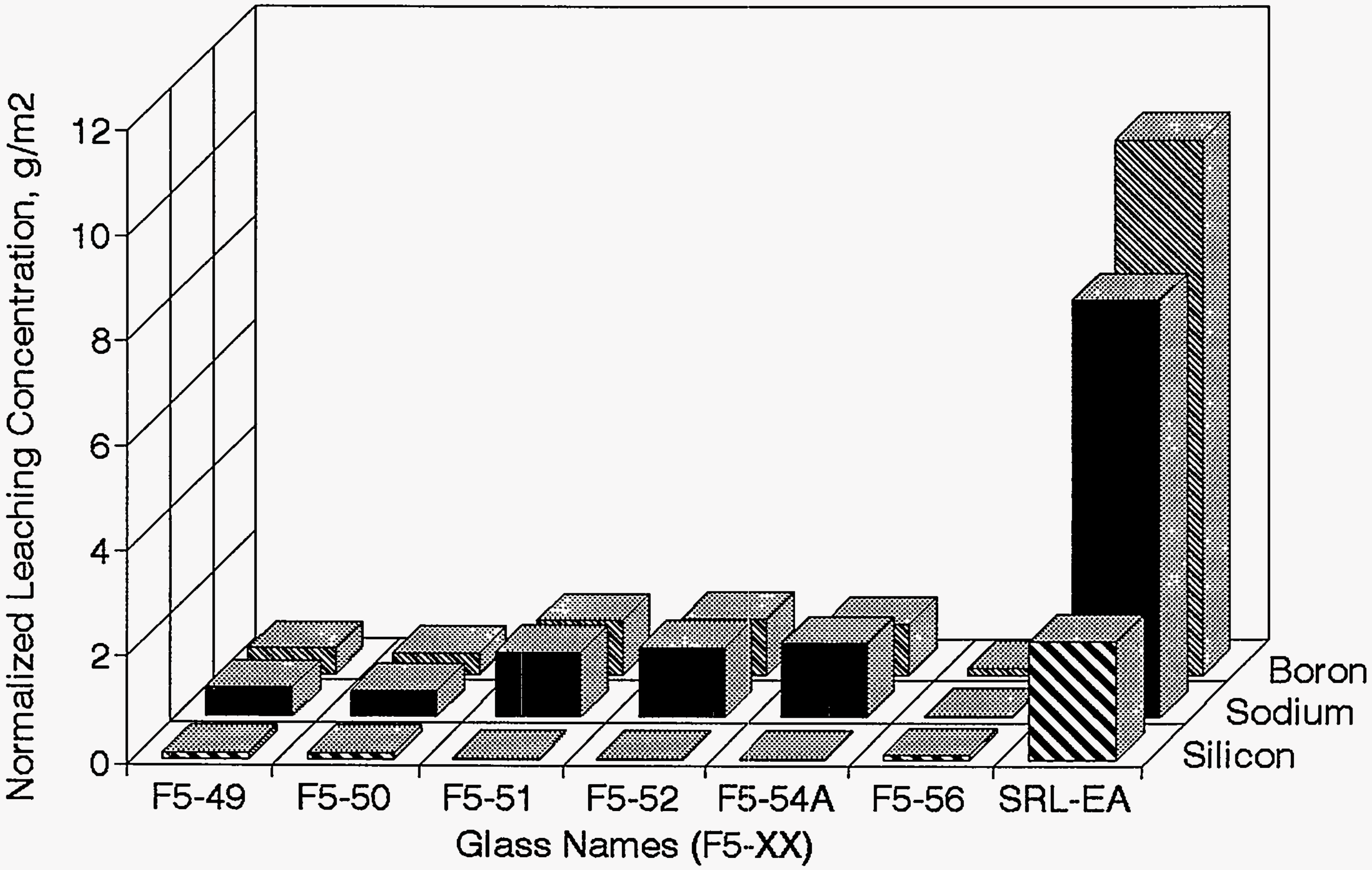


Figure 7.2c
Results from PCT tests on MAWS crucible melts compared to SRL-EA after 7 days

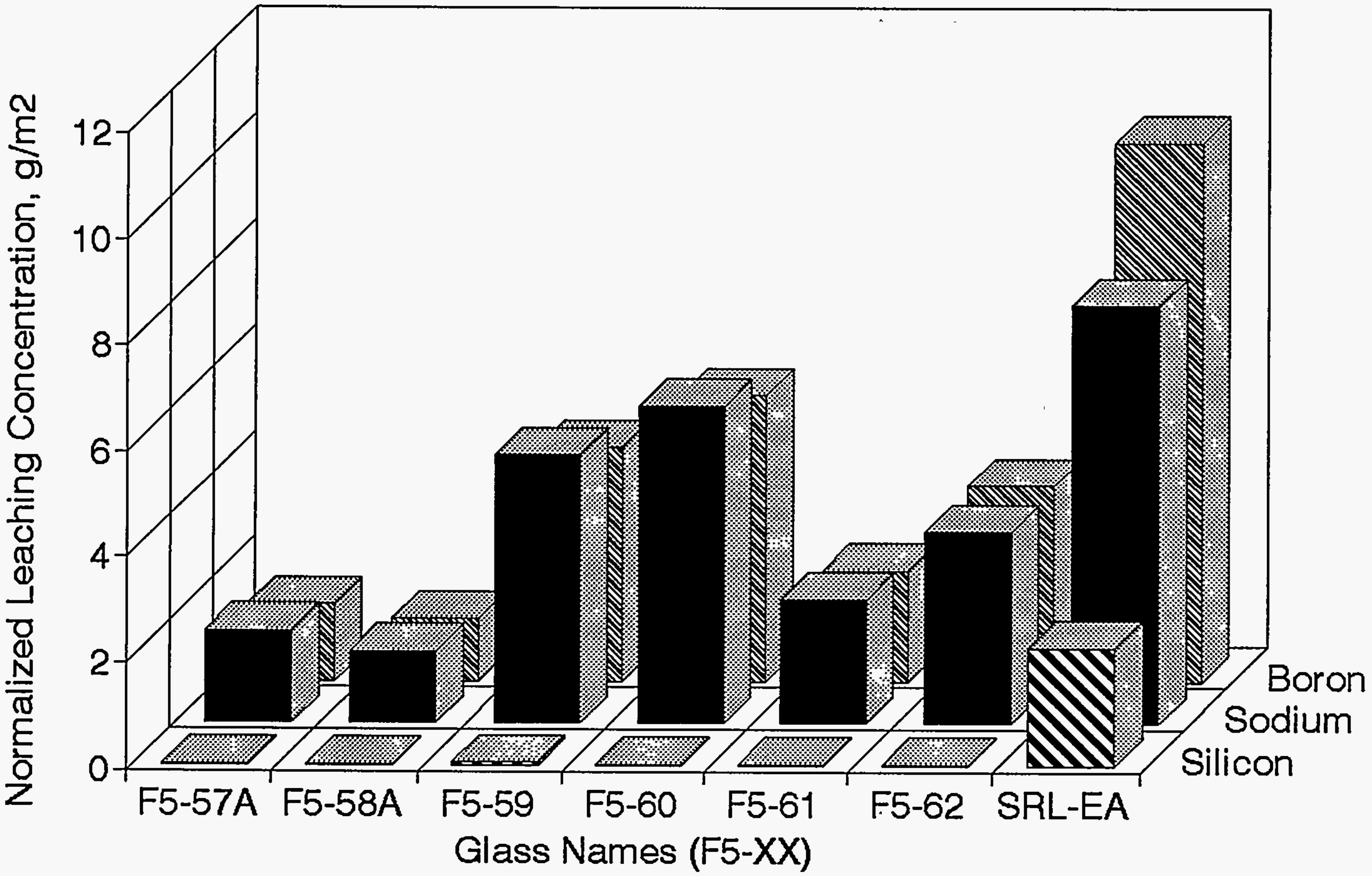


Figure 7.2d

Results from PCT tests on MAWS crucible melts compared to SRL-EA after 7 days

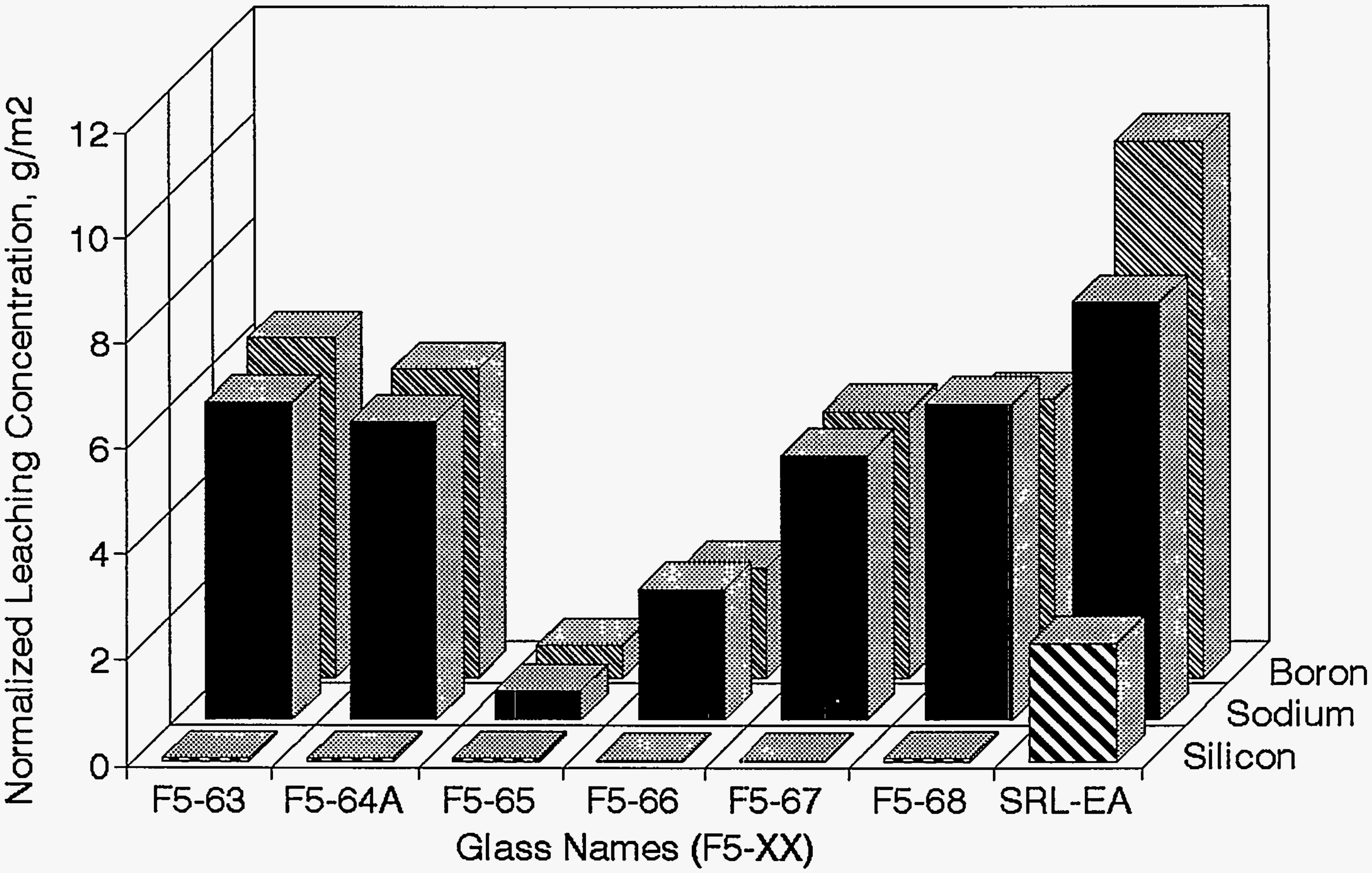


Figure 7.3a
Results from PCT tests on MAWS crucible melts compared to the SRL-EA after 28 days

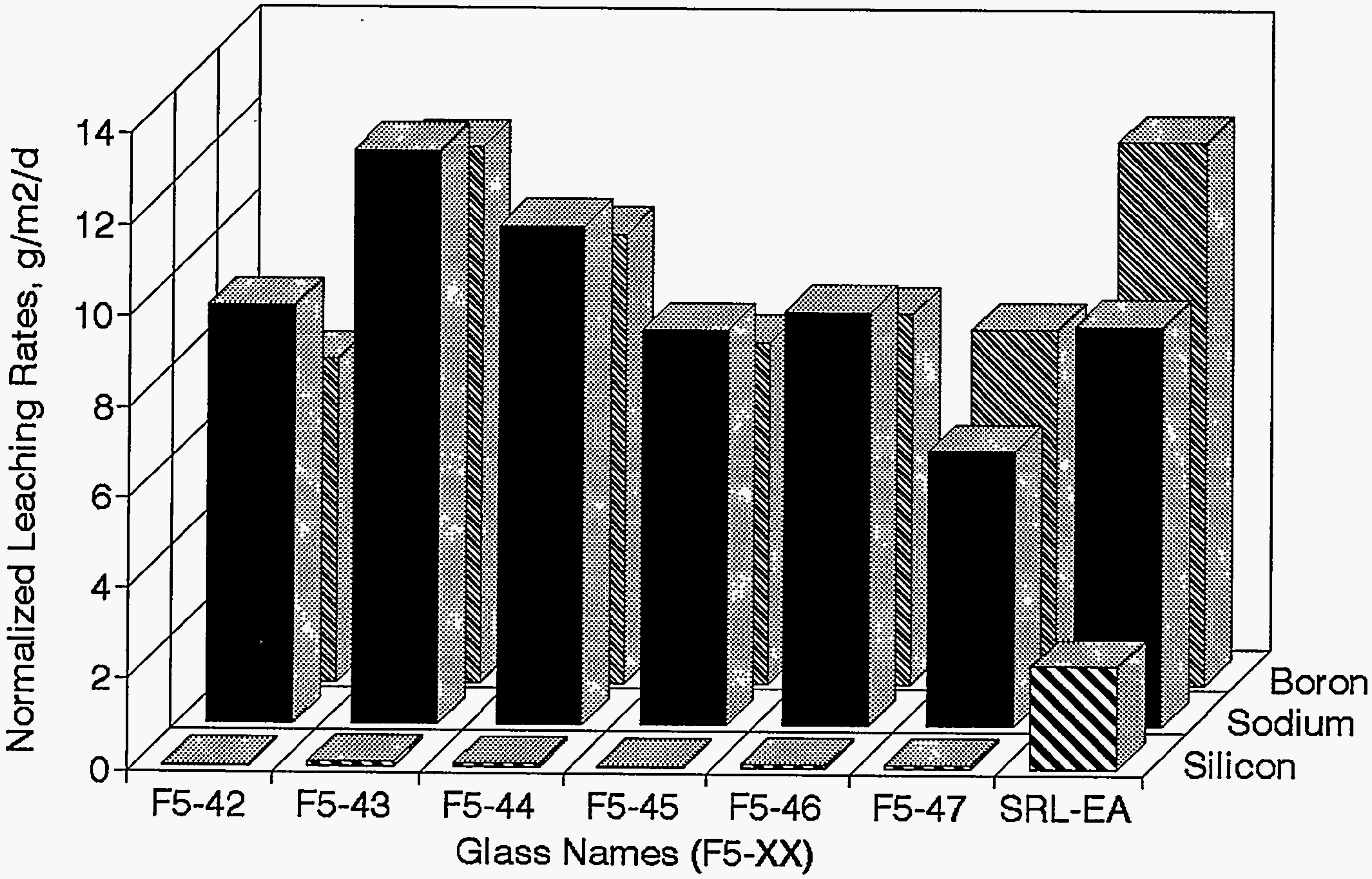


Figure 7.3b

Results from PCT tests on MAWS crucible melts compared to the SRL-EA after 28 days

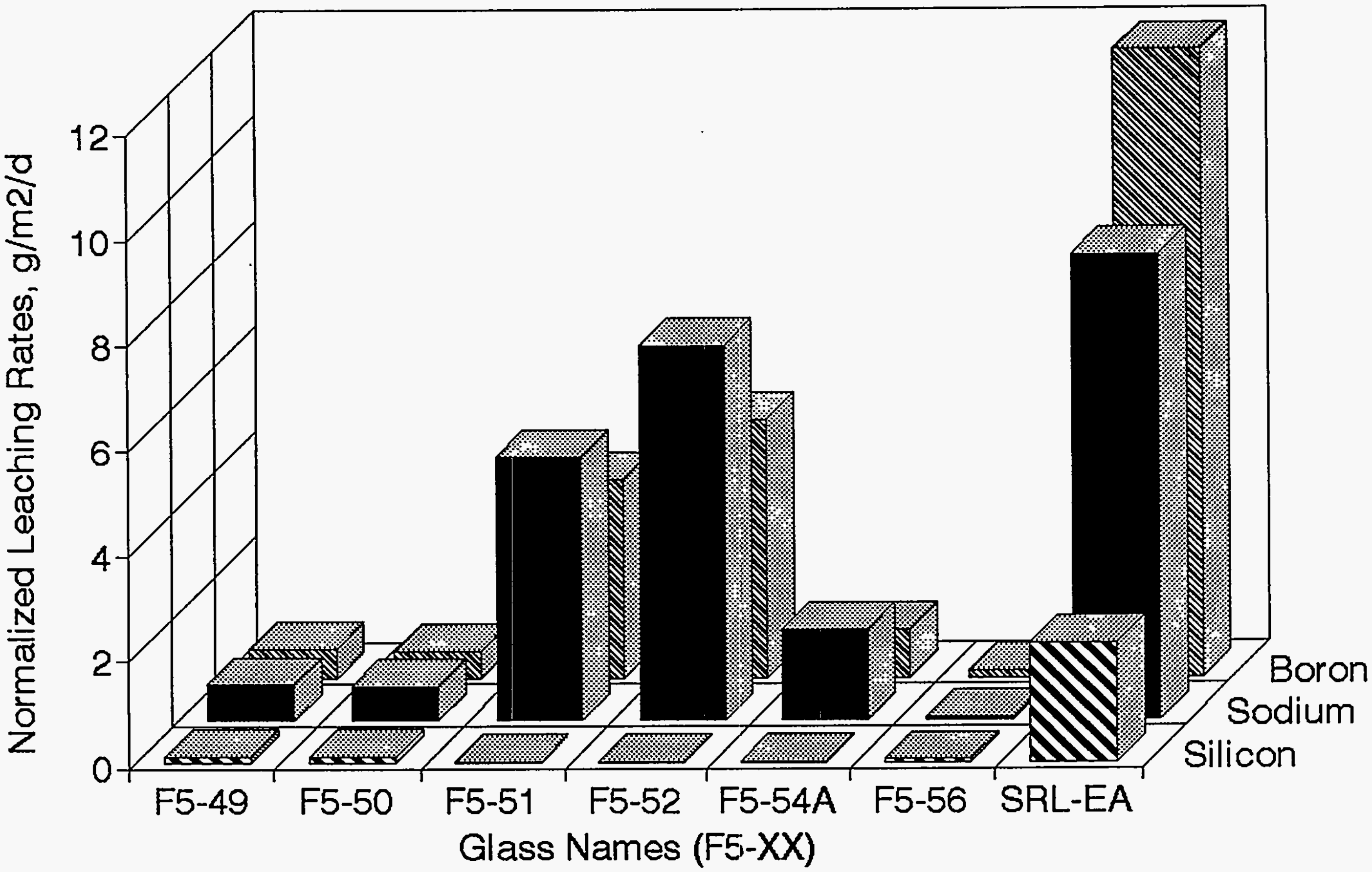


Figure 7.3c

Results from PCT tests on MAWS crucible melts compared to the SRL-EA after 28 days

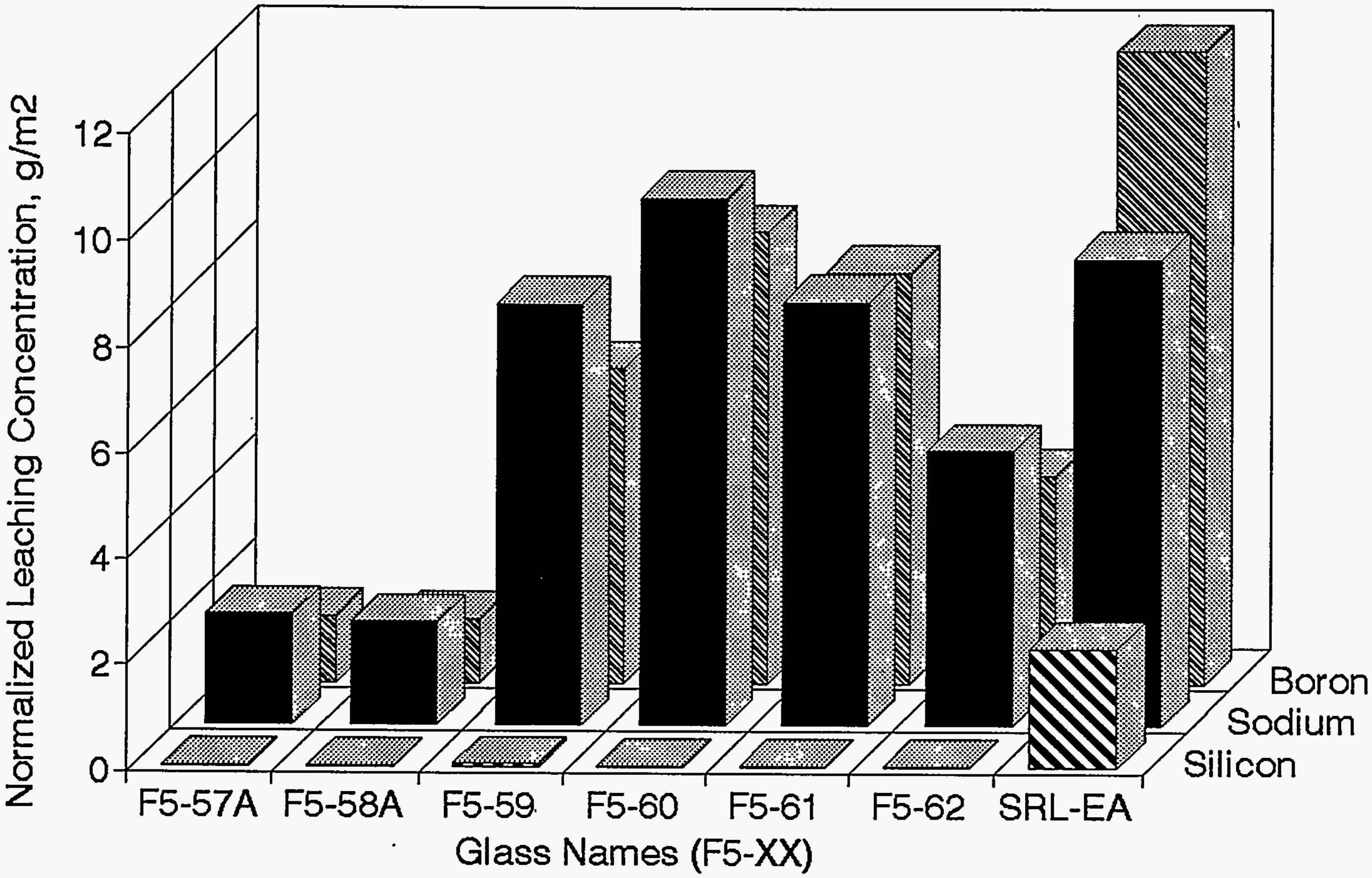


Figure 7.3d

Results from PCT tests on MAWS crucible melts compared to the SRL-EA after 28 days

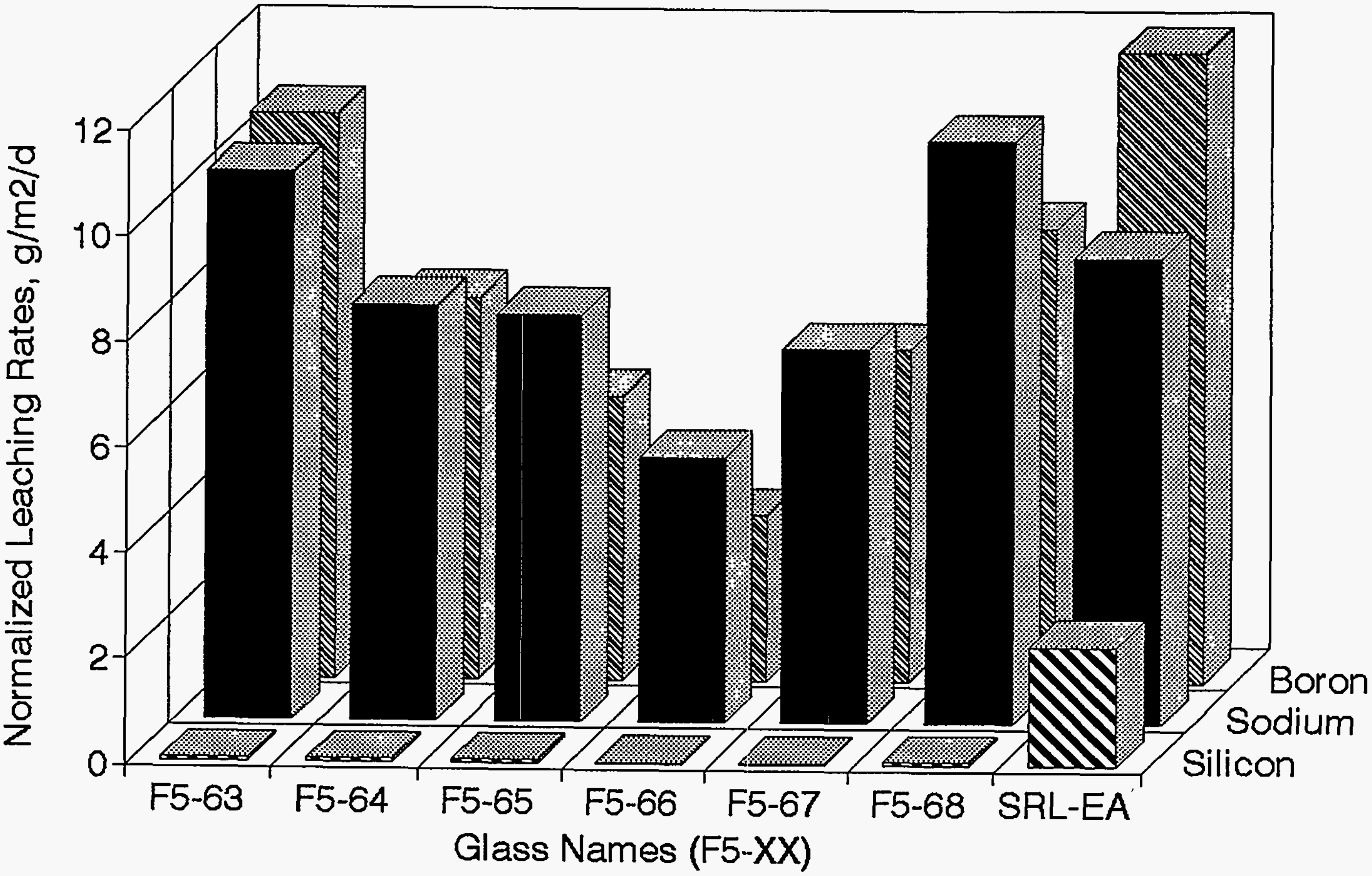


Figure 7.4a
Time dependence of PCT normalized boron release rates for some processable MAWS Glasses

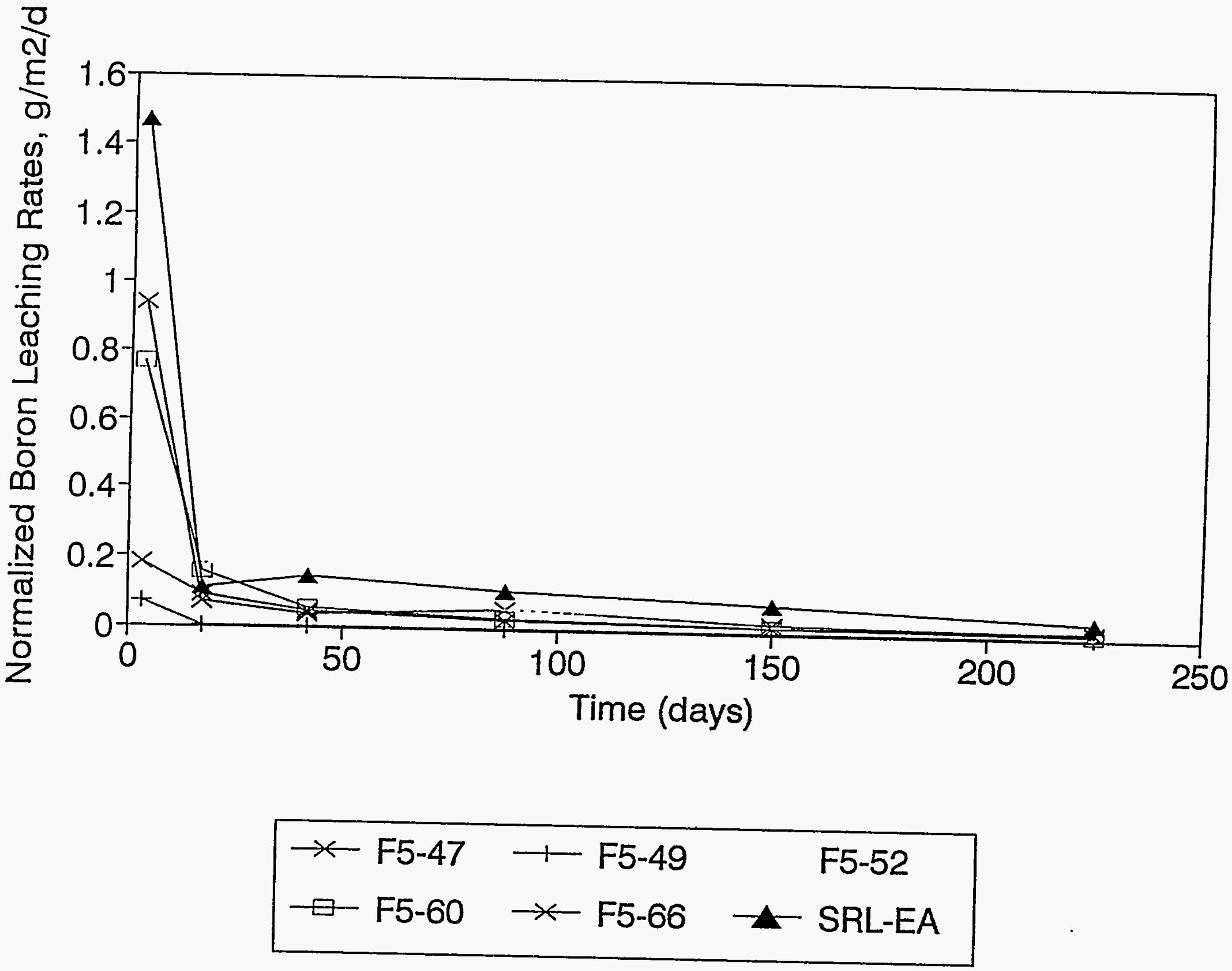


Figure 7.4b

Time dependence of PCT normalized boron release rates for some processable MAWS Glasses plotted on log scale

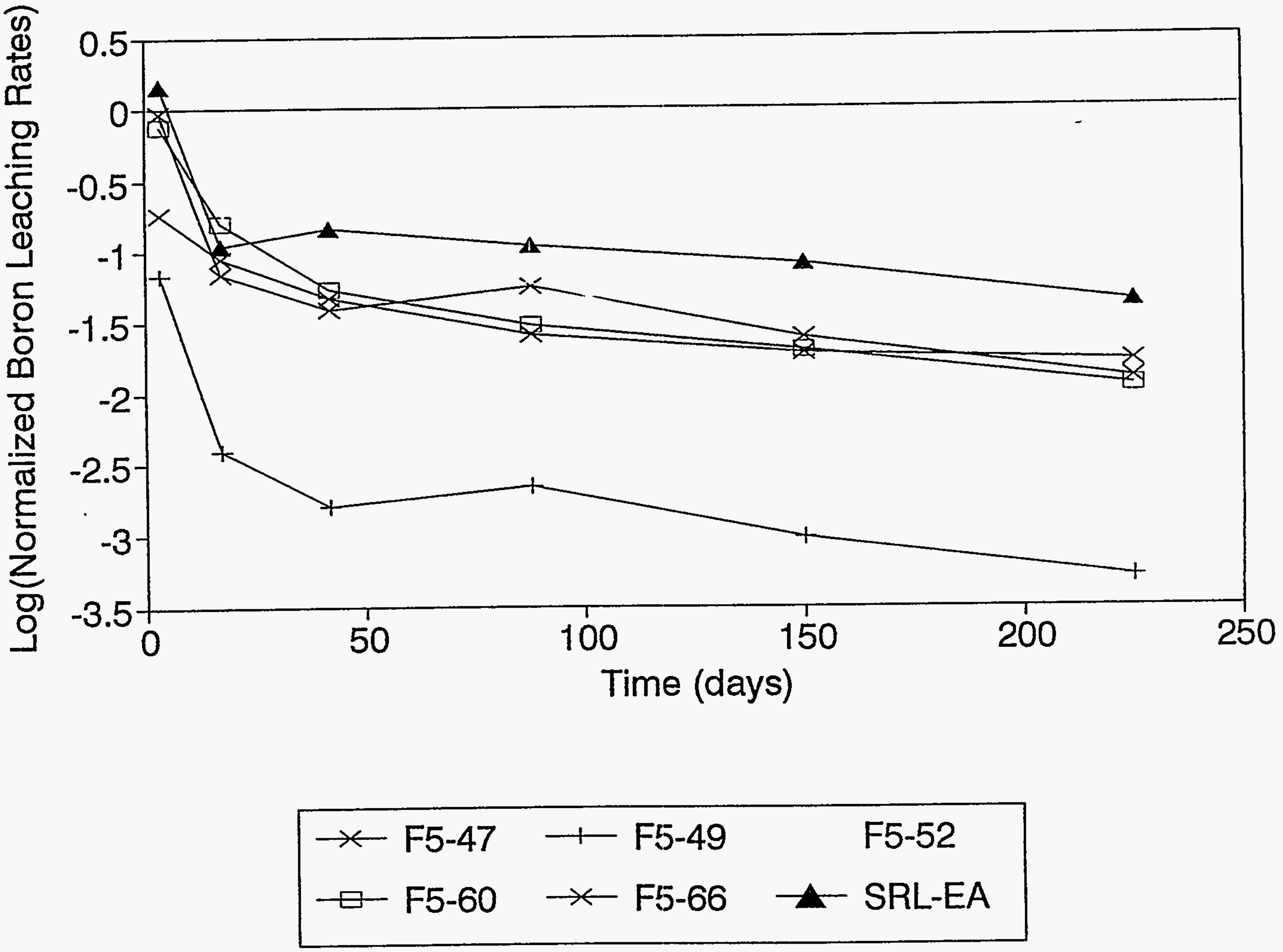


Table 7.5
Summary of Effects of Major Fernald Glass Constituents on Glass Properties

Constituent Increased	Viscosity	Conductivity	Chemical Durability		Liquidus Temperature[*]
			PCT	TCLP	
Al	Increases	Decreases	Increases (more than TCLP	Increases	Usually increases
B	Decreases	Increases	Decreases	Decreases	Decreases
Ca	Decreases	Increases	Usually increases at low levels, effect depends at high levels		Depends
F	Decreases	Increases	Decreases	Decreases	Decreases from 0-10 wt.%, Increases above ~10 wt.%
Mg	Decreases	Increases	Similar to Ca		Depends
Na	Decreases	Increases	Decreases	Decreases	Decreases except at high levels
Si	Increases	Decreases	Increases	Increases	Increases

[*] Effect on liquidus temperature is very strongly dependent on concentration of other components

<u>Note</u>: Specific effect of increase of one constituent depends on how the increase is compensated (since total is still 100%); here we have assumed increase and renormalize.

SECTION 8.0
Systems Engineering

8.1 Introduction

Duramelters™ 10, 100 and 300 represent an upscaling path in the development of the full-scale system for the vitrification of FEMP waste streams. Besides ever increasing complexity related to physical size, operational constraints and safety demands, the whole family has been designed around a single concept from the overall system engineering point-of-view. A major constraint imposed is that each must be a zero-waste system. Since only a minor part (~30%) of the waste forms the final glass product, it follows that the bulk of the material (largely as water and carbon dioxide) is to be processed by the off-gas system. The variety of chemicals passing through the system combined with large amounts of moisture are likely to produce secondary waste streams, an undesirable consequence. The zero-waste concept requires that no secondary waste stream will be generated, thus challenging process design in four major ways:

- No volume increase (e.g. condensation) is allowed in the ECS (emissions control system such as scrubbers, filters, etc.) system
- All material accumulated by various ECS's are recycled
- Efficiency of various ECS's are not compromised in the "zero waste" mode of operation.
- The high fluorine content of FEMP wastes causes significant volatilization of HF from the melt. Thus, the ability to capture and recycle fluorides is crucial to the success of the process. This also introduces additional material compatibility considerations.

To meet these challenges a computer model was developed to handle the material and energy balances of the systems in addition to an innovative evaporative quencher - scrubber device that was introduced to collect and recycle any contaminants and glass forming components escaping the melter cavity.

8.2 System Modelling

Each Duramelter™ system consists of a feed system, melter with glass discharge and off-gas system. To establish the design criteria and proper sizing for each of the systems, the material balance is required in order to match the target glass product composition with feed characteristics, amount of additives, and the desired processing rate. A numerical model has been developed which transforms process input parameters into major engineering specifications for the equipment. An example output for Duramelter™ 300 system is provided in Figure 8.1a-d.

One can see that the Durameltertm 300 is actually designed to handle three times its nominal production capacity. Based upon the output of the modelling program, the detailed Process Flow Diagram (PFD) can be constructed.

8.3 Process Description

Here again the Durameltertm 300 system serves as an example. All the other systems are specifically discussed later on. The following process description refers to the symbolics of the PFD given in Figure 8.2. However, the specific functional details including process control elements can be extracted more clearly by following full Process and Instrumentation Diagram (P&ID, Figures 8.3a-b).

The feed to the glass melter consists of a toxic, radioactive waste in the form of either a sludge (S1), a liquid, a solid (S2, S3, S4) or their combination. Specifically, the FEMP waste contains large amounts of magnesium fluoride in addition to transition metals, uranium and thorium. The feed generally also contains other additives (A1) necessary to produce a stable glass product which can be safely disposed. The feed is introduced to the melter in the form of slurry (S6), after all the components have been thoroughly blended in the correct proportions (S5). The solid portion of the slurry forms glass while the gaseous byproducts (mostly CO_2 and steam) together with some solid particulates leave the melter via off-gas conduit (S8) carrying with them considerable amounts of heat (H8). The energy supplied to the melter (H1) must be sufficient to make up for this loss in addition to the loss in the melting process itself (equal to the loss by glass discharge, H5) and radiative losses of the melter (H2). Stirring of the melter is accomplished by bubbling air through the glass pool (A3). The temperature of the exhaust gases is adjusted first by air dilution (A4) which simultaneously provides the air mass excess necessary to carry the moisture through the system (S9) and to allow for subsequent evaporative cooling in the quencher-scrubber solid recovery unit.

The quencher and solid recovery scrubber unit plays the dual roles of lowering the temperature of the hot inlet gas (S9) and at the same time, entrapping contaminants from the gas stream into the liquid streams (S12). The hot exhaust gases are cooled when the liquid scrubber solution evaporates while the contaminants of the exhaust gas react with a suitable reagent (such as sodium hydroxide in the case of acidic contaminants) and the product is collected in the scrubbing solution (S10). Since the solution is continuously recycled (S12), the concentration of the scrubbing reagent will be diminished as the scrubbing proceeds. On the other hand, the concentration of the scrubbing product in the solution will rise, and eventually exceed its solubility limit. As saturation is reached, the scrubbing products begin to precipitate and are collected at the bottom of the scrubber. The scrubbing reagents are continuously replenished to the scrubber. The precipitates at the bottom can be either continuously or intermittently removed from the scrubber (S23).

The secondary scrubber is a more conventional wet scrubber which uses reagents and a water spray to scrub out the tailing of any contaminants that might have escaped the solid recovery scrubber. In addition, the exhaust gas entering the secondary scrubber (S11) is cooled below its dew point which results in condensation of water in the scrubber. The scrubber solution temperature is adjusted by a heat exchanger (SHX) interlocked to a level controller. The objective is to keep the volume of scrubber solution constant so there will not be any secondary waste solution generated during scrubbing (S14). Based on this requirement, if the volume of the scrubbing solution starts to increase because of a high rate of condensation of the incoming vapors then less heat is removed from the scrubber solution to allow for more evaporation from the secondary scrubber. In contrast, if the volume of the scrubber solution starts to decrease, more heat is removed from the scrubber solution to produce a higher condensation rate. The overall balance is maintained by simultaneous transfer of the water/reagents solution from the secondary scrubber to the solid recovery scrubber. As a result. the total volume of all scrubbing solutions remains fixed. During normal operations. the level of reagents/water in the solid recovery scrubber always falls due to evaporation (which can be regulated to some extent by means of SHX). The liquid is continuously replenished by bringing in solution from the secondary scrubber. The process is controlled by a level sensor in the quencher. Subsequently, the condensation rate will be increased by a lowering of the temperature of the secondary scrubber solution to compensate for the volume transferred to the solid recovery scrubber, which completes the cycle. This cycle constitutes one specific implementation of the zero waste concept in the overall system.

The off-gas (S9) entering the quencher encounters a high velocity, high pressure, rapidly evaporating water/reagent spray jet (S12) which causes the contaminants in the off-gas to be impinged upon and deposited either on the walls of the scrubber or be collected in a turbulent water/reagent sump at the bottom of the scrubber. There are usually several spray nozzles serving recirculating stream S12. The recirculating pump (RPQ) should be of a type that not only can pump liquids containing large fractions of suspended solids (up to about 50%) but it should also resist corrosion due to a high reagent concentration (for example 2-3 molar sodium hydroxide). Progressive cavity pumps or diaphragm air pumps with suitable contact parts are suitable candidates. We have successfully used both types in our systems; the former for the Duramelter™ 100 and 300, and the latter for the 10.

During normal operation of the quencher, especially when acid gases are being scrubbed, the reaction with contaminants occurs above the spray nozzles where a misty curtain of the solution is normally formed. As a result, the scrubbing products tend to deposit onto the walls of the scrubber above and below the nozzles, which may eventually cause clogging of the upper part of the scrubber. To alleviate this problem, a mechanical scrapping mechanism (QCD) is built into the quencher. The scrapping mechanism includes a central shaft which is connected to a variable speed motor. To the shaft are welded rows of horizontal braces at the ends of which are connected vertical chain segments. The chains clear out the inner wall of the scrubber at a tight spacing. The chains are relatively loose lengthwise that gives them enough flexibility to knock down the scrubbing products that are continuously being deposited onto the scrubber walls.

The solid precipitates are transferred (S23) to the separator tank for recycling back to the melter, thus no additional solid or liquid wastes are formed in this operation.

The quenched exhaust gases from the solid recovery scrubber are directed into the secondary scrubber (S11) which is a recirculating, packed-bed type unit. Here final scrubbing of the more volatile or carry-over contaminants takes place.

The scrubber solution (S14) collected in the sump of the secondary scrubber is recycled to the sprayers through return line (S19), pump (RPS) and heat exchanger (SHX). The amount of accumulated solids in the secondary scrubber solution is much smaller than that in the solid recovery scrubber. Nevertheless, pump BPS was selected to be able to handle slurry type liquids.

After a long period (days or weeks depending on the specific application) of operation, the secondary scrubber is expected to have some solid accumulation at the bottom. The solids are then removed by a similar mechanism to that described for the solid recovery scrubber. Reagents are added to the scrubbers from the reagent reservoir by means of metering pumps CPQ and CPS.

Next, the exhaust from the secondary scrubber (S15) passes through a mist eliminator. The gas entering mist eliminator is normally saturated and would produce condensate when brought into contact with a large surface area associated with the mist eliminator. The condensate is returned to the secondary scrubber (S13).

A booster blower (IDB1) following the mist eliminator compensates for the pressure differential across the scrubbers, conduits, and the mist eliminator. The booster blower is equipped with a damper so that the pressure drops in the scrubbers are maintained at optimum operational efficiencies.

In order to be released to the atmosphere, the cleaned exhaust must be filtered through a HEPA filter to remove all remaining airborne particulates. However, to eliminate the possibility of condensation inside the HEPA filter which would render it ineffective, both the exhaust (S17) and the dilution air (A6) must be heated above the dew point of the resulting mixture. This is accomplished by means of the heaters H6 and H7. The HEPA filter assembly consists of a prefilter or a baghouse (depending on the system) and the HEPA unit itself. The solid particulates recovered from the filter are recycled back into the melter (S21). No secondary solid waste is generated and clean air is exhausted through the stack to the atmosphere (E1).

Sampling ports permit analysis of the off-gasses before and/or after the HEPA filter, depending on the system.

In the case of the FEMP wastes, the main function of the solid recovery scrubber is to reclaim solid salts which among others, including sodium, uranium, thorium, and silicon fluorides. The main constituent is sodium fluoride formed by reaction of gaseous hydrogen fluoride from the melter exhaust stream and the liquid sodium hydroxide which is sprayed onto the exhaust gases in the quencher. The ability to recover and recycle fluoride emission is critical for the entire operation. Fluorine is a crucial component in controlling stability of the glass compositions developed for FEMP high-fluoride wastes and its content must be maintained within a narrow range. Utilization of the solid recovery scrubber in the system is therefore absolutely necessary.

The secondary scrubber chemistry is similar to the solid recovery scrubber except that the concentration of sodium fluoride (or salts in general) is maintained below the saturation limit thus no solid phase is intentionally formed here (although some insoluble particulates are always present). The secondary scrubber serves also as a back up recovery system for the solid recovery scrubber to capture any gaseous components or aerosols that escape the quencher.

The process as described above is well suited for treatment of the mixed wastes. Employment of low energy ECS's facilitates operation under negative pressure without overly challenging mechanical design parameters. The probability of catastrophic events is extremely small with this system adding a significant safety factor to the entire operation.

The Process and Instrumentation Diagrams for the Duramelter™ 100 and the Duramelter™ 10 systems are presented in Figures 8.4 and 8.5 for comparison. One can see that these are conceptually similar systems with increasingly complex control provisions dictated by the scale of the process.

```
INITIAL PARAMETERS (ASSUMED):

Raw feed rate (lb/hr)..............:    259.0
Moisture content in feed (%).......:     70.0
Organic matter in feed (as LPE,%)..:      1.0
Sludge content in DRY feed (%).....:     50.0
Gypsum content.in DRY feed (%).....:      0.0
Iron content in DRY feed (%).......:      0.0
Feed rate of flux slurry (lb/hr)...:     68.5
Moisture content in flux slurry (%):     70.0
Na/Si frit c. (%, Na[- =CO3;+ =OH]):    -98.5
Min. carbon combustion fraction (%):     99.0
Sulfate.decomposition fraction (%).:      5.0
CaSO4 cont. of Na2SO4/CaSO4 eut.(%):     50.0
Air demand scaling factor (>=1)....:      2.0
Air inleakage, melter (scfm).......:     16.6
Air inleakage, shaft (scfm)........:     11.1
Ambient humidity (relative, %).....:     80.0
Ambient temperature (°F)...........:     85.0
Service water temperature (°F).....:     70.0
Melt temperature (°F)..............:     2200
Ind. pressure drop in melter (" WH):      6.0
Melt surface area (ft²)............:     3.55
Maximum melt depth (ft)............:     1.90
Minimum reactive slurry.depth (in).:     0.25
Maximum reactive slurry depth (in).:     1.50
Minimum idling glass depth (in)....:    16.00
Load security factor (>=1).........:     1.00
Quench water flow (gpm; - =recirc.):    -3.00
Max. allow. sump temperature (°F)..:      120
Air to quench duct (scfm)..........:       62
Air to stack (calc; scfm)..........:     1050
Desired stack temperature (calc;°F):       84
Tower sump capacity (gal.).........:      200
---------------------------------------------

MELTER MATERIAL BALANCE:

   INPUT (lb/hr)             OUTPUT (lb/hr)
=====================================================
Raw feed total...:   259.0 Melt total.......:    84.0
   Sludge........:    37.6    Glass.........:    82.7 .TOTAL GLASS per DAY......=   0.993 short tons/da
   Soil..........:    37.5    Slug total....:     1.3 .TOTAL SLUG per DAY.......=      30 lb/day
   Gypsum........:     0.0       Na+Ca eut..:     0.6 .TOTAL (SOLIDS) per DAY...=   1.008 short tons/da
   Iron..........:     0.0       Na2SO4.....:     0.6
   Carbon(as LPE):     2.6       CaSO4......:     0.0
   Moisture......:   181.3 Gases total......:   214.4
Flux slurry total:    68.5    Permanent tot.:   194.6
   Sodium precur.:    20.2       Air........:   165.2
   Sand..........:     0.3       N2(atm.)...:    29.4
   Moisture......:    48.0    Reactive total:    19.8
Air total........:   203.5       CO2........:    19.8
   Supply........:    76.6       SO2........:     0.0
   Inleakage.....:   126.9 Steam total......:   232.6
                              Moisture......:   229.3
                              Dehydration...:     0.0
                              Combustion....:     3.3
=====================================================
TOTAL INPUT......:   531.0 TOTAL OUTPUT.....:   531.0
```

Figure 8.1a
Sample output from Duramelter™ system modelling software used in system design.

```
INITIAL COMPOSITION DATA:

                            INITIAL COMPOSITION DATA
=================================================================================
         ¦   g1       g2       g3        g4*       g5*       g5*            ¦
COMPOSIT¦(sludge)  (soil)  (gypsum)  (iron)  (a. flux)(b. flux) MASSUMH ¦COMPOSIT
=================================================================================
 SiO2   ¦   14.0     54.4      0.0       0.0       1.5       1.5      26.0 ¦  SiO2
 Na2O   ¦    1.7      2.2      0.0       0.0      57.6      76.3      13.3 ¦  Na2O
 MgO    ¦   25.7      5.1      0.0       0.0       0.0       0.0      11.6 ¦  MgO
 CaO    ¦   37.2     21.3     38.6       0.0       0.0       0.0      22.0 ¦  CaO
 Al2O3  ¦    2.1      7.3      0.0       0.0       0.0       0.0       3.5 ¦ Al2O3
 Fe2O3  ¦    3.2      3.3      0.0     143.0       0.0       0.0       2.5 ¦ Fe2O3
 SO3    ¦    0.0      0.1      2.8       0.0       0.0       0.0       0.0 ¦  SO3
 Others ¦    7.4      4.4      0.1       0.0       0.0       0.0       4.4 ¦ Others
---------------------------------------------------------------------------------
MASSUMV ¦   34.3     36.8      0.0       0.0      12.2      16.0      83.3 ¦ MASSUMV
=================================================================================
H2O(cr) ¦    0.0      0.0      6.1       0.0       0.0       0.0       0.0 ¦H2O(cr)
H2O(ch) ¦    0.0      0.0      0.0       0.0       0.0      22.2       0.0 ¦H2O(ch)
 CO2    ¦    8.7      0.0      0.0       0.0      40.9       0.0      11.7 ¦   CO2
 SO3    ¦    0.0      1.9     52.4       0.0       0.0       0.0       0.7 ¦   SO3
---------------------------------------------------------------------------------
MASSUMV ¦    3.3      0.7      0.0       0.0       8.4       4.6      12.4 ¦ MASSUMV
=================================================================================
O2(ch)  ¦    0.0      0.0      0.0     -43.0       0.0       0.0      -0.0 ¦ O2(ch)
---------------------------------------------------------------------------------
MASSUMV ¦    0.0      0.0      0.0      -0.0       0.0       0.0      -0.0 ¦ MASSUMV
=================================================================================
GMASSUMV¦   37.6     37.5      0.0       0.0      20.6      20.6      95.7 ¦GMASSUMV
=================================================================================

FINAL COMPOSITION DATA:

                  FINAL COMPOSITION DATA
====================================================
        ¦ lb/hr*   lb/hr*    gt(%)   ga*(%)  [ga-gt]*
COMPOSIT¦in glass net loss (target) (calc.) (deviat.)
====================================================
 SiO2   ¦  26.0      0.0     31.4     31.4     0.0
 Na2O   ¦  12.9      0.4     15.5     15.6     0.1
 MgO    ¦  11.6      0.0     13.0     14.0     1.0
 CaO    ¦  21.8      0.1     26.8     26.4    -0.4
 Al2O3  ¦   3.5      0.0      3.7      4.3     0.6
 Fe2O3  ¦   2.5      0.0      2.6      3.0     0.4
 SO3    ¦   0.0      0.0      0.0      0.0     0.0
 Others ¦   4.4      0.0      7.0      5.4    -1.6
----------------------------------------------------
 TOTAL  ¦  82.7      0.5    100.0    100.0     *
====================================================
  # - includes 9.2% B2O3 distributed equally between SiO2 & Na2O
```

Figure 8.1b
Sample output from Duramelter™ system modelling software used in system design.

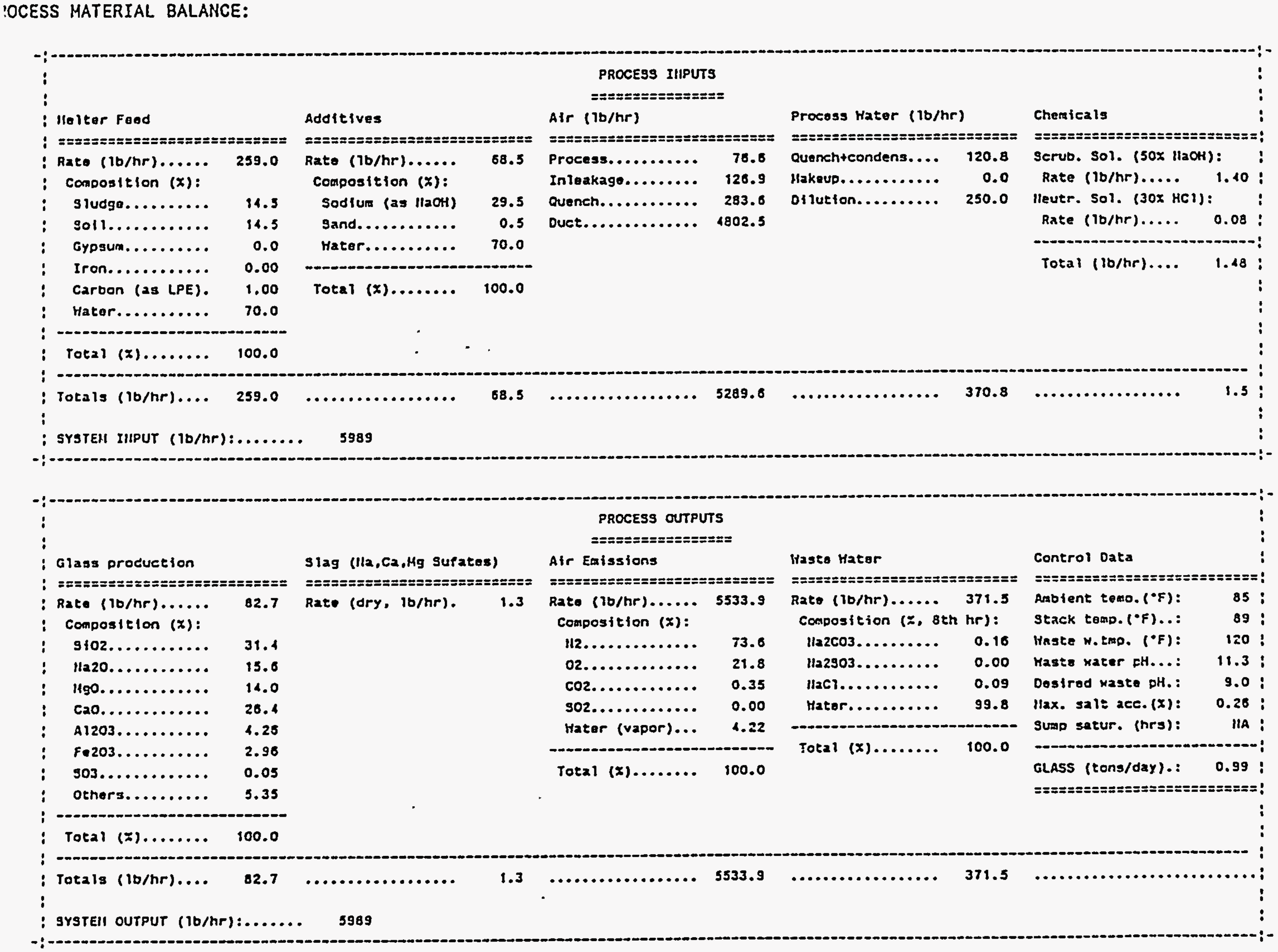
```
SUMMARY OF DESIGN PARAMETERS:

                         SUMMARY OF DESIGN PARAMETERS
 ============================================================================
 SYSTEM ¦ Quench :    R    [Na2CO3]:    0.25% Sump pH:    11.3          ¦ SYSTEM
 ----------------------------------------------------------------------------
Temperatures (°F):                   Supply/drain lines:
------------------                   -------------------

Ambient temp.............:        85 Air:                        (scfm)   (acfm)
Service water temp.......:        70  Dilution air to quencher.:     62       65
Melt temp................:      2200  Dilution air to stack....:   1050     1100
Melter exit temp.........:       669  TOTAL flow through tower.:    157      175
Quencher inlet temp......:       512  TOTAL flow through stack.:   1206     1274
Tower inlet temp (satur.).:      177  Emergency air to bypass..:    482      506
Internal tower spray temp.:       95  TOTAL emergency flow.....:    639      872
Sump water temp..........:       120 Water (gpm):
Tower gas exit temp.......:      120  Makeup / overflow (- / +):   0.24
Stack temp. (diluted).....:       89   Minimum quench flow.....:   0.07
Max. allowable duct temp..:      250   Minimum spray flow......:   11.0
                                       Min. tower recirculation:   10.9
Miscellanous:                         Min. serv. water dem.(HX):   10.8
-------------                         Min. util. w. dem. (mkup):   0.00
Ambient humidity (%, rel.):       80  Dilution to sump.........:   0.5
Max. allow. salt conc. (%):        1 Wastewater (gpm)..........:   0.74
                                     Chemicals (gph):
Cooling requirements (tc):            50% NaOH (scrubber)......:  0.109
--------------------------            30% HCl (neutralizer)....:  0.009
 Heat exchanger...........:     11.2
 #Cond. at satur. temp....:      0.0 Power requirements (kW):
 *Cond. at sump water temp:     11.2 ------------------------
 #Cond. at ambient temp...:     16.3 Req. for vitrification...:   14.4
 Air conditioning.........:      8.8 Radiative losses.........:   16.6
TOTAL cooling demand......:     20.0 Off-gas losses...........:   63.2
                                     TOTAL power demand........:   94.2
=============================================================================
 * - basis for calculation; # - data for comparision
 R - Recirculated quench water; X - eXternal quench water

Maximum melter capacity (lb)...............:    1150
Usefull melter capacity (lb)...............:     265
Time to accumul. reactive sludge layer (hr).:   11.0
Glass to accumul. before sludge reacts (lb).:    909
```

Figure 8.1c
Sample output from Duramelter™ system modelling software used in system design.

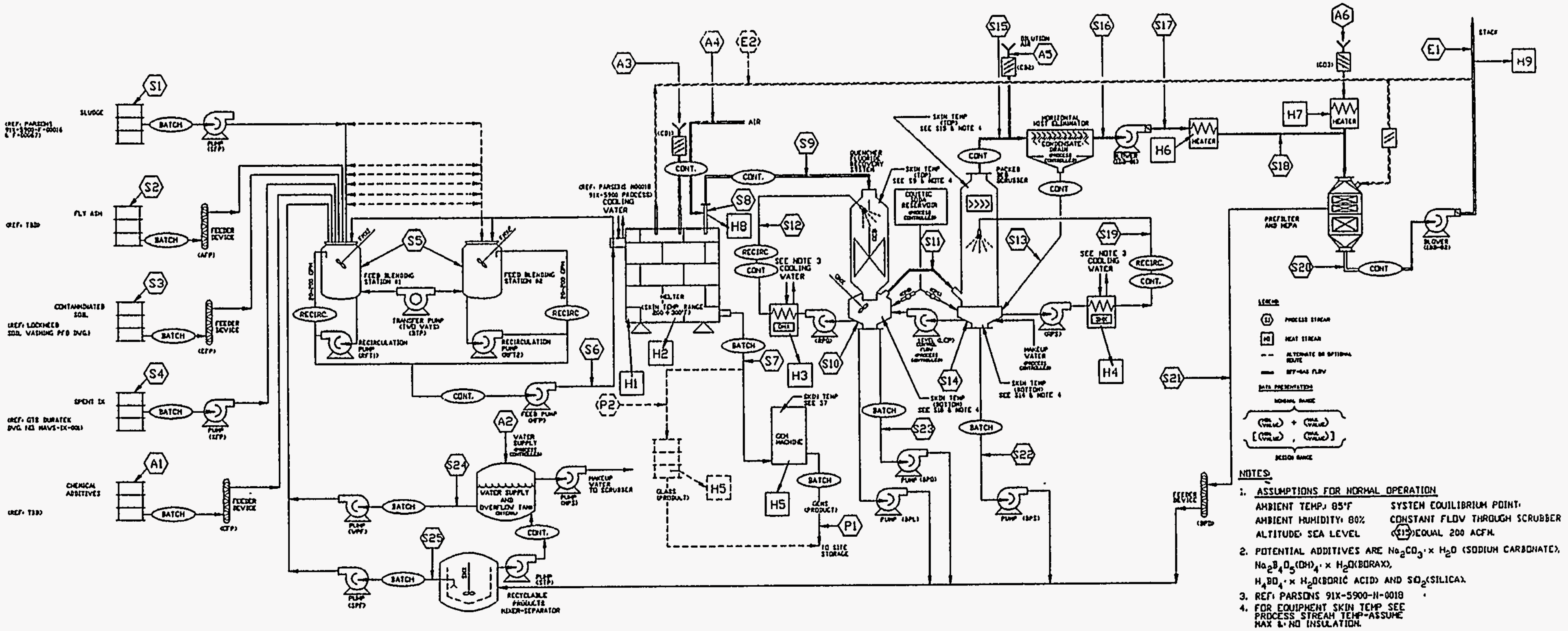


```
OCESS MATERIAL BALANCE:

-¦-------------------------------------------------------------------------------------------------------------------------------------------------¦-
 ¦                                                                 PROCESS INPUTS                                                                 ¦
 ¦                                                                ================                                                                ¦
 ¦ Melter Feed                  Additives                    Air (lb/hr)                  Process Water (lb/hr)        Chemicals                  ¦
 ¦ ==========================   ==========================   ==========================   ==========================   ==========================¦
 ¦ Rate (lb/hr)......   259.0   Rate (lb/hr)......    68.5   Process...........    78.6   Quench+condens....   120.8   Scrub. Sol. (50% NaOH):    ¦
 ¦  Composition (%):             Composition (%):            Inleakage.........   126.9   Makeup............     0.0    Rate (lb/hr).....    1.40 ¦
 ¦   Sludge..........    14.5     Sodium (as NaOH)    29.5   Quench............   283.6   Dilution..........   250.0   Neutr. Sol. (30% HCl):     ¦
 ¦   Soil............    14.5     Sand............     0.5   Duct..............  4802.5                                 Rate (lb/hr).....    0.08 ¦
 ¦   Gypsum..........     0.0     Water...........    70.0                                                             --------------------------¦
 ¦   Iron............    0.00   --------------------------                                                              Total (lb/hr)....    1.48 ¦
 ¦   Carbon (as LPE).    1.00    Total (%)........   100.0                                                                                        ¦
 ¦   Water...........    70.0                                                                                                                     ¦
 ¦ --------------------------                                                                                                                     ¦
 ¦  Total (%)........   100.0                                                                                                                     ¦
 ¦ ---------------------------------------------------------------------------------------------------------------------------------------------- ¦
 ¦ Totals (lb/hr)....   259.0   ..................    68.5   ..................  5289.6   ..................   370.8   ..................     1.5 ¦
 ¦                                                                                                                                                ¦
 ¦ SYSTEM INPUT (lb/hr):........     5989                                                                                                         ¦
-¦-------------------------------------------------------------------------------------------------------------------------------------------------¦-

-¦-------------------------------------------------------------------------------------------------------------------------------------------------¦-
 ¦                                                                 PROCESS OUTPUTS                                                                ¦
 ¦                                                                =================                                                               ¦
 ¦ Glass production             Slag (Na,Ca,Mg Sufates)      Air Emissions                Waste Water                  Control Data               ¦
 ¦ ==========================   ==========================   ==========================   ==========================   ==========================¦
 ¦ Rate (lb/hr)......    82.7   Rate (dry, lb/hr).     1.3   Rate (lb/hr)......  5533.9   Rate (lb/hr)......   371.5   Ambient temp.(°F):      85 ¦
 ¦  Composition (%):                                          Composition (%):             Composition (%, 8th hr):    Stack temp.(°F)..:      89 ¦
 ¦   SiO2............    31.4                                  N2..............    73.6     Na2CO3..........    0.16   Waste w.tmp. (°F):     120 ¦
 ¦   Na2O............    15.6                                  O2..............    21.8     Na2SO3..........    0.00   Waste water pH...:    11.3 ¦
 ¦   MgO.............    14.0                                  CO2.............    0.35     NaCl............    0.09   Desired waste pH.:     9.0 ¦
 ¦   CaO.............    26.4                                  SO2.............    0.00     Water...........    99.8   Max. salt acc.(%):    0.26 ¦
 ¦   Al2O3...........    4.26                                  Water (vapor)...    4.22   --------------------------   Sump satur. (hrs):      NA ¦
 ¦   Fe2O3...........    2.96                              --------------------------    Total (%)........   100.0   --------------------------¦
 ¦   SO3.............    0.05                                 Total (%)........   100.0                                GLASS (tons/day).:    0.99 ¦
 ¦   Others..........    5.35                                                                                          ==========================¦
 ¦ --------------------------                                                                                                                     ¦
 ¦  Total (%)........   100.0                                                                                                                     ¦
 ¦ ---------------------------------------------------------------------------------------------------------------------------------------------- ¦
 ¦ Totals (lb/hr)....    82.7   ..................     1.3   ..................  5533.9   ..................   371.5   ..........................¦
 ¦                                                                                                                                                ¦
 ¦ SYSTEM OUTPUT (lb/hr):.......     5989                                                                                                         ¦
-¦-------------------------------------------------------------------------------------------------------------------------------------------------¦-
```

Figure 8.1d
Sample output from Duramelter™ system modelling software used in system design.



NOTES:

1. ASSUMPTIONS FOR NORMAL OPERATION
   AMBIENT TEMP: 85°F
   AMBIENT HUMIDITY: 80%
   ALTITUDE: SEA LEVEL
   SYSTEM EQUILIBRIUM POINT:
   CONSTANT FLOW THROUGH SCRUBBER
   (S15) EQUAL 200 ACFM.
2. POTENTIAL ADDITIVES ARE $Na_2CO_3 \cdot x\ H_2O$ (SODIUM CARBONATE), $Na_2B_4O_5(OH)_4 \cdot x\ H_2O$ (BORAX), $H_4BO_4 \cdot x\ H_2O$ (BORIC ACID) AND SiO_2 (SILICA).
3. REF: PARSONS 91X-5900-H-0018
4. FOR EQUIPMENT SKIN TEMP SEE PROCESS STREAM TEMP-ASSUME MAX & NO INSULATION.

PROCESS STREAM	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
STREAM DESCRIPTION STREAM TYPE	SLUDGE SUSPENDED SOLIDS	FLY ASH DRY SOLIDS	CONTAMIN. SOIL DRY SOLIDS	SPENT IX MEDIA	BLENDED FEED (BATCH) SLURRY	MELTER FEED SLURRY	MOLTEN GLASS LIQUID	MELTER OFF-GAS	MELTER OFF-GAS (DILUTED)	QUENCHER SUMP (BATCH) SLURRY	MELTER OFF-GAS (QUENCHED)	QUENCHER RECIRC. SOLUTION	CONDENSATE DRAIN LIQUID
CHARACTIZATION	40-70%H_2O	<10%H_2O	<30%H_2O	<10%H_2O	30-70%H_2O 5 DAY CYCLE	50-70%H_2O	VISCOSITY 10 ÷ 20 POISE 6 HR. CYCLE	UNDERSATUR. GAS	UNDERSATUR. GAS	SUPERNAT 3M NaOH 1M F-	SATURATED GAS & MIST	3M NaOH NaF SAT	WATER
TEMP. (°F)	85 [32, 100]	85 [0, 100]	85 [0, 100]	85 [0, 100]	85 [32, 100]	85 [32, 100]	2102 [1900, 2200]	536 ÷ 684 [0, 750]	203 ÷ 420 [0, 750]	111 ÷ 165 [70, 195]	111 ÷ 165 [0, 195]	111 ÷ 165 [70, 195]	100 ÷ 120 [70, 160]
PRESS. (AS INDICATED)	N/A	N/A	N/A	N/A	N/A	< 10psig [0, 5]psig	FREE FLOW	-6 ÷ -3in.w.c. [-6, -0]in.w.c.	-6 ÷ -3in.w.c. [-6, 0]in.w.c.	-5 ÷ -3in.w.c. [-6, 0]in.w.c.	-5 ÷ -3in.w.c. [-6, 0]in.w.c.	30 ÷ 40psig [25, 45]psig	FREE FLOW
GAS FLOW (SCFH)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	101 ÷ 122 [0, 150]	165 ÷ 237 [0, 300]	N/A	180 ÷ 330 [0, 350]	N/A	N/A
MASS FLOW (LB/H)	2800 ÷ 14500 [0, 15000]	160 ÷ 430 [0, 1000]	480 ÷ 1450 [0, 1000]	138 [0, 1000]	BATCH SIZE (48500) LB	69.5 ÷ 336 [0, 350]	27 ÷ 85 [0, 90]	185 ÷ 441 [0, 500]	894 ÷ 1078 [0, 1200]	BATCH SIZE (500) LB	904 ÷ 1112 [0, 1200]	MIN. REC (01)GPM	VARY, MAX (01)GPM
DENSITY (LB/SCF)	156 ÷ 218 [62.4, 249]	105 ÷ 133 [62.4, 249]	105 ÷ 133 [62.4, 249]	VARY [62.4, 249]	VARY [62.4, 249]	VARY [62.4, 249]	148 ÷ 164 [125, 187]	0.063 ÷ 0.081 [0.060, 0.200]	0.070 ÷ 0.090 [0.060, 0.200]	VARY [62.4, 81.2]	0.068 ÷ 0.086 [0.060, 0.200]	VARY [62.4, 74.9]	62.4 [62.4]
SERVICE SEVERITY	ABRASIVE	ABRASIVE	ABRASIVE	ABRASIVE	ABRASIVE	ABRASIVE	HIGH TEMP CORR. (ALK, F-)	HIGH TEMP. CORR. GAS W/ ABRASIVE	MED. TEMP CORR. GAS W/, ABRASIVE	CORROSIVE NaF, pH=14	MED. TEMP CORR. GAS W/ ABRASIVE	CORROSIVE (ALK, F-)	pH < 11

PROCESS STREAM	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25
STREAM DESCRIPTION STREAM TYPE	SCRUBBER SUMP (BATCH) SOLUTION	SCRUBBER EXHAUST GAS	DEMISTER EXHAUST GAS	BOOSTER BLOWER EXHAUST GAS	REHEATER EXHAUST GAS	SCRUBBER RECIRC. SOLUTION	HEPA EXHAUST GAS	BAGHOUSE RECYCLE SOLID	SCRUBBER DISCHARGE SLURRY	QUENCHER DISCHARGE SLURRY	PROCESS WATER SOLUTION	INTEGRATED RECYCLE SLURRY
CHARACTIZATION	SUPERNAT 0.7 M Na+ 1.6 M [illegible]	SATURATED GAS & MIST	SATURATED GAS	SATURATED GAS	UNSATURATED GAS	0.005 M NaOH 0.6 M NaF max.	UNDERSATUR. OR SATUR. GAS	ALL PARTICULATES [illegible]	96-99.73%H_2O	30-70%H_2O	DILUTED VARYING COMP.	20-70% H_2O
TEMP. (°F)	101 ÷ 120 [70, 160]	101 ÷ 120 [70, 160]	100 ÷ 120 [70, 160]	102 ÷ 125 [70, 160]	110 ÷ 140 [70, 160]	90 ÷ 95 [70, 120]	107 ÷ 130 [70, 160]	85 [0, 100]	101 ÷ 120 [70, 160]	111 ÷ 165 [70, 195]	85 [40, 100]	85 [40, 100]
PRESS. (AS INDICATED)	N/A	-4 ÷ -3in.w.c. [-6, 0]in.w.c.	-4 ÷ -3in.w.c. [-6, 0]in.w.c.	-3 ÷ -1in.w.c. [-6, 0]in.w.c.	-3 ÷ -1in.w.c. [-6, 0]in.w.c.	30 ÷ 40psig [25, 45]psig	ATM [0]in.w.c.	ATM [0]in.w.c. [0, 0.5][illegible] CONTR	TO MATCH LINE ΔP	TO MATCH LINE ΔP	TO MATCH LINE ΔP	TO MATCH LINE ΔP
GAS FLOW (SCFH)	N/A	SEE NOTE 1 [145, 175] ACFM	100 ÷ 190 [0, 215]	180 ÷ 190 [0, 300]	180 ÷ 190 [0, 300]	N/A	1670 ÷ 1970 [0, 2500]	N/A	N/A	N/A	N/A	N/A
MASS FLOW (LB/H)	BATCH SIZE (500) LB	698 ÷ 961 [912]	818 ÷ 889 [0, 980]	818 ÷ 889 [0, 1370]	818 ÷ 889 [0, 1370]	MIN. REC (10)GPM	TBD [0, 11250]	TBD [0, 0.002]	0 ÷ 9.6 [0, 15]	2.7 ÷ 10.7 [0, 15]	VARY [0, 40]	8.7 ÷ 28.3 [0, 300]
DENSITY (LB/SCF)	VARY [62.4, 68.7]	0.075 ÷ 0.076 [0.076]	0.075 ÷ 0.076 [0.076]	0.075 ÷ 0.076 [0.076]	0.075 ÷ 0.076 [0.076]	VARY [62.4, 68.7]	0.075 ÷ 0.076 [0.076]	TBD [60, 560]	VARY [62.4, 68.7]	VARY [62.4, 81.2]	62.4 [62.4]	VARY [62.4, 81.2]
SERVICE SEVERITY	CORROSIVE NaF, pH=13	MOIST AIR	MOIST AIR	MOIST AIR	WARM AIR	CORROSIVE (ALK, F-)	AIR	FINE DUST	CORROSIVE NaF, pH=13	CORROSIVE NaF, pH=14	MILD CORR. pH < 11	CORR., ABR. pH=14

PROCESS STREAM	A1	A2	A3	A4	A5	A6	P1	P2	E1	E2
STREAM DESCRIPTION STREAM TYPE	CHEMICAL DRY SOLIDS	PROCESS WATER ADDITIVE	INLEAKAGE AND PROCESS AIR	DILUTION AIR (QUENCHER)	DILUTION AIR (LINE)	DILUTION AIR (STACK)	GLASS GEMS	BULK GLASS	PROCESS EXHAUST	EMERGENCY EXHAUST
CHARACTIZATION	SEE NOTE 2	NON CHLOR WATER	ASSUMED INLEAKAGE [illegible] LB/H	AMBIENT AIR	AMBIENT AIR	AMBIENT AIR	6 HR. CYCLE	6 HR CYCLE	DILUTED HEPA EXH	DESIGN PARAM. ONLY
TEMP. (°F)	85 [32, 100]	85 [40, 120]	85 [0, 100]	85 [0, 100]	85 [0, 100]	85 [0, 100]	85 ÷ 1400 [0, 1500]	85 ÷ 2100 [0, 2500]	85 ÷ 96 [41, 101]	(750)
PRESS (AS INDICATED)	N/A	AS SUPPLIED	0 ÷ 7psig [0, 10]psig	0 ÷ 7psig [0, 20]psig	ATM (ATM)	ATM (ATM)	N/A	N/A	ATM (0)in.w.c.	(-85)in.w.c.
GAS FLOW (SCFH)	N/A	N/A	313 ÷ 458 [0, 530]	135 ÷ 155 [0, 173]	75 ÷ 155 [0, 173]	1450 ÷ 1700 [0, 2200]	N/A	N/A	1670 ÷ 1980 [0, 2500]	(750)
MASS FLOW (LB/H)	1.3 ÷ 3.0 [0, 10]	VARY [0, 40]	143 ÷ 209 [0, 250]	617 ÷ 709 [0, 800]	343 - 572 [0, 800]	6000 ÷ 8100 [0, 10,000]	27 ÷ 85 [0, 90]	27 ÷ 85 [0, 90]	7615 ÷ 9029 [0, 10,000]	(3500)
DENSITY (LB/SCF)	VARY [62.4, 249]	62.4 (62.4)	0.076 (0.076)	0.076 (0.076)	0.076 (0.076)	0.076 (0.076)	150 ÷ 162 (156)	150 ÷ 162 (156)	0.076 (0.076)	(0.076)
SERVICE SEVERITY	BORAX CARBONATE	WATER	AIR	AIR	AIR	AIR	MOLT. GLASS SOLIDIFYING	MOLT. GLASS SOLIDIFYING	HUMID AIR MAY BE CONDENSING	HIGH TEMP CORR. GAS W/ ABRASIVE

HEAT STREAM	VALUE	NOTE
H1	34.4 ÷ 95.7kW [0, 120]kW	TOTAL ELECTRIC
H2	< (17)kW	RADIATIVE LOSS
H3	0 ÷ 0.8TC [0, 2]TC	TONS OF COOLING TO HEXCH.
H4	8.2 ÷ 10.3TC [0, 20]TC	TONS OF COOLING TO HEXCH.
H5	6.1 ÷ 8.8TC [0, 10]TC	HEAT DUMPED TO ENVIR.
H6	<(22)kW	POWER TO HEATER (ELECTRIC)
H7	<(18)kW	POWER TO HEATER (ELECTRIC)
H8	13.3 ÷ 64.0kW [0, 80]kW	TOTAL HEAT LOSS THROUGH OFF-GAS
H9 (LESS H7)	12.4 ÷ 27.9kW [0, 80]kW	HEAT LOSS THROUGH STACK

Figure 8.2
Process Flow Diagram-
MAWS (Fernald) Process

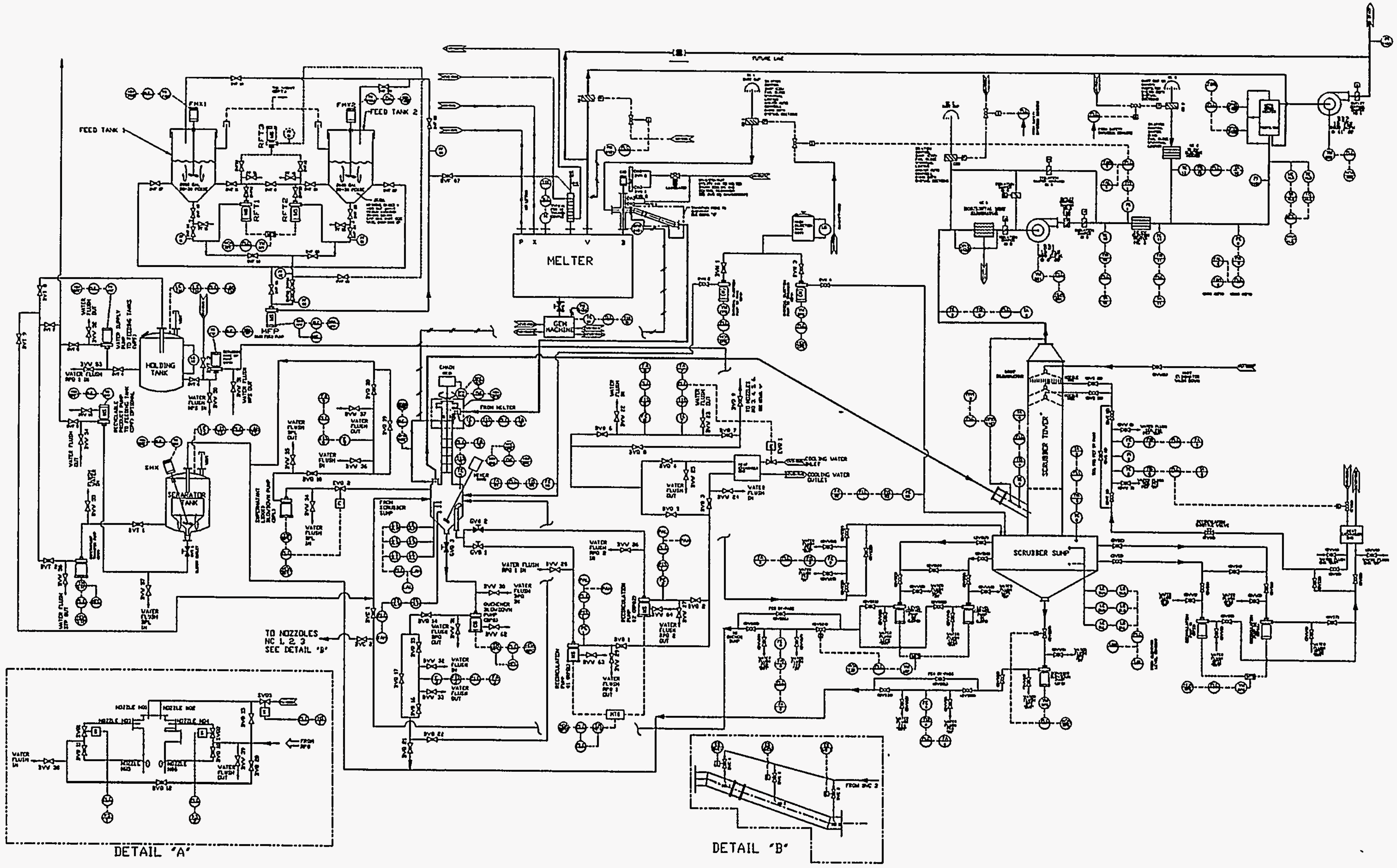
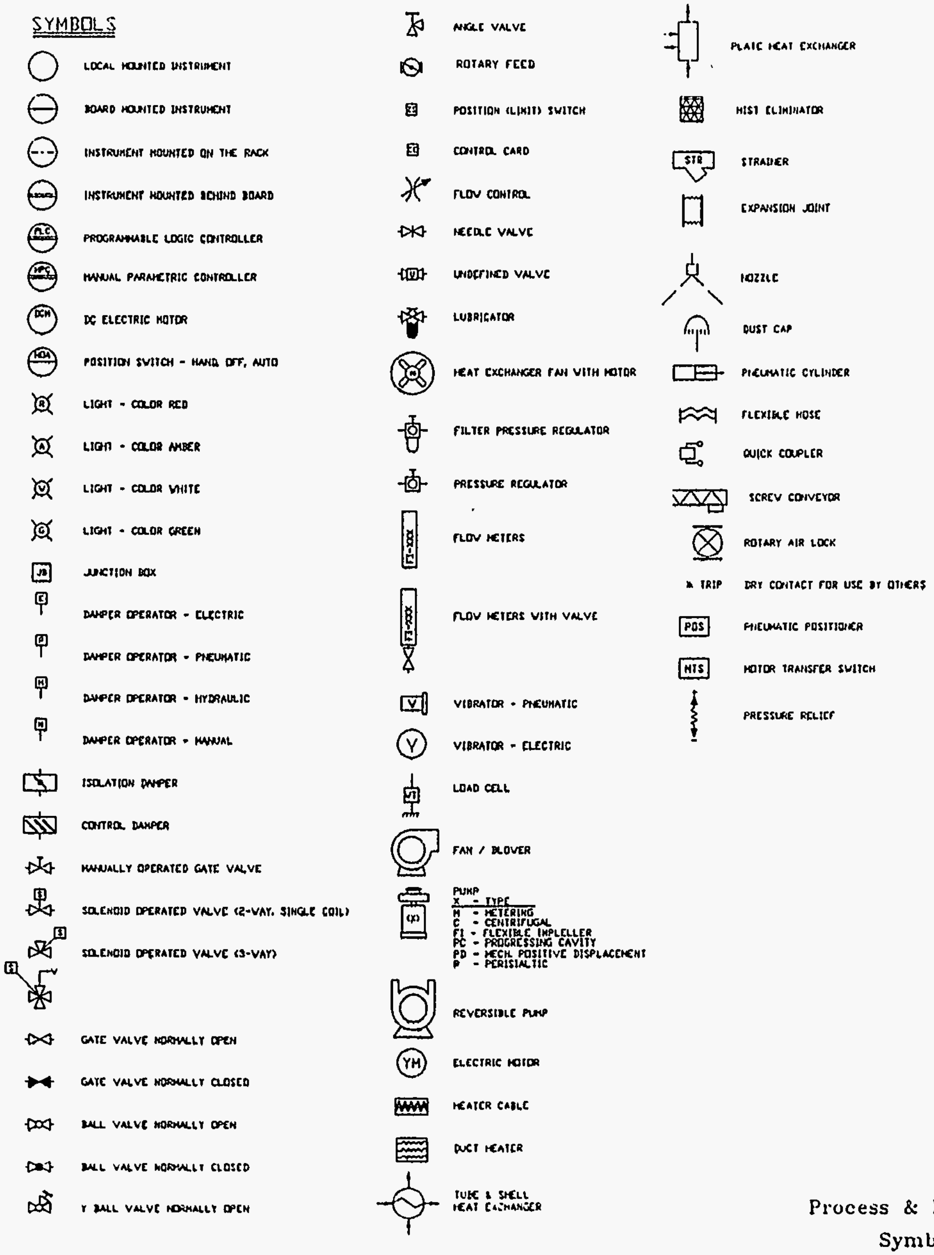


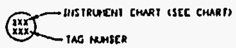
Figure 8.3a
Process & Instrumentation Diagram–
Duramelter™ 300 System at Fernald

APPENDIX 1B: P & ID LEGENDS AND SYMBOLS

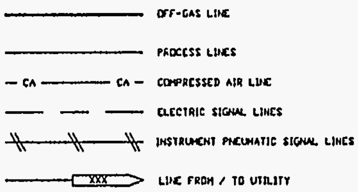
SYMBOLS



INSTRUMENT IDENTIFICATION



LINE IDENTIFICATION



	FIRST LETTER		SUCCEEDING LETTERS		
	MEASURED OR INITIATING VARIABLE	MODIFIER	READOUT OR PASSIVE FUNCTION	OUTPUT FUNCTION	MODIFIER
A	ANALYSIS		ALARM		
B	BURNER FLAME		USER'S CHOICE	USER'S CHOICE	USER'S CHOICE
C	CONDUCTIVITY (ELECTRICAL)			CONTROL	
D	DENSITY (MASS) OR SPECIFIC GRAVITY	DIFFERENTIAL			
E	VOLTAGE (EMF)		PRIMARY ELEMENT		
F	FLOW RATE	RATIO (FRACTION)			
G	GAGING (DIMENSIONAL)		GLASS		
H	HAND (MANUALLY INITIATED)				HIGH
I	CURRENT (ELECTRICAL)		INDICATE		
J	POWER	SCAN			
K	TIME OR TIME-SCHEDULE			CONTROL STATION	
L	LEVEL		LIGHT (PILOT)		LOW
M	MOISTURE OR HUMIDITY				MIDDLE OR INTERMEDIATE
N	USER'S CHOICE		USER'S CHOICE	USER'S CHOICE	USER'S CHOICE
O	USER'S CHOICE		ORIFICE (RESTRICTION)		
P	PRESSURE OR VACUUM		POINT (TEST CONNECTION)	PRESSURE	
Q	QUANTITY OR EVENT	INTEGRATE OR TOTALIZE			
R	RADIOACTIVITY		RECORD OR PRINT		
S	SPEED OR FREQUENCY	SAFETY		SWITCH	
T	TEMPERATURE			TRANSMIT	
U	MULTIVARIABLE		MULTIFUNCTION	MULTIFUNCTION	MULTIFUNCTION
V	VIBRATION			VALVE, DAMPER, OR LOUVER	
W	WEIGHT OR FORCE		WELL		
X	UNCLASSIFIED		UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED
Y	SOLID			RELAY OR COMPUTE	
Z	POSITION			DRIVE, ACTUATE OR UNCLASSIFIED FINAL CONTROL ELEMENT	

THIS TABLE APPLIES ONLY TO THE FUNCTIONAL IDENTIFICATION OF INSTRUMENTS.

Figure 8.3b
Process & Instrumentation Diagrams–
Symbols & Abbreviations

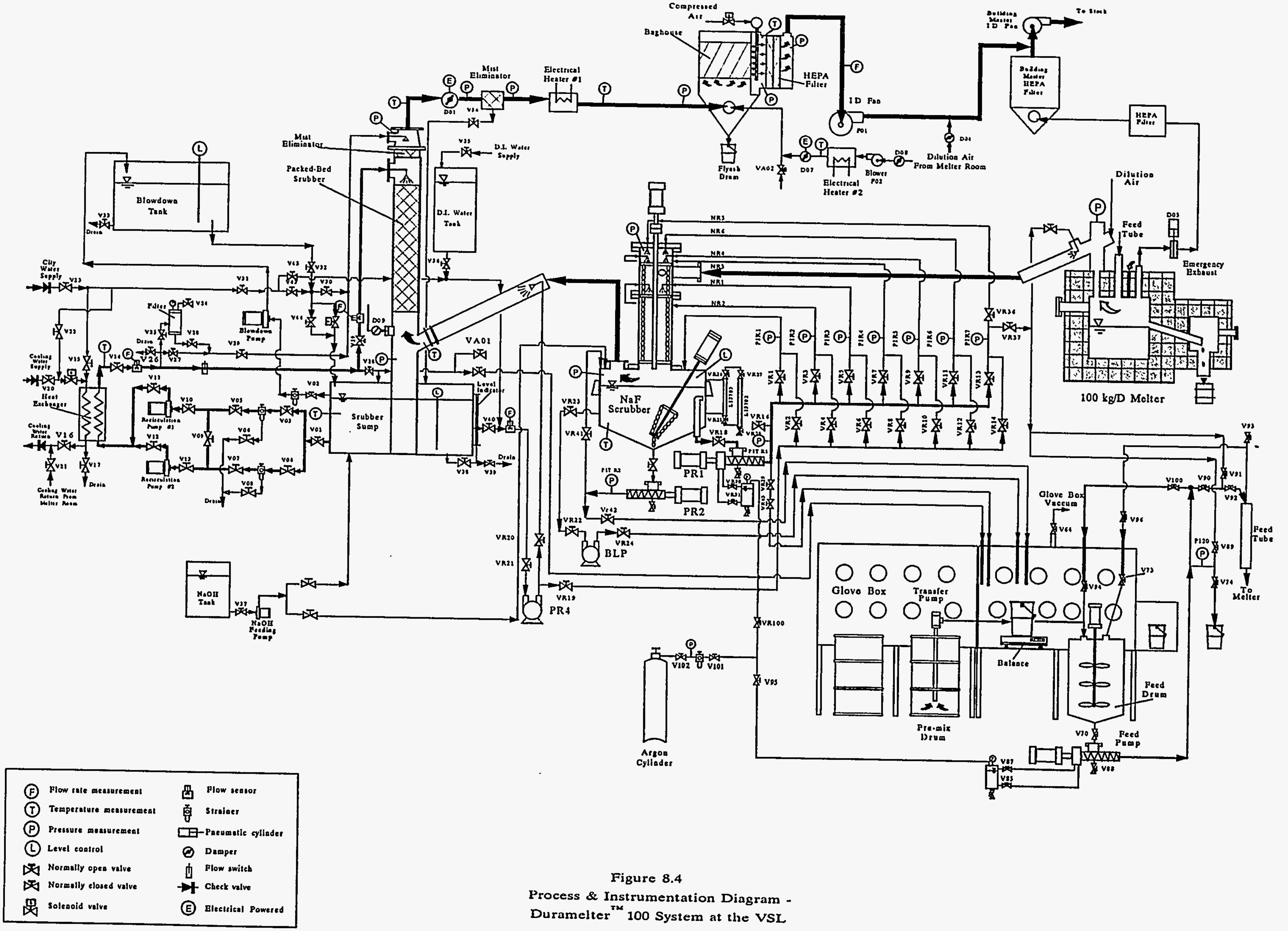


Figure 8.4
Process & Instrumentation Diagram -
Duramelter™ 100 System at the VSL

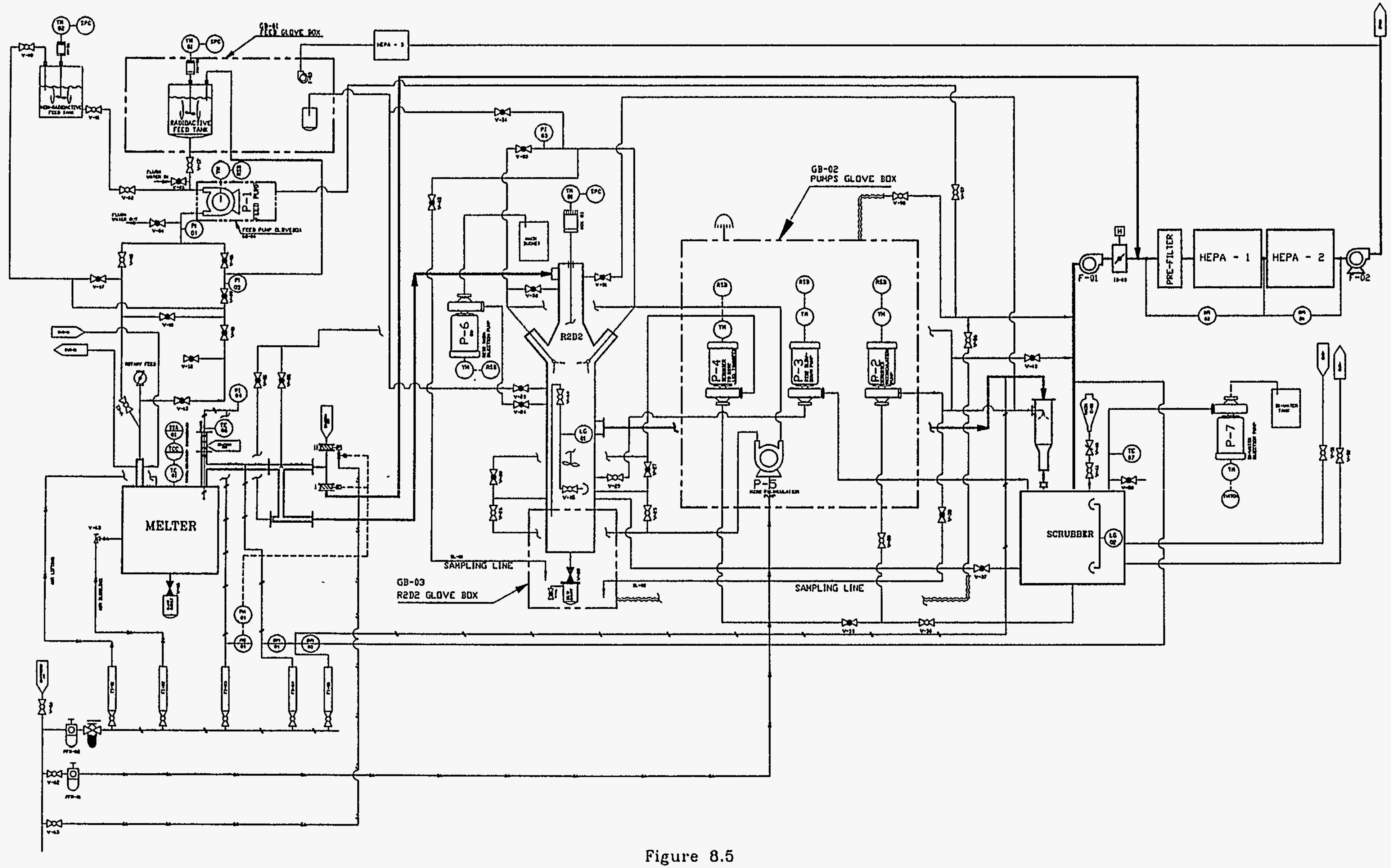


Figure 8.5
Process & Instrumentation Diagram–
Duramelter™ 10 System at the VSL

SECTION 9.0
Duramelter™ 10 Runs

9.1 Introduction

The crucible melt studies discussed in the previous sections demonstrate that a number of the MAWS glasses meet the requirements for processability and leach resistance. The requirements that were determined for processing wastes in a joule-heated melter are that the viscosity is in the range of 2-80 poise, the conductivity is in the range of 0.05-0.55 S/cm at 1100-1150°C and that the glass has a liquidus temperature below 1050°C. Crystallization was identified as one of the most constraining factors for these melts, but we determined several viable compositions containing 5-12 wt.% fluoride. Using FE1 sludge, the high-fluoride end of that range effectively sets the high end of FE1 (Pit 5) waste loadings at 75-80% FE1 (wet basis). When combined with Lockheed soil-wash fractions and NaF recovered from our scrubber system, total waste loadings can be as high as 96 wt.%. Four surrogate compositions were tested using a Duramelter™ joule-heated vitrification system, with a nominal glass output rate of 10 kg/day. Subsequently, two compositions employing FE1 (Pit 5 sludge), Fernald soils and Lockheed soil-wash fractions were used to make two radioactive glasses in the Duramelter™ 10 system. Recycled NaF was also added to these feeds.

These small-scale continuous melter tests provide essential information that cannot be obtained from crucible melts and such studies are necessary for several reasons: (1) to determine the off-gas release and potential off-gas system needs and performance; (2) to examine the effect of cold caps on both throughput rates and in mitigation of off-gas release; and (3) to demonstrate the recycle of the fluoride and other components that are lost to the off-gas system. The last point is especially important for these glasses because we have seen that significant amounts of fluoride are lost when the MAWS wastes or glasses are heated to temperatures above about 1000°C. The fluoride recycle system that we have demonstrated uses a NaOH scrubber solution which combines with the off-gas stream to form NaF. The system operates in such a way that the NaF can be removed from the scrubber solution as a solid in slurry form which is then used as an additive for the next batch of feed. This stream provides part of the sodium required for the batch. This method of recycling the fluoride lost during vitrification is shown schematically in Figure 9.1.

In this section we present the results of four surrogate 10 kg/day melter runs and two radioactive runs. Batch compositions that were determined to be processable and leach resistant based on the data presented in the previous sections were used to produce processable leach resistant glasses from the melter runs.

9.2 Results for Non-radioactive Surrogate Runs

Extensive system tests were performed with fluoride-containing, but non-radioactive, surrogate feeds which cover the range of compositions shown in Table 9.1. Note that some of the components lie outside the range (given in Table 6.6) of processable compositions demonstrated in crucible studies. The data and experience gained with the crucible melt studies permit us to make small extrapolations beyond that range with reasonable confidence, however. Thus, some runs used slightly higher Al_2O_3 and MgF_2 levels to account for small variations in sludge composition, and higher sodium levels to test a wider conductivity range in the melter. Four of the individual feed compositions, both in terms of components added to the batch and the target compositions, are given in Table 9.2. These runs were performed in order to test a variety of system modifications that were made for these high-fluoride feeds prior to radioactive operations. Note that in one surrogate run, we used non-radioactive Fernald whole soil as part of the feed. This enabled us to determine that our simple feed system could handle soil particles < 75 microns (passing mesh #200). Over 100 kg of glass was produced in the surrogate runs. Analysis of the glasses produced from the feeds listed in Table 9.2 are shown in Table 9.3. The glass MIC2-138A was produced by feeding five batches (each batch producing 2.4 kg glass) of MICRO-6A feed. This many batches of the same feed produced about 80% turnover of the glass in the melter; hence the analyzed glass is close to its target composition. The glass MIC2-142A was produced from five batches of a different feed: MICRO-8A. Again, because we fed enough of the same feed, the targeted and analyzed compositions are very close with the exception of fluoride. For all of the surrogate runs, we had large amounts of idling time, producing more fluoride loss from the glass than desired. The glasses MIC3-36A and MIC3-42A were produced from MICRO-4B and MICRO-7B feeds, respectively. Both of these glasses were drained before enough feed was added to achieve a one-half turnover of the glass in the melter. As a result, the glasses were off the target compositions.

The glasses produced from these four surrogate runs were also analyzed to determine their viscosities and conductivities over a range of temperatures, with the results shown in Tables 9.4(a) and 9.4(b). All four glasses have processable viscosities and conductivities in the temperature range of 1100-1150°C. It is not possible to compare the viscosities and conductivities of these surrogate glasses to the crucible melts due to a number of factors: (1) the surrogate compositions were used to encompass a range of compositions rather than imitate exactly the crucible melts. This is important as continuous melters process a range of compositions until complete turnover is reached. (2) The wastes contain elements which result in another 5 wt.% oxides that are not present in the surrogates. Small amounts of other components, such as Li_2O, will affect the viscosity and conductivity of the melts. The important aspect of these surrogate runs is that within the composition envelope used, the glasses produced processable viscosities and conductivities at 1100-1150°C, similar to the range observed from the crucible studies.

Both TCLP and PCT leach tests were performed on the glasses produced from these four surrogate runs. The results of the TCLP tests are shown in Table 9.5. All of the glasses passed the TCLP test, although MIC2-142A is questionable. We believe that the Se value is closer to 0.5 ppm because adding a 1.0 ppm spike of Se to the leachate produced an analyzed concentration of 1.5 ppm Se. The standard deviation for many of the Se values in Table 9.5 was 0.5 ppm. With such a high standard deviation, it is difficult to determine if Se concentrations in the leachate passed or failed the EPA limits. These numbers are even more suspect since no Se had been put in the melter at prior to the draining of these glasses. The results of the PCT tests are presented in Table 9.6 as the average of each triplicate PCT test leachate concentration and as normalized leachate concentrations in Figure 9.2a. We compare our glasses from the 10 kg/day melter runs to the Savannah River EA glass, a standard for high-level radioactive waste disposal. All of our surrogate glasses except MIC3-42A have lower normalized leachate concentrations than the high-level waste disposal standard. Figure 9.2b shows the behavior of the normalized boron leach rates vs. time for these glasses. The rates fall rapidly and appear to remain low and stable at longer times.

9.3 Results for Radioactive Runs

In this section, we discuss the compositional range of MAWS wastes tested in the 10 kg/day melter, data collected, observations made during the runs, the leach resistance of the final glass, and analysis of the off-gas from the 10 kg/day melter. These runs successfully demonstrated that FEMP FE1 (Pit 5) waste along with radioactive Lockheed soil-wash fractions (FE 7) can be processed in a Duramelter joule-heated vitrification system, with over 99% of the uranium and 95% of the RCRA metals retained within the glass before recycling of the scrubber sludge (i.e. volatilization of UF_6 is not a problem), and that the resulting glasses passed the EPA TCLP test for the eight RCRA metals

The two types of feed used for the radioactive 10 kg/day melter runs are listed in Tables 9.7a and 9.7b. The feeds are based on (but not identical to) crucible melts F5-47 and F5-49 which proved to be both processable (Sections 4.0, 5.0, and 6.0) and leach resistant (Tables 7.1 and 7.2). As seen from Tables 9.7a and 9.7b, the major component of the feeds is FE1 (Pit 5) sludge, with the main variations between the feeds being the type of soil used and the presence or absence of added iron. The feed compositions shown in Table 9.7b contain 80% Pit 5 sludge, 8% soil-wash fractions and 4% recovered NaF, producing a total waste loading of 92 wt.%. Note that both feeds used NaF recycled from the off-gas scrubber: as such, it is not an additive but part of the waste for vitrification. Multiple batches of each of these feeds were made in order to complete the vitrification runs, but neither of the runs achieved complete turnover.

The two feeds were fed into the melter and processed without any major difficulties. While feeding was taking place, the feed rate ranged from 30-80 ml/min. The feed slurries produced approximately 500 g glass per liter of feed. The overall glass production rate during these two runs was approximately 6 kg/day, less than the nominal 10 kg/day design basis. The major constraint on exceeding a production rate of 6 kg/day was the feed system itself which tended to clog periodically; a more reliable feed system would undoubtedly have permitted even higher production rates, and, in fact, rates of up to 57 kg/day were sustainable between clogging events. We do not consider this to be a significant processing problem for scaled up systems in view of the slow feed rate required for the 10 kg/d melter. The flow rate for continuous slurry feeding to attain the nominal 10 kg/day glass production is approximately 14 ml/min while it is approximately 420 ml/min for 300 kg/day glass production. Clogging in feed lines is less likely when higher flow rates are used since slower feed rates allow settling in the feed lines.

The temperature and electrode power ranges used during these runs are summarized in Table 9.8. The difference in power consumption during idling at constant temperature and during feeding at the same temperature, together with the measured glass production rate, permits an estimate of power required per kg of glass produced. An approximate average value of 0.6 kW hr/kg was obtained by this method, somewhat smaller than expected in view of the large water content of the feeds. The plenum temperature range is a function of both the power being supplied to the lid heaters and the size of the cold cap.

The glasses produced from these two feeds behaved well in the melter and showed no evidence of crystallization in the melt pool at the processing temperatures. Some difficulties were noted in draining the glass which were probably due to crystallization in the drain tube, since a small section of the drain tube was at times below 1000°C. This problem was addressed in the 100 kg/day melter by incorporating design modifications to ensure higher temperatures in this region.

The glasses produced from the radioactive feeds were called MIC3-58A and MIC3-62A, respectively. Their analyzed compositions, using combined DCP and fluoride analyses, are shown in Table 9.9. The amount of fluoride retained in the glass was less than the targeted amount due to long idling times.

Table 9.10 summarizes the viscosity and conductivity measurements of glasses produced from these radioactive runs. These measurements show that over the processing temperature range of 1100°C to 1150°C the melt viscosities were about 2 to 4 Poise, within the Duramelter's processing range.

The leach resistance of the radioactive glasses was measured by both TCLP and PCT procedures. The results of the TCLP test on MIC3-58A and MIC3-62A glasses are presented in Table 9.11. Both glasses pass the EPA limits for all eight RCRA metals, as would be expected from the crucible melt studies. Table 9.12 shows the PCT results after seven days for MIC3-58A and MIC3-62A glasses; these results are compared with those for the SRL-EA glass in Figure 9.3a. The normalized boron leach rates are plotted and compared to the Savannah River EA glass in Figure 9.3. Both of our glasses compare well to the high-level nuclear waste standard especially at longer leach times. Because we did not achieve complete turnover for the radioactive runs, the resulting glasses do not have the same compositions as specific crucible melts, but rather a combination of crucible melts. The important point is that the glasses produced were within the compositional range predicted from crucible studies, and had processable viscosities, conductivities, and liquidus temperatures, and produced leach rates similar to the (processable) MAWS crucible melts.

9.3.1 Off-Gas Analysis

A major factor determining overall system performance and, in particular, the performance of the off-gas system, is the fractional partition of the hazardous and radioactive elements in the glass and the melter exhaust stream. The concentration of the gaseous element is a function of both the volatility of the element and the concentration of the elements in the feed. For equivalent concentration in the feed, the more volatile species will have higher concentrations in the vapor phase. For instance, if there are 10 moles of sodium and 0.001 moles of cesium in the feed composition, there will be a higher concentration of sodium in the vapor phase above the melter than the cesium, even though cesium is more volatile. The hazardous and radioactive elements must be efficiently captured in the off-gas system in order to meet emission standards. A variety of analyses were performed in order to quantify the partition of various elements between the glass and off-gas system components and pre-HEPA filter emissions.

Figures 9.4-9.6 show the total mass distributions of various components that accumulated in (i) the scrubber solutions (ii) the solid NaF stream, and (iii) the glass, as a function of time during sequential continuous melter runs (shown as one run for these purposes); note the scale differences. The first two glasses resulted from approximately 50 hours of continuous melter operation while feeding Pit 5 - soil blends for a research and development effort supported separately by FEMP (results reported previously). The second two glasses resulted from approximately 60 hours of continuous melter operation for the MAWS program. These runs were performed sequentially in order to obtain the largest possible running time.

Figures 9.4a and 9.4b show the uranium distributions during the runs. For both ^{238}U and ^{235}U, there is of the order of 1000-fold more uranium contained in the glass than in the off-gas system. This is particularly important in view of the high fluoride concentrations in these melts since it indicates that volatilization of uranium as UF_6 is not significant. Note that the $^{238}U/^{235}U$ ratio is on the order of 100 in both the glasses and scrubber solutions which is consistent with the measured ratio in FE1 (Pit 5); one would expect these ratios to be preserved since the chemistry of these isotopes is the same.

From Figures 9.4a and 9.4b, it seems that the quantity of both U-235 and U-238 decreases after 75 hours. This decrease of uranium in solution should be compensated by a concomitant rise in the amount of uranium in the NaF solid. This discrepancy is probably due to not obtaining a representative sample of the scrubber solid at the end of the run. The discrepancy is on the order of one milligram. It is likely that in our attempts to homogenize over one kilogram of scrubber solid, we were not successful in evenly distributing this one milligram of uranium. When the approximately 20 ml aliquot was taken for analysis, the uranium was not sufficiently represented and therefore not measured.

Figure 9.5 shows the corresponding data for ^{232}Th in which approximately 10^4 times more thorium is in the glass than is in the off-gas system. Other isotopes of thorium would, of course, be expected to behave similarly.

In addition to analyzing glass, scrubber solutions, and scrubber solids, emission measurements were made by sampling the exhaust after the scrubbers but *before* the HEPA filtration stage. This was done by drawing exhaust air at a constant rate through a gas scrubbing bottle containing NaOH solution for a known period of time. The solution was then analyzed by use of an ion selective electrode to determine the fluoride concentration, and by ICP-MS and DCP for other elements. These data, along with those collected from the glass, scrubber solutions and scrubber solids, give the elemental distributions summarized in Table 9.13. All RCRA metals analyzed show greater than 95% retention in the glass. Even mercury which is very volatile, shows excellent retention in the glass. In fact, almost all elements examined are held in the glass at levels greater than 95% and most are held in the glass at levels greater than 99%.

Fluoride differs from many of the other constituents in that it is present in high concentrations in the Pit 5 sludge and it readily volatilizes from the melt. Thus, the ability to capture and effectively recycle the fluoride is one of the major features required of the off-gas system for FE1 (Pit 5) waste vitrification. The-off gas system employed for the 10 kg/day Duramelter performed well in this respect. Concentrations of HF in the final off-gas stream amounted to less than 0.4% of the total fluoride. The fluoride data given in Table 9.13 and illustrated in Figure 9.6 show that greater than 50% of the fluoride fed into the melter is retained in the glass before accounting for recycling of NaF solids. This low value is indicative of a melter run which had relatively long idling time. In that campaign, the melter was idle at least 50% of the time. However, the overall fluoride retention was over 99.6% when recycled fluoride was taken into consideration.

Emissions from the vitrification scrubber system are given in Table 9.14. All values are less than 1 ppm and most are less than 0.1 ppm even though the air was sampled after the scrubbers but *before* the HEPA filtration stage. All RCRA metals and radionuclides are present at less than 30 ppb in the emission air and many are present at less than 1 ppb. Fluoride emissions were below 1 ppm; for comparison the Occupational Safety and Health Act (OSHA) limit for the workplace is 3 ppm. Both Ru and Tc are expected to be quite volatile and, indeed, Ru was detected in the off-gas emissions, as shown in Table 9.14. Unfortunately, the presence of Ru-99 increases our detection limit for analysis of Tc-99 by ICP-MS but despite this, our upper bound for Tc emissions is still extremely low (Table 9.14).

9.4 Summary

Results presented in this section demonstrate that feed compositions obtained from the crucible melts studies can be processed through the continuous melter system. In addition, the results demonstrate that the Duramelter off-gas system captures fluoride emissions from the melter and produces a recyclable sludge which can be recycled to the subsequent feed batches. These are two major objectives of the MAWS Phase I program. While a small system such as the one employed in these tests is not optimal for assessing off-gas emissions and processing rates, the results obtained are very encouraging and support the progression to large scale tests; the results of such tests are discussed in the following sections.

Table 9.1

Range of Target Compositions used for Duramelter™ 10 Surrogate Runs

Components	Wt% (analyzed)
Al_2O_3	3.1-7.7
B_2O_3	8.5-9.6
BaO	0.7-1.0
CaO	19.1-24.8
Fe_2O_3	2.5-5.0
K_2O	0.7-1.0
MgO	0-1.7
MgF_2	16.7-20.4
Na_2O	0-10.4
NaF	5.1-9.6
SiO_2	29.4-32.5
TiO_2	0-0.4

Table 9.2
Four of the Surrogate Feeds for 10 kg/day Melter Runs

Glass Produced	MIC2-138A		MIC2-142A		MIC3-36A		MIC3-42A	
Feed Name	FEED MICRO-6A		FEED MICRO-8A		FEED MICRO-4B		FEED MICRO-7B	
Components	wt. of components (kg)	target composition (wt.%)	wt. of components (kg)	target composition (wt.%)	wt. of components (kg)	target composition (wt.%)	wt. of components (kg)	target composition (wt.%)
Fernald Whole Soil*	1.5		0		0		0	
Al_2O_3	0.25		0.16		0.38		0.16	
H_3BO_3	0.8		0.77		0.82		0.76	
BaO	0		0.047		0.05		0.046	
$CaCO_3$	1.4		2.71		2.16		2.67	
$Fe(OH)_3$ slurry	1.0		0.88		1.64		0.87	
K_2CO_3	0.015		0.05		0.07		0.05	
$MgCO_3$	0		0.17		0.08		0.16	
MgF_2	0.98		1.16		1.06		1.14	
NaF	0.45		0		0.48		0.31	
Na_2CO_3	0		0.55		0		0.06	
SiO_2	0.70		1.62		1.50		1.60	
TiO_2	0.015		0		0.014		0	
Al_2O_3		7.3		3.26		7.5		3.21
B_2O_3		9.8		8.68		9		8.54
BaO		0.0		0.93		1.05		0.92
CaO		19.3		24.8		19.32		24.41
Fe_2O_3		4.1		2.57		4.7		2.53
K_2O		0.2		0.73		0.98		0.72
MgO		1.3		1.59		0.81		1.57
MgF_2		18.7		19.65		17.62		19.34
NaF		9.8		0		9.4		6.1
Na_2O		0.24		5.3		0		0.6
SiO_2		29.0		32.45		29.34		31.94
TiO_2		0.3		0		0.27		0
Total		100.04		99.96		99.99		99.88

*Passing mesh #50

Note: Four batches of feed previous to MICRO-6A were spiked with 100 times the amount of As, Cd, Cr, and Pb found in Pit 5 FE1 sludge.

Table 9.3

Combined DCP and Fluoride Analysis of Glasses Produced from 10 kg/day Surrogate Runs

Wt.% Oxide	MIC2-138A				MIC2-142A				MIC3-36A				MIC3-42A			
	target	anal(1)	anal(2)	anal(3)	target	anal(1)	anal(2)	anal(3)	target	anal(1)	anal(2)	anal(3)	target	anal(1)	anal(2)	anal(3)
Al_2O_3	7.3	7.57	7.37	7.11	3.26	3.31	3.37	3.48	7.5	4.83	4.70	4.68	3.21	5.12	5.41	5.69
B_2O_3	9.8	9.06	9.01	8.94	8.68	8.17	8.14	8.29	9	8.56	8.66	8.60	8.54	7.69	7.88	7.82
BaO	0.0	0.09	0.09	0.09	0.93	0.42	0.43	0.43	1.05	0.78	0.79	0.79	0.92	0.86	0.85	0.85
CaO	19.3	22.16	22.04	21.58	24.8	28.48	28.46	28.25	19.32	26.00	26.00	25.67	24.41	27.19	26.65	25.57
Fe_2O_3	4.1	3.39	3.38	3.31	2.57	2.47	2.53	2.55	4.7	2.91	2.90	2.88	2.53	2.70	2.76	2.76
K_2O	0.2	0.90	0.89	0.91	0.73	0.85	0.86	0.86	0.98	0.92	0.94	0.93	0.72	0.94	0.92	0.90
Li_2O	0.0	0.19	0.18	0.18	0.0	0.35	0.35	0.35	0.0	0.44	0.45	0.45	0.0	0.24	0.24	0.23
MgO	1.3	4.21[*]	4.22[*]	3.92[*]	1.59	5.82[*]	5.89[*]	5.83[*]	0.81	4.72[*]	4.88[*]	4.61[*]	1.57	3.09[*]	2.36[*]	1.62[*]
MgF_2	18.7	14.12[*]	14.12[*]	14.12[*]	19.65	12.48[*]	12.48[*]	12.48[*]	17.62	12.48[*]	12.48[*]	12.48[*]	19.34	17.25[*]	17.25[*]	17.25[*]
Na_2O	0.24[′]	7.17[′]	7.06[′]	6.79[′]	5.3	5.42	5.47	5.65	0.0[′]	6.23[′]	6.12[′]	6.12[′]	0.6[′]	5.53[′]	5.82[′]	5.98[′]
NaF	9.8[′]	0.0[′]	0.0[′]	0.0[′]	0.0	0.0	0.0	0.0	9.4[′]	0.0[′]	0.0[′]	0.0[′]	6.1[′]	0.0[′]	0.0[′]	0.0[′]
SiO_2	29.0	33.23	32.89	32.23	32.45	34.98	35.01	34.74	29.34	33.96	34.27	33.74	31.94	33.74	33.15	31.69
Total	99.74	102.15	101.31	99.23	99.96	102.90	103.14	103.0	99.72	101.99	102.31	101.03	99.88	104.51	103.42	100.57

[*] All the analyzed F is reported as; excess Mg is reported as MgO

[′] Although we fed NaF into the melter, we expected the amount of fluoride associated with Na to be lost as HF in the melter and recycled back as NaF from reaction with scrubber solution (NaOH). Note that 7.17 wt.% Na_2O corresponds to 9.71 wt.% NaF.

Table 9.4(a)
Viscosity of Four Surrogate Glasses

	Viscosity (poise)			
Temperature	MIC2-138A	MIC2-142A	MIC3-36A	MIC3-42A
950°C	unstable	unstable	unstable	crystallized
1000°C	unstable	12.1	17.0	12.8
1050°C	7.9	7.3	9.0	7.1
1100°C	5.0	4.7	5.1	4.4
1150°C	3.9	3.1	3.1	3.0
1200°C	3.3	2.1	2.0	NA

NA = Not Analyzed

Table 9.4(b)
Conductivity of Four Surrogate Glasses

	Conductivity (S/cm)			
Temperature	MIC2-138A	MIC2-142A	MIC3-36A	MIC3-42A
950°C	NA	0.05	NA	NA
1000°C	0.09	0.08	0.08	0.09
1050°C	0.14	0.12	0.11	0.14
1100°C	0.21	0.18	0.14	0.21
1150°C	0.30	0.25	0.18	0.28

Table 9.5
TCLP Data of Four Surrogate 10 Kg/day Melter Runs
RCRA Metals (ppm)

Elements (ppm)	MIC2-138A	MIC2-142A	MIC3-36A	MIC3-42A	EPA Limits
As	0.26	0.46	0.41	0.06	5
Se	0.80	1.0*	0.05	0.89	1
Cd	0.04	0.03	0.06	0.02	1
Hg	0.04	0.08	0.19	0.15	0.2
Ag	0.00	0.00	0.02	0.01	5
Pb	1.70	1.95	2.00	1.86	5
Cr	0.10	0.10	0.71	0.20	5
Ba	0.18	0.65	2.17	3.47	100

*Adding a 1.0 ppm spike of Se to this sample gave 1.5 ppm Se.

Table 9.6
PCT Leach Test Results for Glasses Produced in 10 kg/day Surrogate Runs
(7 days, 90°C, 100-200 mesh)

Elements (ppm)	MIC2-138A	MIC2-142A	MIC3-31A	MIC3-42A
B	248	262	244	364
Si	6.05	5.31	6.82	4.04
Na	413	388	368	712
pH	11.01	10.69	10.69	11.34
Al	2.10	3.46	4.93	1.53
Ba	3.83	4.26	0.15	0.73
Ca	106	158	122	155
Cr	1.01	0.19	0.41	0.34
Fe	0.00	0.00	0.00	0.00
K	16.1	6.97	16.1	14.6
Li	11.1	2.20	1.10	3.61
Mg	0.00	0.00	0.03	0.05
Mn	0.06	0.05	0.04	0.03
Ni	0.14	0.11	0.09	0.14
P	1.41	1.51	0.24	0.23
Sr	0.64	0.87	0.35	0.92
Ti	0.09	0.08	0.07	0.11
Zr	0.12	0.10	0.05	0.07

Note: Averages of triplicate samples.

Table 9.7(a)
First Radioactive Feed Used for 10 Kg/day Melter Runs

	F1B-1		F1B-2	
	Mass (kg)	Wt %	Mass (kg)	Wt %
FE1 (Pit 5) Sludge	7.0	75	3.5	74.5
Fernald Soil	0.46	4.9	0.23	5.0
H_3BO_3	0.59	6.4	0.30	6.5
SiO_2	0.60	6.5	0.30	6.5
Recovered NaF	0.15	1.6	0.07	1.6
$Fe(OH)_3$ Slurry	0.55	5.9	0.27	5.9

Table 9.7(b)
Second Radioactive Feed Used for 10 Kg/Day Melter Runs

	Target Feed		Typical Feed	
	Mass (kg)	Wt %	Mass (kg)	Wt %
FE1 (Pit 5) Sludge	8.50	80.6	4.3	83
Lockheed Soil-wash Fractions	0.88	8.3	0.44	8.5
H_3BO_3	0.56	5.3	0.28	5.4
SiO_2	0.20	1.9	0.1	1.9
Recovered NaF (40% water)	0.40	3.8	0.05	1.1

Table 9.8
Parameters Used for Continuous Melter Runs of Fernald Glasses

Glass Temperature Range	1034 - 1150°C
Plenum Temperature Range	756 - 858°C
Brick Temperature Range	755 - 859°C
Electrode Power Range	1.1 - 3.3 kW

Table 9.9
DCP and Fluoride Analysis of MIC3-58A and MIC3-62A Glasses Produced in 10 kg/d Continuous Melter Runs (wt%)

	MIC3-58A		MIC3-62A	
Elements	DCP Analysis (w/o fluoride)	Analysis (with fluoride)	DCP Analysis (w/o fluoride)	Analysis (with fluoride)
Al_2O_3	3.1	3.1	4.9	4.9
B_2O_3	9.3	9.3	10.4	10.4
BaO	1.0	1.0	1.2	1.2
CaO	18.7	18.7	21.3	21.3
Cr_2O_3	0.1	0.1	0.2	0.2
Fe_2O_3	3.8	3.8	5.2	5.2
K_2O	0.4	0.4	1.0	1.0
Li_2O	0.1	0.1	0.7	0.7
MgO	13.8	6.0	14.5	8.0
MgF_2	NA	12.1	NA	10.0
MnO_2	0.1	0.1	0.3	0.3
Na_2O	6.6	6.6	6.3	6.3
NiO	0.3	0.3	0.4	0.4
P_2O_5	0.9	0.9	0.6	0.6
SiO_2	33.7	33.7	29.0	29.0
SrO	0.04	0.04	0.04	0.04
TiO_2	0.1	0.1	0.3	0.3
U_3O_8	0.7	0.7	0.4	0.4
ZrO_2	0.1	0.1	0.3	0.3
Total	92.67	96.27	97.04	101.04
Measured Fluoride (wt.%)	7.4%		6.1%	

Table 9.10

Viscosity and Conductivity Measurements Interpolated to Standard Temperatures for MIC3-58A and MIC3-62A Glass Produced from 10 kg/day Continuous Melter Runs.

	Viscosity (Poise)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
MIC3-58A	21.84	9.53	5.42	3.61	2.65
MIC3-62A	18.75	7.76	4.27	2.78	2.01
	Conductivity (S/cm)				
Glass ID	@ 950°C	@ 1000°C	@ 1050°C	@ 1100°C	@ 1150°C
MIC3-58A	0.06	0.09	0.14	0.20	0.27
MIC3-62A	0.07	0.10	0.15	0.22	0.30

NA = Not Analyzed

Table 9.11

TCLP Data (ppm) for Glasses Produced from 10 kg/day Continuous Melter Runs

	As	Se	Cd	Hg	Ag	Pb	Cr	Ba
MIC3-58A	0.66	0.47*	0.04	0.19	0.01	1.56	1.99	9.80
MIC3-62A	0.67	0.30*	0.02	0.17	0.01	1.69	0.95	12.39
EPA Limit	5	1	1	0.2	5	5	5	100

* Se data were below the standard deviation of the measurement

Table 9.12
PCT Results of Glasses from Radioactive Runs
(7 days, 90°C, 100-200 mesh)

Elements (ppm)	MIC3-58A	MIC3-62A
B	271	177
Si	10.5	5.20
Na	579	301
pH	10.10	10.65
Al	0.44	0.91
Ba	1.44	2.23
Ca	44.5	107
Cr	1.42	0.51
Fe	0.04	0.00
K	46.7	24.0
Li	1.26	8.69
Mg	0.05	0.04
Mn	0.05	0.04
Ni	0.13	0.12
P	0.05	0.08
Sr	0.34	0.75
Ti	0.00	0.02
U	0.33	0.39
Zr	0.00	0.02

Note: Averages of triplicate samples.

Table 9.13

Percentage Distribution, by Weight, of Elements between Glass, Quencher and Scrubber Liquid, and NaF Slurry after Completion of Duramelter™ 10 Radioactive Runs

Component	Glass (MIC3-62A)	Liquid from Quencher and Scrubber	NaF Slurry	Pre-HEPA Off-Gas
Ba	99.62	0.05	0.289	0.04
Cd	96.44	0	0.235	3.33
Cr	96.95	1.44	0.680	0.93
Hg	95.44	4.56	<0.01	<0.01
Ni	99.40	0.06	0.452	0.09
Pb	98.89	0.03	0.051	1.03
Sb	98.68	0.37	0.395	0.55
F	54.88	4.87	39.85	0.39
P	99.28	0.51	0.21	0
B	95.89	3.43	0.50	0.18
Si	99.66	0.06	0.21	0.07
Ti	99.71	0	0.30	<0.01
Mn	99.67	0.05	0.28	<0.01
Mg	99.68	0.02	0.25	0.06
Fe	99.64	0.02	0.32	0.02
Al	99.64	0.03	0.27	0.06
Zr	99.87	0.01	0.12	<0.01
Sr	96.06	0.02	0.71	3.21
Ca	99.52	0.01	0.35	0.12
Rb	95.03	0.50	0.35	4.13
Mo	97.57	0.61	0.43	1.40
Ru	58.98	8.01	12.30	20.64
Sn	99.72	0.05	0.19	0.04
Cs	95.31	1.07	0.13	3.49
Ce	99.97	0.01	0.02	<0.01
Nd	99.80	0.01	0.20	0.01
W	99.14	0	0.60	0.03
Th 232	99.77	0.03	0.21	<0.01
U 235	99.88	0.12	0	<0.01
U 238	99.87	0.07	0.06	<0.01

Table 9.14
Air Emissions from 10 kg/day MAWS Radioactive Run

Element	Concentration in off-gas before HEPA-Filter (ppm)
Cr	0.026
B	0.095
Si	0.144
Ni	0.0043
Mn	<0.001
Mg	0.073
Fe	0.012
Al	0.024
Sr	0.015
Ca	0.26
Ba	0.0061
Rb	0.0021
Mo	0.0072
Tc	<0.0002
Ru	0.0025
Cd	0.0003
Sn	0.0001
Sb	0.0001
Cs	0.0021
W	0.0004
Hg	<0.1 ppb
Tl	0.0045
Pb	0.0064
Th 230	<0.1 ppb
Th 232	<0.1 ppb
U 235	<0.1 ppb
U 238	0.0037
F	0.73
As	<0.5
Se	<0.5
Ag	<0.5

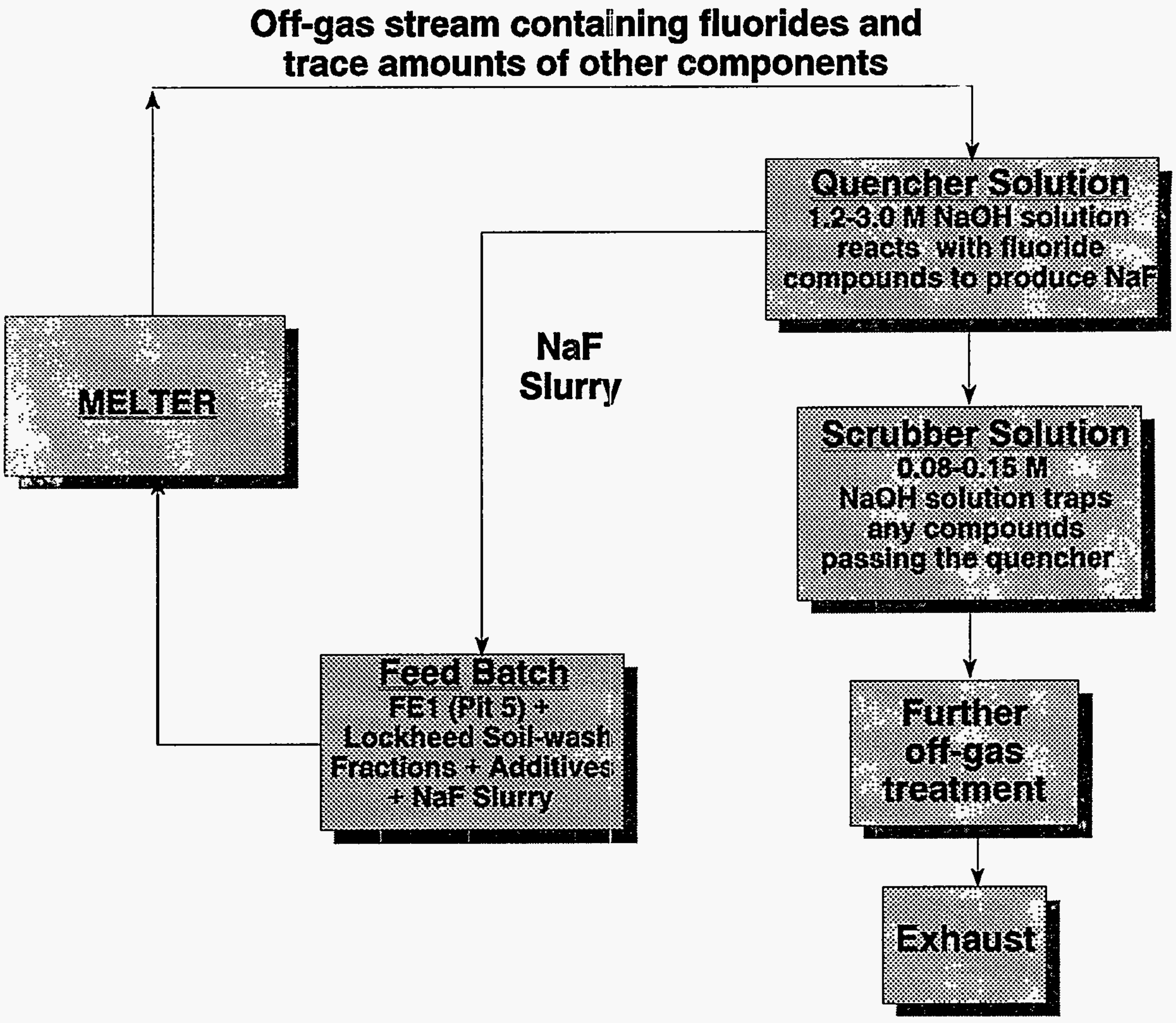


Figure 9.1.
Schematic of Continuous Melter Flow Showing Fluoride Recycle

Figure 9.2(a)
Normalized leaching concentration of Duramelter™ 10 surrogate glasses compared to the high-level waste standard glass (SRL-EA) after 7 days.

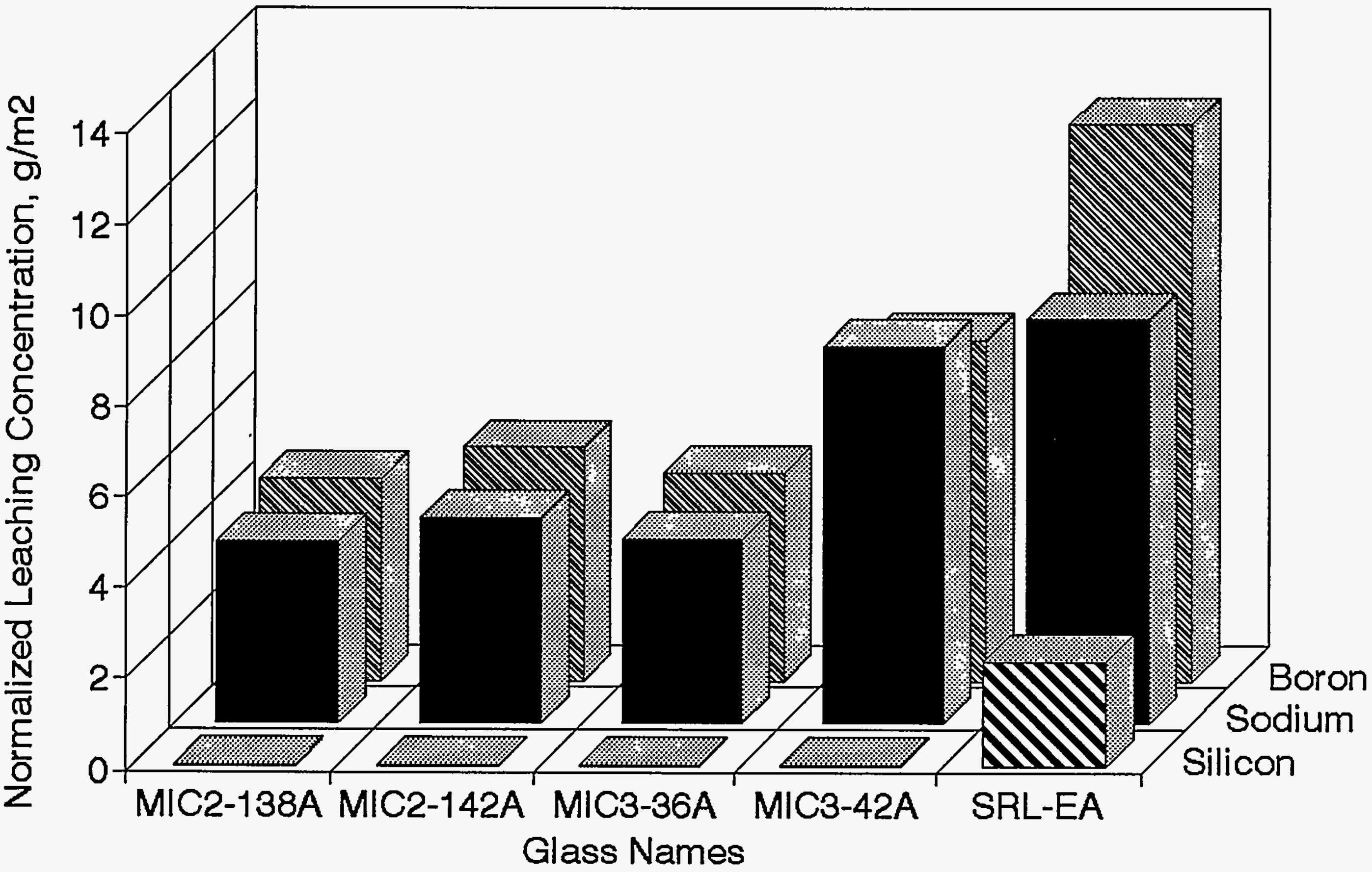


Figure 9.2(b)
Time dependence of PCT normalized leachate rates (boron)

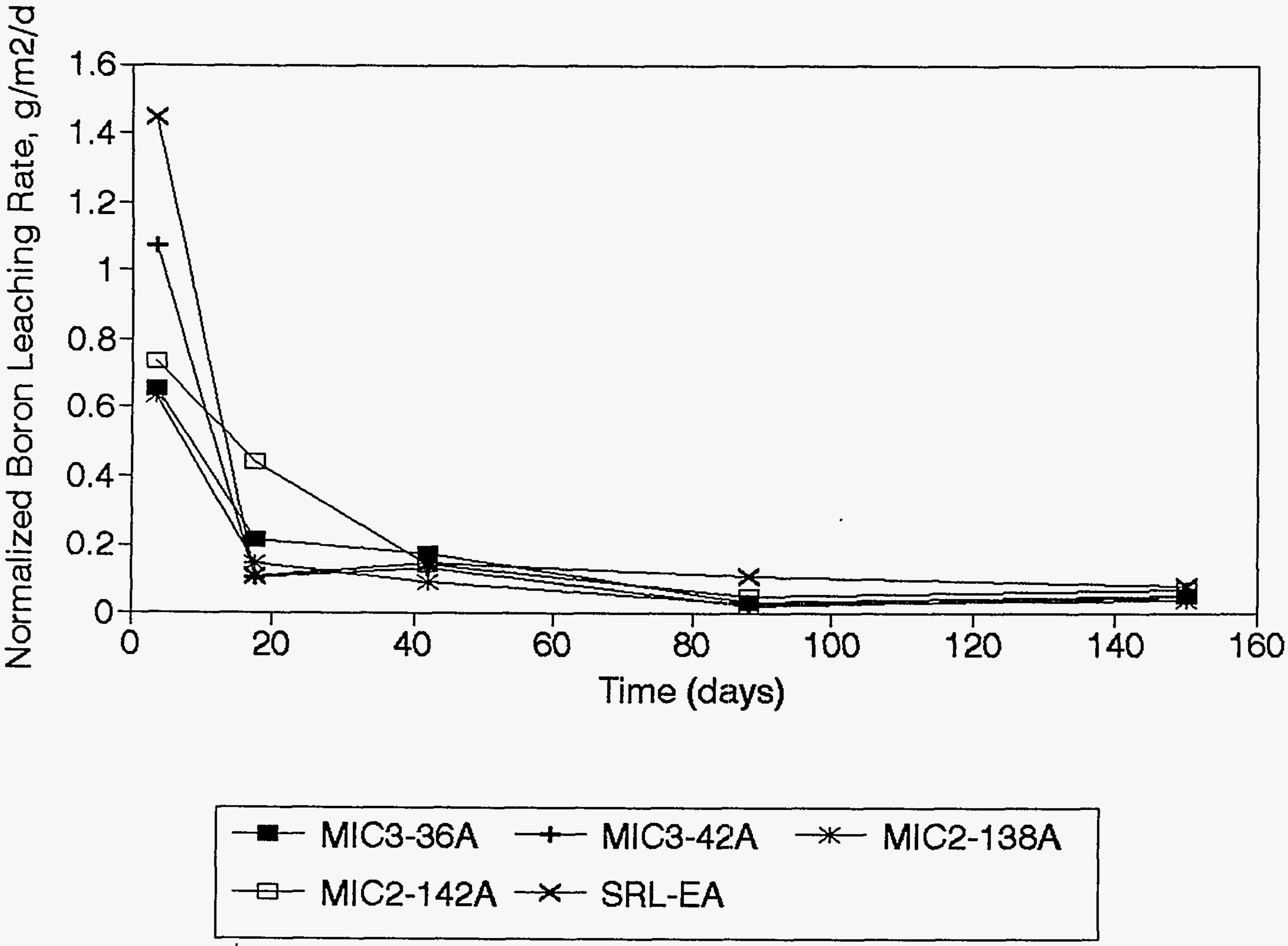


Figure 9.2(b) (continued)
Time dependence of PCT normalized leachate rates (boron) plotted on log scale

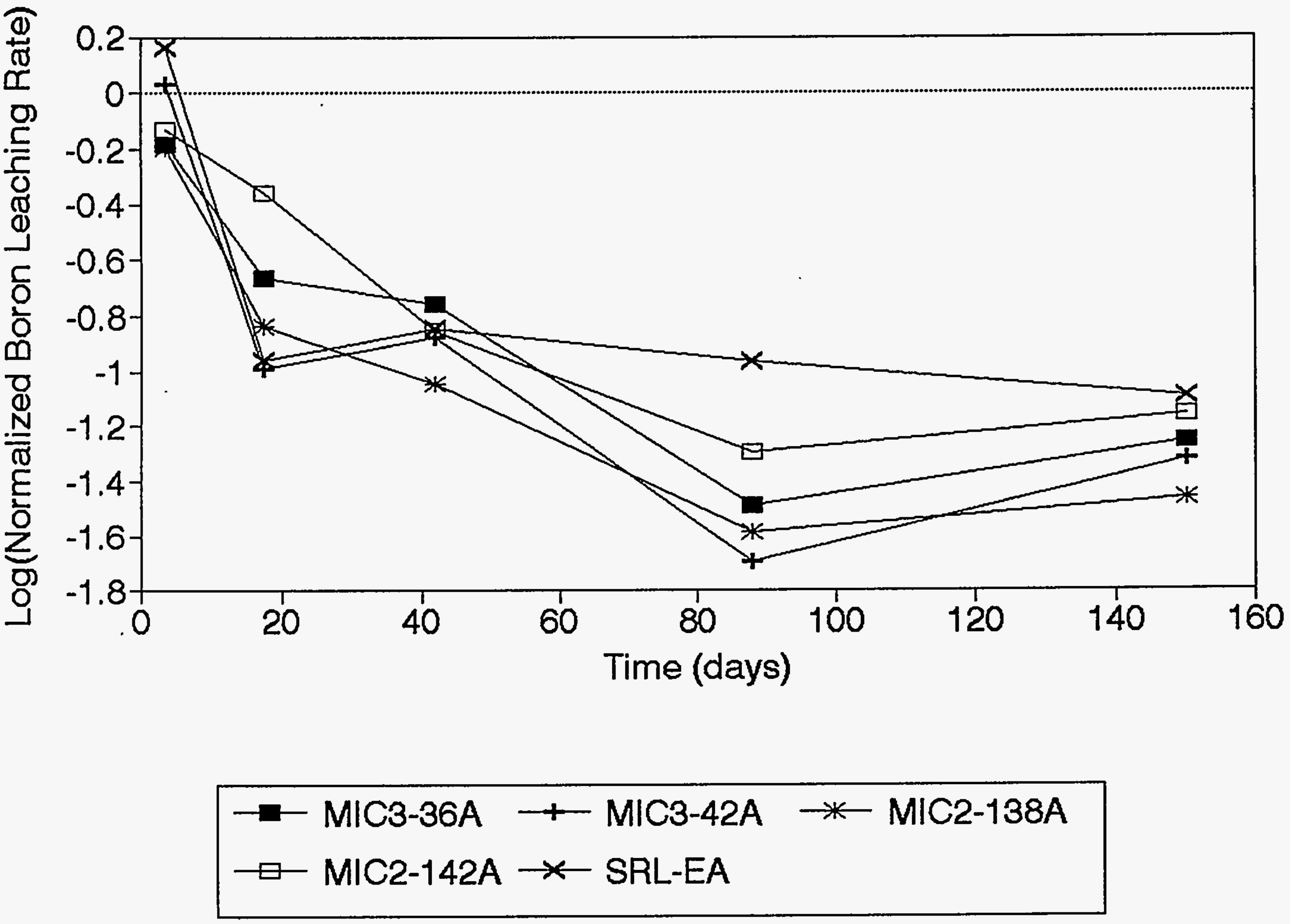


Figure 9.3(a)

Normalized leaching concentration of Duramelter™ 10 radioactive glasses compared to the high-level waste standard glass (SRL-EA) after 7 days.

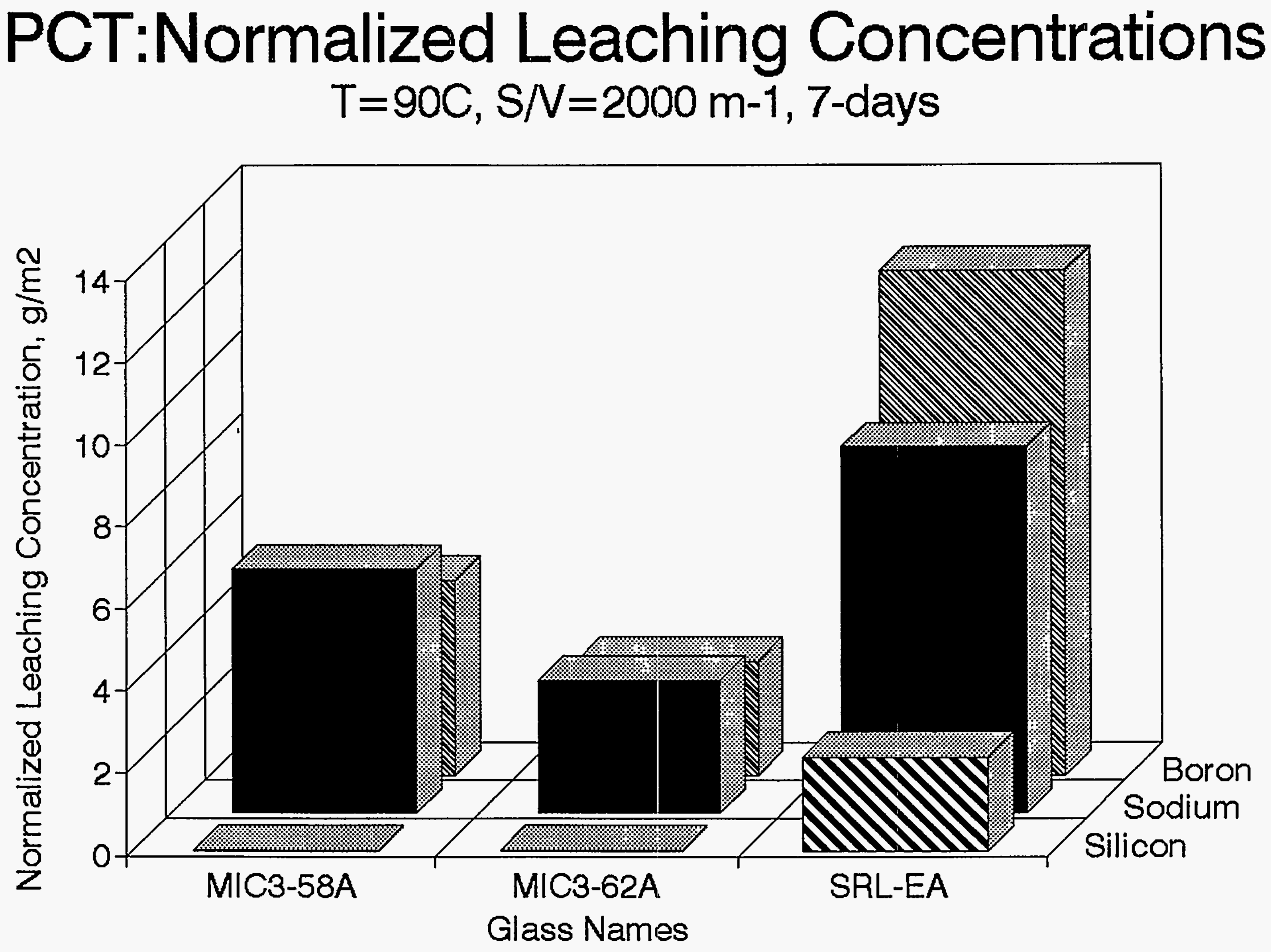


Figure 9.3(b)
Time dependence of PCT normalized leachate rates (boron)

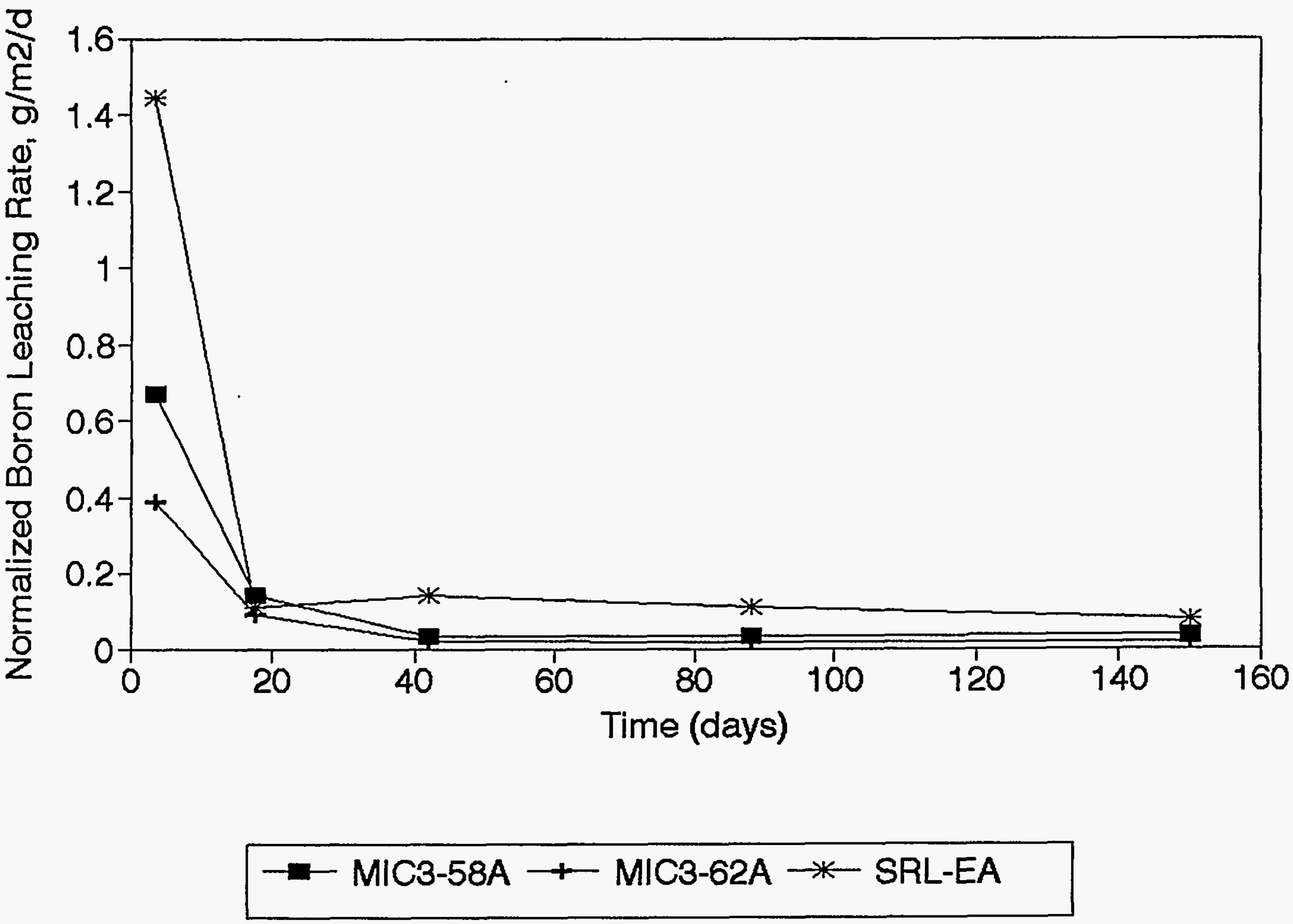


Figure 9.3(b) (continued)

Time dependence of PCT normalized leachate rates (boron) plotted on log scale

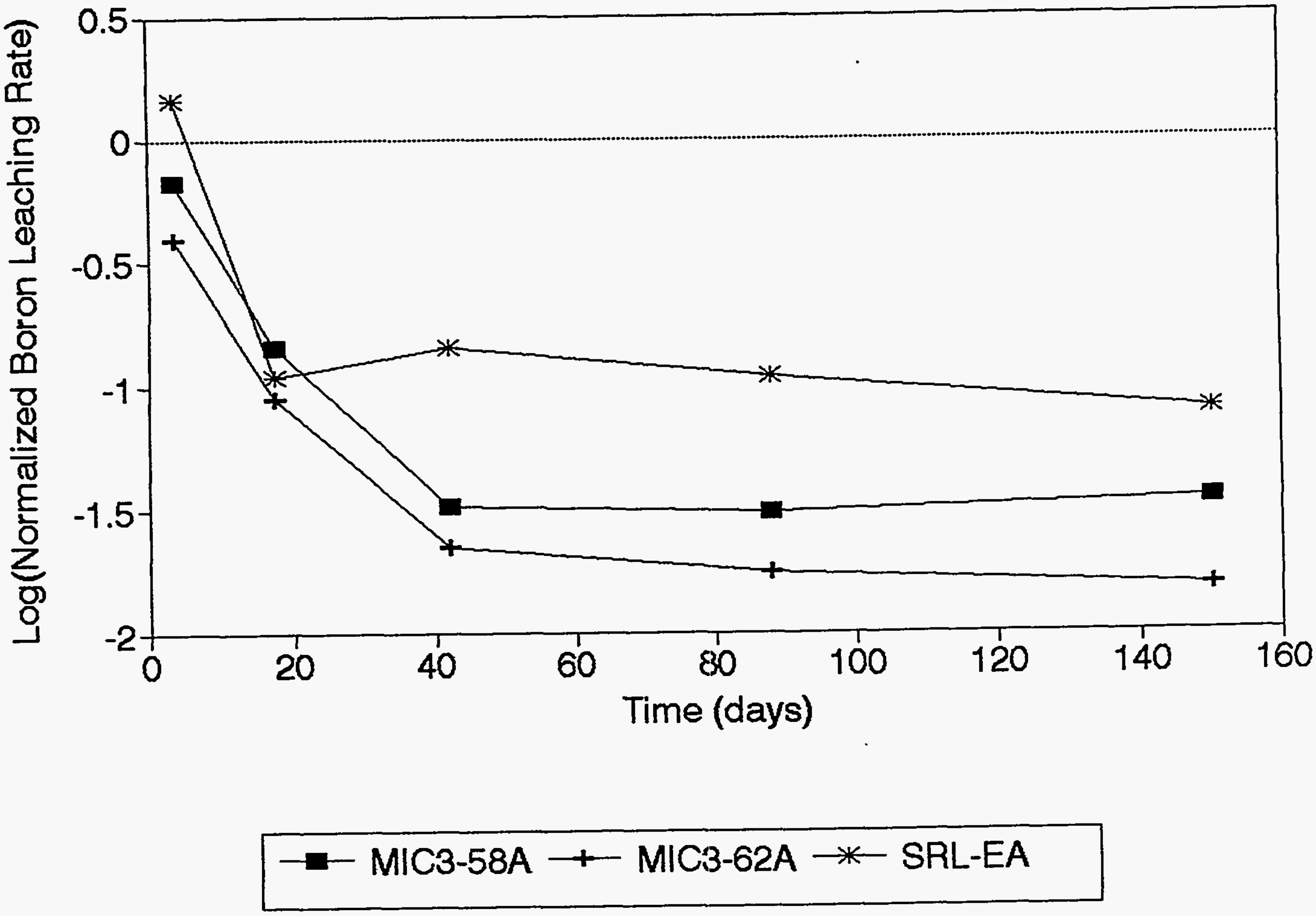


Figure 9.4a
Total mass of ^{235}U accumulated in glasses, scrubber solutions, and scrubber solids during Duramelter™ 10 campaign

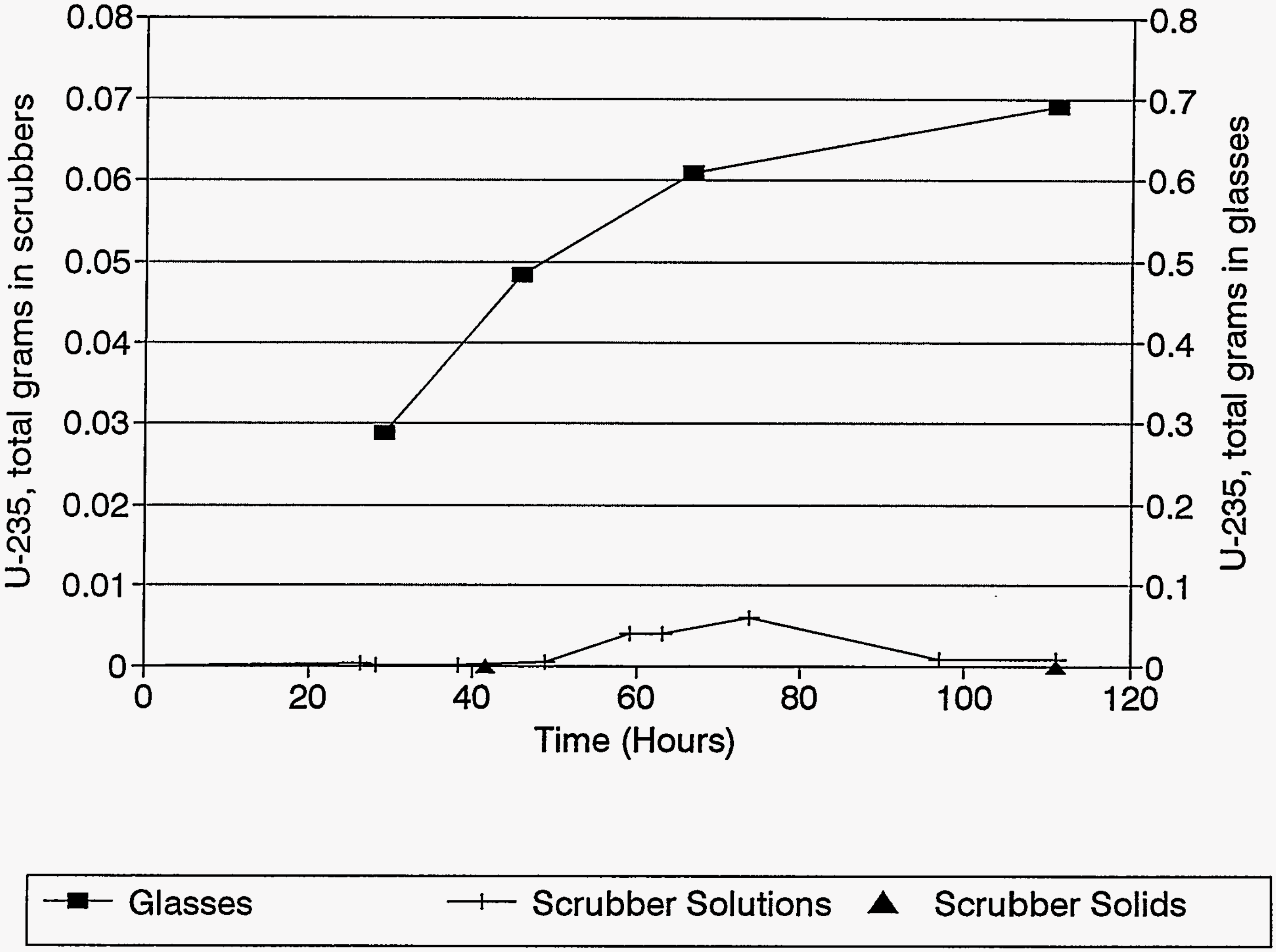


Figure 9.4b

Total mass of ^{238}U accumulated in glasses, scrubber solutions, and scrubber solids during Duramelter™ 10 campaign

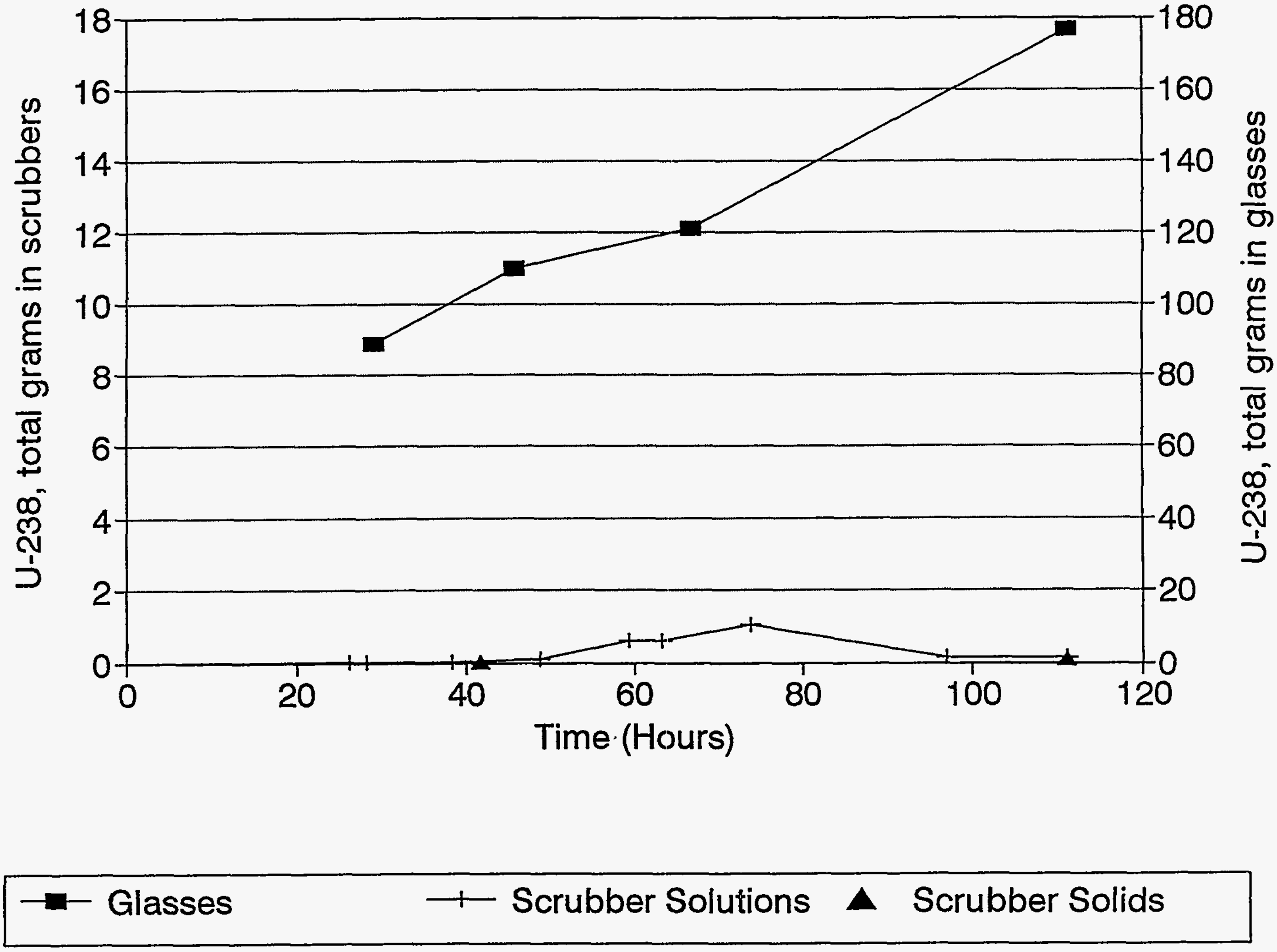


Figure 9.5
Total mass of ^{232}Th accumulated in glasses, scrubber solutions, and scrubber solids during Duramelter™ 10 campaign

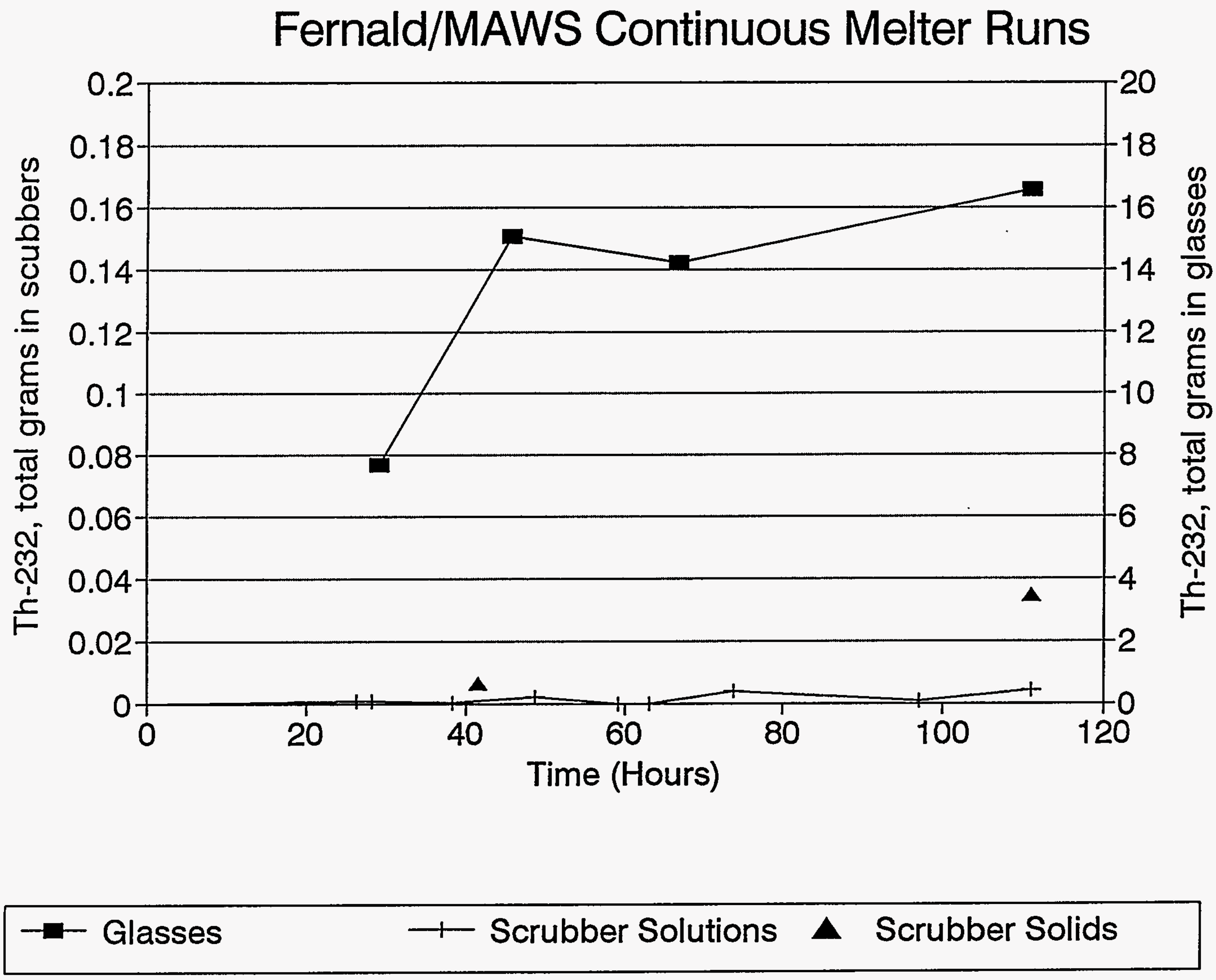
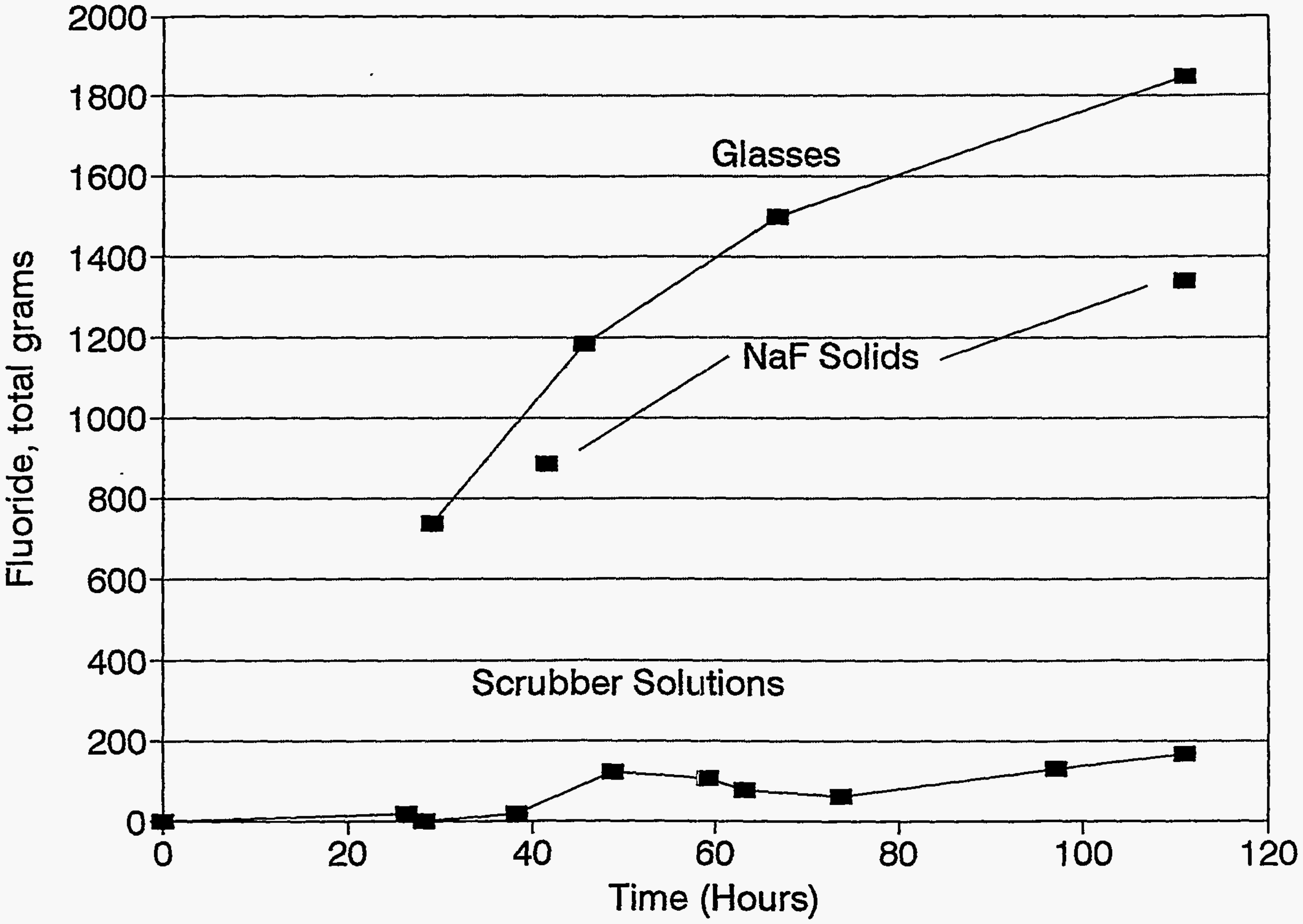


Figure 9.6
Total mass of F accumulated in scrubber solutions, NaF solids, and glass during Duramelter™ 10 campaign



SECTION 10.0
Duramelter™ 100 Runs

10.1 Introduction

The crucible melt studies and Duramelter™ 10 melter runs discussed in the previous sections demonstrate that a number of the MAWS glasses meet the requirements for processability and leach resistance. The next scale-up step that was tested was vitrification of these blends in the Duramelter™ 100, a continuously fed melter with a nominal glass output of 100 kg/day. Before the Fernald surrogate and radioactive compositions were processed, the melter produced about 1000 kg of borosilicate glass. The purpose of producing the borosilicate glass was twofold: first to test the components of the Duramelter™ 100 with the ability to make modifications easily, and, second, to produce frit for the starting up of the Duramelter™ 300 at FEMP. Three surrogate compositions were tested using the Duramelter™ 100 joule-heated vitrification system. Subsequently, compositions employing various Pit 5 sludges and Lockheed soil-wash fractions were used to make over 250 kg of radioactive glass in the Duramelter™ 100. Recycled NaF was also added to these feeds.

These mid-scale continuous melter tests provide essential information that cannot be obtained from crucible melts and 10 kg/day melter runs in that they more closely represent the processes involved in actual on-site vitrification. They also permit economical research and development on problems indicative of larger melter operations. The Duramelter™ 100 off-gas system is almost identical to the Duramelter™ 300 system at FEMP and therefore provides off-gas data pertinent to operation on site at Fernald. Predictions of potential contaminant release for the Duramelter™ 300 system would be considerably more reliable based on results from the Duramelter™ 100 system than the 10 kg/day system.

10.2 Duramelter™ 100 Operational Overview

Duramelter 100 System

The Duramelter™ 100 system consists of a feed system, melter, and off-gas system, as illustrated in Figure 10.1a-c. Each system is discussed separately below.

Feed System

Preparation and handling of radioactive feed must be done in a glovebox. The Duramelter™ 100 system employs a large glove box with three sealable ports on the floor section for feed and mixing barrels, as shown in Figure 10.1a. One of the ports is for sealed 55-gallon drums containing radioactive sludge. A rubber skirt is placed around the top of the drum and positioned around the lip of the drum port (inside the glovebox) to ensure containment of the radioactive sludge. Once the installation of the drum is complete, an electric mixer is placed into the drum to homogenize the sludge. A transfer pump is then used to move a pre-determined amount of sludge into the second 55-gallon drum for mixing. The amount of sludge transferred is measured on a volume basis using a graduated rod. Pre-measured amounts of soil-wash fractions and additives are brought into the glovebox using the pass-through. They are added to the sludge in the mixing drum one at a time as an electric mixer keeps the batch homogenized. Recovered sodium fluoride slurry (also containing other captured contaminants) from the quencher is brought into the glovebox through piping connecting the solid scrubber to the glovebox. The appropriate amount of sodium fluoride slurry is weighed on the balance in the glovebox and added to the batch in the mixing drum. Solution from the scrubber is pumped into the glovebox and added to the batch in the mixing drum when necessary to facilitate mixing. Once all of the ingredients of the batch are homogenized, they are transferred to the third drum for feeding. This feed drum is permanently mounted and mixed. Feed is pumped from a bottom discharge to a water cooled feeding tube on top of the melter.

Melter

The Duramelter™ 100 is a joule-heated melter containing two rectangular plate electrodes that supply the main source of heat to the glass pool. The melter also has four lid heaters spaced evenly above the glass pool. A schematic representation of the melter is shown in Figure 10.1c. The size of the melter was designed to guarantee a minimum glass output of 100 kg/day. The feed is pumped into the melter from the feed tank. A cold cap is maintained on top of the melt pool to help keep volatiles contained within the glass melt. A bubbler assembly in the glass pool helps to mix the slurry into the glass. From the melt cavity, three exit ports are provided: a bottom drain, a surface sulfate layer drain, and a side discharge to a riser and pour spout, which is activated by an airlift mechanism. The primary route of glass discharge is through the sidewall to an Inconel 690 riser and pour trough. The glass is discharged into 5-gallon steel buckets or 1-gallon clay crucibles and allowed to cool before analysis.

Off-Gas System

The off-gas treatment system has been designed specifically to handle the high fluoride content of Pit 5. The two major components of the off-gas system are the quencher, which operates as a spray-drying wet scrubber, and a more conventional wet scrubber. The hot off-gases flow from the melter into the quencher into which a 2-3 M sodium hydroxide solution is sprayed and evaporated to aid in decreasing the off-gas temperature. Fluoride in the off-gas reacts with the sodium hydroxide to form a sodium fluoride solid. The solids fall to the bottom of the quencher and are recycled back into the melter through the feed system. The wet scrubber is a secondary cleaner of the gases and uses a lower concentration of sodium hydroxide (approximately 0.1 M). From the liquid scrubber, the gases travel through various units connected in-line (mist eliminator, heater, baghouse, off-gas sampler, etc.) prior to the stack. The off-gases are pulled through the system by a blower connected in-line after the pre-filter and HEPA filters. The melter is maintained under negative pressure by the blower and in the event that the melter pressure rises too close to ambient, the melter's emergency vent line is automatically activated. The emergency vent line is also used during bake-out or when modifications to the off-gas system are necessary.

Isokinetic sampling of off-gas emissions was accomplished by pulling air representative of that in the emissions through sodium hydroxide and nitric acid solutions. The linear velocity of the exhaust air is measured and the sampling system pulls air through the solutions at the same linear velocity.

10.3 Duramelter™ 100 Operational Summary

Bakeout of the Duramelter™ 100 commenced in January 1993. The heating of the melter from room temperature to 750°C was accomplished using the four lid heaters above the main chamber and the four discharge heaters. The bakeout process is performed slowly enough to allow for trapped water and binders to escape from the refractories without causing the refractories to fracture. Once the temperature in the main glass chamber attained 750°C, about 100 kg a of borosilicate frit was fed into the melter in batches of 25 kg through a port on the lid. The lid heaters provided enough heat to form a molten pool of glass that covered the electrodes. The electrodes were energized and the main off-gas system was put online. A slurry feed formulated to result in a glass of borosilicate composition was then fed to the melter. Approximately 25 batches of the borosilicate composition were fed into the melter, with each batch producing about 43 kg of glass. During the four months of this production, modifications continued on the system to ready it for the surrogate and radioactive runs. Modifications included insulating the baghouse, installing a glovebox for the feed system, and adding additional valves and piping to support the quencher and feed systems. Procedures were prepared and operators were trained.

Two bottom draining operations were performed on the melter. The first bottom draining was performed to allow maintenance on the melter. The melter was visually inspected for corrosion and wear. There were no rounding of the edges of the electrodes which would indicate wear. The refractories containing the molten glass pool also looked in good condition. The bottom drain heaters were replaced due to the molten glass seeping into the heating elements and shorting them. The second bottom drain was performed to retrieve a section of the bubbler that failed at a weld and separated from the bubbler. The full contents of the melter was drained and the 12" piece of Inconel was retrieved. We were able to successfully bottom drain two times, but it is a method not recommended for routine operations. It should be used only when the entire glass pool is to be removed from the melter.

The first fluoride run commenced on June 22, 1993. The first composition, FEED 100-F1 (Table 10.2), was previously used in the Duramelter™ 10 and was easily processed. Two other compositions were also processed in the Duramelter™ 100, FEED 100-F2 and FEED 100-F3 which contained less magnesium fluoride and more calcium carbonate. The changes to the feed composition were made based on results of the analysis of the third and fourth drums of Pit 5 wastes (FE14 and FE16). These compositions produced processable homogenous glass.

Radioactive operations began on July 1, 1993. The total run time for the radioactive runs was 43 hours. During this time, five feed compositions were fed into the melter: FEED 1, FEED 2, FEED 3, FEED 4A, FEED 5A, and FEED 5B. Feed compositions 1-4 (Table 10.6) were made using Pit 5 material, soil-wash fractions, recycled NaF and additives. As seen in Table 10.7(b), FEED 5A and 5B used simulated Pit 5 waste materials (Table 10.7(a)). The feed batches 5A and 5B were also spiked with RCRA metals for TCLP analysis. We spiked the surrogate feed with RCRA metals at ten times the level found in Pit 5 material to ensure that our fluoride glasses could retain RCRA metals at higher concentrations, if needed. The surrogate Pit 5 material was made to prolong the run times due to Pit 5 material arriving late to VSL.

10.4 Results for Non-radioactive Surrogate Runs

Extensive system tests were performed with non-radioactive, fluoride-containing surrogate feeds which cover a range of compositions (Table 10.1). Individual feed compositions are given in Table 10.2. Glass is discharged from the melter when the level of molten glass reaches a given point. As a result, there is always carry over from one feed batch to another and often several glasses are drained from a given feed batch. Therefore. several different glasses can be attributed to a given feed batch but each reflects differing degrees of compositional turn-over. Some of the glasses analyzed from these feeds are noted at the top of Table 10.2. These runs were performed in order to test a variety of system modifications that were made for these high-fluoride feeds prior to radioactive operations. Over 500 kg of glass was produced in these runs. Analysis of typical surrogate glasses converted to oxide form are given in Table 10.3. Note that 100-2-32A, 100-2-36A, and 100-2-38A all have the same target glass of feed 100-F2; the glass drains with increasing numbers represent increasing turnover, and hence increasing match with the target compositions. The fluoride content was not analyzed for these samples and therefore all data is reported in oxide form. As a result, the oxides do not total 100%. If the appropriate amount oxides were converted to fluorides they would come close to 100%. Typical glass viscosity, conductivity, and TCLP results are given in Tables 10.4 and 10.5. The cation content of glass 100-2-44B is similar to the cation content of MIC3-36A, a glass from the Duramelter™ 10 runs. Comparing the viscosities and conductivities of the two glasses suggest that 100-2-44B has a lower fluoride content than MIC3-36A since 100-2-44B has higher viscosity and lower conductivity than MIC3-36A at the same temperatures.

10.5 Results for Radioactive Runs

In this section, we discuss the compositional range of MAWS glasses melted in the Duramelter™ 100. In addition, operational data, leach resistance of the glass product, and analysis of the off-gas will be described. These runs successfully demonstrated that three different Pit 5 waste samples together with 12 different samples of radioactive soil-wash fractions could be processed in a Duramelter™ vitrification system. In addition, over 99% of the uranium and 95% of the RCRA metals were contained within the glass before recycling of the quencher sludge (i.e. volatilization of UF_6 is not a problem).

The five compositions of feed used for the radioactive Duramelter™ 100 runs are listed in Tables 10.6, 10.7a, 10.7b. The feeds are based on (but not identical to) radioactive and surrogate glasses processed in the Duramelter™ 10 which had been shown to be processable and leach resistant. Each feed batch is based on optimum waste loading. The various feed components are analyzed and mixed to minimize additives while staying within the compositional range established by the crucible melts. Magnesium fluoride was added to the FEED 1-4 due to less MgF_2 in FE14, FE15, and FE16 Pit 5 sludge. It was found from the crucible melts and Duramelter™ 10 runs that the glass has less tendency to crystallize when 7-11% fluoride is present in the glass. (Note that MgF_2 did not need to be added to the feeds for the Duramelter™ 10 batches as seen in Tables 9.7(a) and (b)). Note that the first four feeds are composed of combined Pit 5 sludges FE14, FE15, and FE16, with soil-wash fractions, recovered NaF, and additives. After using FE14, FE15, and FE16 Pit 5 sludge, our inventory was exhausted and shipments of further drums from Fernald were delayed. In order to extend the melter runs, we produced a simulated Pit 5 sludge as shown in Table 10.7a, to which we added soil-wash fractions, additives, U_3O_8, ThO_2, and RCRA metals, as shown in Table 10.7b. The amount of RCRA metals added to the blend was about 10 times greater than the levels found in Pit 5 sludge. The feed compositions shown in Table 10.6 contain approximately 75-79 wt.% Pit 5 sludge, 10-15 wt.% Lockheed soil-wash fractions, and 3-4 wt.% recycled NaF. After taking into account the added soil and recycled NaF, the feed is only 7-8% additives. Although the four MAWS feeds appear to be different, the target compositions of all of them are actually very close based on oxide wt% (Table 10.9). Since the Pit 5 sludges and soil-wash fractions vary in composition, different batch recipes are used in order to compensate for these changes. Our two radioactive runs consisted of using only the inorganic soil-wash fractions in the first run and using organic soil-wash fractions in the second run.

All four MAWS blends produced stable slurries which processed without any major difficulties. The feed slurries produced approximately 325 g glass per liter of feed. The average glass production rate during these two runs was approximately 184 kg/day, more than the nominal 100 kg/day design basis while rates over 208 kg/day were achieved for long periods of time. The maximum cold cap formation (i.e. fraction of melt surface occluded by unreacted feed) was estimated to be 80%. No unusual events such as foaming were noted during the 100 kg/day melter runs, even during the feeding of slurry containing the organic soil-wash fractions.

The biggest difficulty with the Duramelter™ 100 system was the feed system. During initial operations with the borosilicate composition, the feed tube periodically clogged. This was due to the low flow rate into the melter (approximately 240 ml/min). This was also a problem during the surrogate and radioactive operations. In preparations for radioactive operations, sand was added to the borosilicate feed composition to simulate the coarse grained material of the soil-washed fractions. The coarse grained material proved difficult to feed into the melter due to settling in the feed lines. To help prevent these difficulties, the radioactive feed was strained during transferring from the mixing tank to the feeding tank. This eliminated some of the problems but there was still settling in the line.

The temperature and electrode power ranges used during these runs are summarized in Table 10.8a. The difference in power consumption during idling at constant temperature and during feeding at the same temperature, together with the measured glass production rate, permits an estimate of power required per kg of glass produced. An approximate average value of 5.2 kW hr/kg was obtained by this method, a reasonable value considering that the feeds contained 70-80% water.

The glasses produced from these four feeds (FEED 1-4) behaved well in the melter and showed no evidence of crystallization in the melt pool at the processing temperature. This is consistent with a liquidus temperature below 1050°C, as measured on glasses drained from the melter.

Over 250 kg of radioactive glass was produced during the MAWS runs. This glass is the accumulation of 27 drains, each drain being a unique sample. Each glass produced from the radioactive feeds is named with a number/letter combination as the following: 100U-2-48(A-H), 100U-2-52(A-K) and 100U-56(A-G), shown in Table 10.8b. This rather complicated numbering system is used to identify each glass in the operational notebook with minimum effort. Table 10.9 presents analyzed compositions, using combined DCP and fluoride analyses for glasses drained in the radioactive campaign. Note that the fluoride levels in these glasses are below the target values. This is due to interrupted feeding, which then eliminates the cold cap and increases fluoride loss. Fluoride leaves the molten glass at a much greater rate if there is no cold cap to retain it. Prolonged idling periods (at 1050°C) in the 10 kg/day melter indicate that the glass reaches equilibrium when containing approximately 4% fluoride. We have now run a 72-hour surrogate fluoride campaign in the Duramelter™ 300 at Fernald and analysis of the glasses produced from these runs indicate that we can retain the targeted fluoride values of 10-11 wt.%. Tables 10.10(a) and (b) show results for viscosity and conductivity measurements made on samples of glasses produced in these runs. These measurements show that over the processing temperature range of 1050°C to 1150°C the melt viscosities were between 2 to 11 Poise while the conductivity in the same temperature range was from 0.1-0.3 S/cm, all within the processing range of the Duramelter vitrification system.

TCLP tests on the radioactive glasses demonstrate that they pass the EPA limits for all eight RCRA metals as shown in Table 10.11. Only the Se in glass 100U-2-48A came close to the EPA limit of 1 ppm. This glass was retested and the second test gave a value of 0.27 ppm. In the near future, we hope to enhance the accuracy and precision of our Se analysis with the installation of a hydride generator. Results from PCT tests are presented as the average of three tests on two glasses in Table 10.12 and graphically as the normalized leachate concentrations in Figure 10.2. As can be seen from Figure 10.2, the glasses from the 100 kg/day melter runs compare favorably to the high-level nuclear waste standard of SRL-EA.

10.5.1 Off-Gas Analysis

A major factor determining overall system performance and, in particular, the performance of the off-gas system, is the distribution of the hazardous and radioactive elements between the glass and the melter exhaust system. The concentration of a species in the off-gas is a function of its volatility and the amount in the feed. Although most elements are retained in the glass due to melting parameters such as cold caps, some of the more volatile and highly concentrated species leave the melter and therefore must be efficiently captured in the off-gas system in order to meet emission standards. A variety of analyses were performed in order to quantify the distribution of various elements between the glass, off-gas system components (quencher and scrubber solutions), solid NaF that would be recycled to the melter as feed baghouse particulates (which can also be returned to the melter), and air emissions.

Figures 10.3-10.5 show the accumulation of various components in the quencher and scrubber solutions over time. The two sets of data for each element represent concentrations in the quencher and scrubber solutions. Concentrations of most elements are approximately two orders of magnitude greater in the quencher than in the scrubber. Figure 10.3 shows the concentration of boron, potassium, and silica in the quencher and scrubber for the duration of the radioactive run. The graph shows that there is a steady state situation where there is a fluctuation of about 500 ppm of boron and potassium and that there is no accumulation of the three elements. Figure 10.4 shows the steady state concentration of chromium, iron, aluminum, and magnesium in the quencher and scrubber for the duration of the radioactive run. Figure 10.5 shows the molar concentration of fluoride in the quencher and scrubber. The data shows a fairly steady state condition, except for the value at about 36 hours where the fluoride concentration increases to almost 0.9 molar. The average molarity for the fluoride during the 43-hour run was approximately 0.35. Figure 10.6 shows the steady rise in uranium concentration throughout the radioactive run. The concentration in the quencher rises from 0 ppm initially to about 3.5 ppm at the end of the run. The thorium maintained a low and stable concentration in both the quencher and scrubber. During the MAWS run, solid NaF was removed on five occasions. This yielded the equivalent of approximately 50 kg of dried solid which was used as feed additive. Steady state for many major glass elements (i.e. Si, B, K) was achieved in that continuous removal of solid kept pace with incoming flow from the melter.

Four emission samples, each averaging three hours in duration, were taken during the MAWS runs. The sampling train consisted of three impingers, two with 0.7 M nitric acid (to trap metals) and one with 0.5 M sodium hydroxide (to trap acid anions). The order of the solutions was varied for different samples. In the case of the samples 7/2/93 12:15 and 7/2/93 21:00, the three impinger solutions were combined while with the other samples the three impinger solutions were analyzed separately. The solutions were analyzed by ion chromatography to determine the fluoride and chloride concentrations, and ICP-MS for any other elements that may show significant concentrations in the exit stream. Results of these solution measurements and the applicable detection limits are given in Table 10.13. With the exception of barium and chromium, almost all measurements are below the detection limits.

Solution concentrations were combined with solution volumes, duration of sampling time, and air flow rate through the impingers to calculate concentrations of species in the final emissions air (Table 10.14). All values are less than 25 ppb and most are less than 1 ppb. In most cases the numbers are defined by solution detection limits, and not by how much of the component is actually present. The volatile element F was measured in the emissions below 25 ppb; for comparison the OSHA limit for the workplace is 3 ppm.

Distributions of various components that accumulated in (i) the quencher and scrubber solutions (ii) the solid NaF stream, (iii) the baghouse (iv) the glass and (v) emissions are given in Tables 10.15a and 10.15b. These calculations are based on glass, quencher and scrubber solution, and recovered NaF data collected for an eleven-hour period in the MAWS runs. The off-gas data were taken for time periods immediately before and after the eleven-hour period. The particulates were collected in the baghouse for all the runs so its accumulations were adjusted by the amount of glass produced for that period.

All RCRA metals, with the exception of chromium, show greater than 95% retention in the glass. Many of the metals show greater than 99% retention in the glass. Even mercury which is very volatile, shows excellent retention in the glass. Chromium is a special case in that a large fraction of it comes from the refractory materials and inconel used to construct the melter. Despite its ubiquity in the melter system, over 70% is retained in the glass and all but 0.06% is captured for recycling to the melter feed.

Thorium and uranium were retained in the glass at levels greater than 99.7%. Although uranium accumulated in the quencher solution over time (Figure 10.6), the total amount in the scrubber system was very small compared to the amount in the glass. Neither of these two constituents was measurable in the emissions.

Fluoride differs from many of the other constituents in that it is present in high concentrations in the sludge and it readily volatilizes from the melt. Thus, the ability to capture and effectively recycle the fluoride is one of the major features required of the off-gas system for Pit 5 soil waste vitrification. The Duramelter™ 100 system employed for the continuous melter tests performed well in this respect: fluoride was captured and successfully recycled. No HF in the final off-gas stream was measurable resulting in less than 25 ppb air emissions. Over the course of the entire radioactive runs approximately half of the fluoride is retained in the glass and the other half can be recycled to the feed. Using the present feed, we need to retain 70% of the fluoride in the glass to produce no fluoride sidestreams. This has been accomplished in the surrogate runs of the Duramelter™ 300. Figure 10.5 illustrates how NaF can be recycled to avoid accumulation of fluoride in the scrubber.

10.6 Summary

In this section, we demonstrated that feed compositions obtained from crucible melt studies and Duramelter™ 10 runs can be processed continuously in the Duramelter™ 100. In addition, we demonstrated that the off-gas system for the Duramelter™ 100 removes contaminants from the exhaust to levels below measurable limits and emission standards. Sodium fluoride solid was removed from the quencher and returned to the melter as feed. Virtually all the fluoride put into the melter either stayed in the glass or was recycled back to the melter as feed. Solution concentrations of fluoride in the quencher and scrubber (Figure 10.5) illustrate that there is no net accumulation of fluoride in the solutions. All the fluoride entering the quencher during the runs became solid precipitate. The Duramelters™ 100 and 300 have almost identical off-gas systems therefore these results are a good indication of off-gas system performance. The glasses made during these Duramelter™ 100 runs were both processable and leach resistant.

Table 10.1
Range of Surrogate Feed Compositions Used in the Duramelter™ 100

Components	Wt%
Al_2O_3	2.00-3.4
H_3BO_3	10.6-14
$BaCO_3$	0-0.8
$CaCO_3$	25.3-31.4
$Fe(OH)_3$ Slurry	11.4-18.6
K_2CO_3	0-1.2
$MgCO_3$	0-1.6
MgF_2	10-13.8
NaF	4.5-5.4
SiO_2	18.4-22
TiO_2	0-0.06

Table 10.2
Typical Surrogate Feeds used in Duramelter™ 100

Glass Produced	100-2-26B		100-2-32A, 100-2-36A and 100-2-3-38A		100-2-44B	
Feed Name	FEED 100-F1		FEED 100-F2		FEED 100-F3	
Components (wt.%)	wt. of components (kg)	target composition (wt.%)	wt. of components (kg)	target composition (wt.%)	wt. of components (kg)	target composition (wt.%)
Sand	0		0		7.5	
Al_2O_3	1.0		1.4		0.8	
H_3BO_3	5.3		4.6		4.6	
$BaCO_3$	0.3		0.3		0.0	
$CaCO_3$	10.3		13.0		12.8	
$Fe(OH)_3$ slurry	5.1		7.7		5.1	
K_2CO_3	0.4		0.4		0.0	
$MgCO_3$	0.6		0.3		0.3	
MgF_2	5.3		4.1		4.1	
NaF	1.8		1.8		1.8	
Na_2CO_3	0		0		0	
SiO_2	8.5		8.0		3.0	
TiO_2	0.03		0.03		0.00	
Al_2O_3		4.0		5.6		5.0
B_2O_3		12.0		10.3		10.8
BaO		1.0		1.0		0.0
CaO		19.0		24.0		24.7
Fe_2O_3		3.0		4.5		3.7
K_2O		1.0		1.0		0.7
MgO		1.0		0.5		0.5
MgF_2		18.0		14.0		14.7
NaF		7.0		7.0		7.3
Na_2O		0.0		0.0		0.0
SiO_2		33.9		32.0		32.5
TiO_2		0.1		0.1		0.1
Total		100		100		100

Table 10.3
Typical Compositions of Surrogate Glasses Given in Oxide Form (No Fluoride Analysis)

Components (wt.%)	100-2-26B		100-2-32A		100-2-36A		100-2-38A		100-2-44B	
	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed
Al_2O_3	4.0	4.0	5.6	4.0	5.6	4.9	5.6	5.0	5.0	5.4
B_2O_3	12.0	13.2	10.3	11.7	10.3	10.7	10.3	10.5	10.8	10.2
CaO	19.0	19.5	24.0	21.9	24.0	24.7	24.0	25.3	24.7	26.6
Fe_2O_3	3.0	3.8	4.5	2.7	4.5	3.0	4.5	3.1	3.7	3.0
K_2O	1.0	1.5	1.0	1.2	1.0	1.2	1.0	1.1	0.7	1.1
MgO	1.0	11.2	0.5	11.7	0.5	11.5	0.5	11.0	0.5	10.8
MgF_2	18.0	NA	14.0	NA	14.0	NA	14.0	NA	14.7	NA
Na_2O	5.3	7.4	5.3	6.0	5.3	6.1	5.3	5.8	5.5	5.3
SiO_2	33.9	36.4	32.1	34.7	32.1	33.4	32.1	31.9	32.5	32.0
TiO_2	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	NA
Total	97.3	97.0	97.3	93.9	97.3	95.5	97.3	93.7	98.2	94.8

NA = Not Analyzed

Table 10.4
Viscosity and Conductivity Data for a Typical Surrogate Glass from the Duramelter™ 100 Runs

			Viscosity (Poise)			
Glass Name	950°C	1000°C	1050°C	1100°C	1150°C	1200°C
100-2-44B	54.3	24.1	12.5	7.3	4.6	NA
			Conductivity (S/cm)			
	950°C	1000°C	1050°C	1100°C	1150°C	1200°C
100-2-44B	0.01	0.04	0.08	0.11	0.15	0.19

NA = Not Analyzed

Table 10.5
TCLP Results of Duramelter™ 100 Surrogate Glass
RCRA Metals (ppm)

Elements (ppm)	100-2-38A	EPA Limit
As	0.1	5
Se	0.6	1
Cd	0.00	1
Hg	0.2	0.2
Ag	0.01	5
Pb	1.7	5
Cr	1.1	5
Ba	10.8	100

Table 10.6
Radioactive Feed for Duramelter™ 100

Components	FEED 1		FEED 2		FEED 3		FEED 4	
	Mass (kg)	Wt%	Mass (kg)	Wt%	Mass (kg)	Wt%	Mass (kg)	Wt%
Pit 5 material (combination)	110*	76.1	120*	77.7	104*	78.5	80*	74.6
	Inorganic						Organic	
Soil-wash Fractions (combination)	16	11.1	15.9	10.3	15.0	11.3	15.6	14.5
Recovered NaF (60 wt.% solids)	5.8	4	5.8	3.8	3.9	2.9	3.5	3.3
MgF_2	4.1	2.8	4.1	2.6	3.8	2.9	3.1	2.9
H_3BO_3	8.7	6.0	8.7	5.6	5.8	4.4	5.1	4.87

*Approximated mass of Pit 5 sludge by using a density of 1.3 kg/l.

Table 10.7(a)
Target and Actual Composition of the Pit 5 Surrogate Sludge Used for Simulated Radioactive Runs

Surrogate Pit 5 Sludge Components	Target Weight (kg)	MIX 3A (actual) (kg)	MIX 3B (actual) (kg)
$Fe(OH)_3$ Slurry	4.95	4.98	5.0
Al_2O_3	0.45	0.45	0.45
$BaCO_3$	0.6	0.6	0.6
$CaCO_3$	18.3	18.3	18.3
K_2CO_3	0.1	0.1	0.1
MgF_2	10.0	10.0	10.0
$MgCO_3$	0.71	0.7	0.7
Na_2CO_3	0.47	0.5	0.5
SiO_2	3.1	3.2	3.2

Table 10.7(b)
Simulated Radioactive Feed

Components	FEED 5A		FEED 5B	
	mass	wt.%	mass	wt.%
Surrogate Pit 5 Sludge	38.8 kg (Mix 3A)	51 (Mix 3A)	38.8 kg (Mix 3B)	49.1 (Mix 3B)
Soil-wash Fractions	23.1 kg	30.4	26.1 kg	33
H_3BO_3	8.3 kg	10.9	8.3 kg	10.5
Recovered NaF (60% solids)	5.3 kg	7.0	5.2 kg	6.6
U_3O_8	250 g	0.3	250 g	0.3
ThO_2	1.9 g	0.002	1.9 g	0.002
As_2O_3	3.76 g	0.005	3.59 g	0.005
CdO	4.93 g	0.006	4.51 g	0.006
Cr_2O_3	59.6 g	0.08	58.8 g	0.07
Pb_3O_4	268 g	0.35	268 g	0.34
HgO	0.4 g	0.0005	0.4 g	0.0005

Table 10.8a
Parameters Used for Duramelter™ 100 Runs

Glass Temperature Range	1079 - 1151°C
Plenum Temperature Range	600 - 800°C
Refractory Temperature Range	820 - 880°C
Discharge Temperature Range	905 - 1090°C
Temperature Range of Scrubber Liquid	45 - 70°C
Baghouse Temperature Range	35 - 70°C
Dilution Air Temperature Range	55 - 125°C
Electrode Power Range (avg)	38-42 kW

Table 10.8b
Run Time, Feed Batch, and Glass Drain Identification for
Duramelter™ 100 Radioactive Runs

Run Time (hr)	Feed Batch	Glass Drained
0	#1	--
7	#1	100U-2-48A*
11.17	#2	100U-2-48B
12.33	#2	100U-2-48C
13.17	#2	100U-2-48D
14.17	#2	100U-2-48E
15.17	#2	100U-2-48F
15.42	#2	100U-2-48G
15.82	#3	--
16.58	#3	100U-2-48H
17.5	#3	100U-2-52A
18.67	#3	100U-2-52B
19.5	#3	100U-2-52C
20.5	#4	--
20.58	#4	100U-2-52D*
21.25	#4	100U-2-52E
22.5	#4	100U-2-52F
23.5	#4	100U-2-52G
24.5	#4	100U-2-52H
25.0	#4	100U-2-52I
26.5	#4	100U-2-52J*
27.5	#4	100U-2-52K
28.5	#4	100U-2-56A*
29.5	#4	100U-2-56B*
30.83	#4	100U-2-56C
31.75	#4	100U-2-56D
32.5	#5	--
33.5	#5	100U-2-56E
37.0	#5	100U-2-56F
43.3	#5	100U-2-56G
49.3	#5	100U-2-60A

*Glasses analyzed in Table 10.9 and 10.10.

Table 10.9
DCP and Fluoride Analysis of Radioactive Glasses from Duramelter™ 100 Runs

Oxide (wt.%)	100U-2-48A	100U-2-48G	100U-2-52D	100U-2-52J	100U-2-56A	100U-2-56B
Al_2O_3	5.27	5.41	5.08	5.19	5.22	5.71
B_2O_3	10.80	10.74	10.87	10.88	11.06	10.52
BaO	NA	NA	NA	NA	NA	NA
CaO	25.70	23.82	24.32	25.75	23.84	23.09
Cr_2O_3	NA	NA	NA	NA	NA	NA
Fe_2O_3	3.51	3.20	3.41	3.04	3.09	2.87
K_2O	1.01	0.93	1.01	0.98	1.00	0.92
Li_2O	0.19	0.18	0.23	0.19	0.21	0.17
MgO	4.84	5.36	5.21	4.77	4.78	3.96
MgF_2	9.67	10.74	10.59	10.18	10.18	10.62
MnO_2	0.04	0.07	0.07	0.10	0.06	0.07
Na_2O	5.57	6.66	6.35	6.09	6.80	6.57
NaF	0.0	0.0	0.0	0.0	0.0	0.0
NiO	0.10	0.02	0.00	0.00	0.00	0.00
P_2O_5	0.45	0.51	0.52	0.48	0.51	0.50
SiO_2	30.46	28.65	29.32	29.80	28.24	28.61
SrO	NA	NA	NA	NA	NA	NA
TiO_2	0.12	0.25	0.22	0.18	0.25	0.27
U_3O_8	0.20	0.35	0.33	0.26	0.36	0.34
Total	97.94	96.89	97.53	97.81	95.60	94.22

NA = Not Analyzed

Table 10.10(a)
Viscosity Measurements of Duramelter™ 100 Glasses (Poise)

Temperature	100U-2-48A	100U-2-52D	100U-2-56B
950°C	51.4	31.4	27.2
1000°C	21.5	13.3	13.1
1050°C	11.0	7.2	7.1
1100°C	6.5	4.5	4.1
1150°C	4.2	3.2	2.6
1200°C	3.0	2.4	1.7

Table 10.10(b)
Conductivity Measurements of Duramelter™ 100 Glasses (S/cm)

Temperature	100U-2-48A	100U-2-52D	100U-2-56B
1000°C	0.06	0.07	0.11
1050°C	0.09	0.12	0.15
1100°C	0.13	0.17	0.21
1150°C	0.19	0.23	0.29
1200°C	0.27	0.30	0.39

Table 10.11
TCLP Results of Duramelter™ 100 Glasses
RCRA Metals (ppm)

Elements (ppm)	100U-2-48A		100U-2-52B	100U-2-52C	100U-2-56C	100U-2-56E	EPA Limit
	Test #1	Test #2					
As	0.53	0.64	0.85	0.82	0.60	0.73	5
Se	0.73	0.27	0.00	0.00	0.05	0.06	1
Cd	0.01	0.05	0.02	0.03	0.04	0.04	1
Hg	0.09	0.02	0.06	0.07	0.03	0.07	0.2
Ag	0.01	0.01	0.01	0.01	0.01	0.01	5
Pb	1.73	1.80	1.72	1.73	1.70	1.78	5
Cr	0.33	0.15	0.25	0.20	0.17	0.30	5
Ba	8.53	12.0	9.93	9.41	11.83	11.0	100

Table 10.12
PCT Results for Duramelter™ 100 Glasses
(7 days, 90°C, 100-200 mesh) (ppm)

Elements (ppm)	100U-2-48A	100U-2-56B
B	177	169
Si	5.85	8.03
Na	252	307
pH	10.8	10.7
Al	1.98	1.19
Ba	9.87	2.54
Ca	134	93.2
Cr	0.29	0.32
Fe	0.00	0.00
K	46.8	42.6
Li	0.80	0.63
Mg	0.00	0.01
Mn	0.02	0.00
Ni	0.03	0.11
P	0.87	0.48
Sr	0.59	0.58
Ti	0.08	0.07
U	1.70	1.10
Zr	0.03	0.05

Note: Averages of triplicate samples.

Table 10.13
Solution Measurements of Off-Gas Samples from Duramelter™ 100
(Combined ICPMS and Ion Chromatography Measurements) (ppb)

Sample	Detection Limit (ppb)	Date/Time							
		7/1/93 16:40 HNO_3(1)	7/1/93 16:40 HNO_3(2)	7/1/93 16:40 NaOH(3)	7/1/93 22:38 NaOH(1)	7/1/93 22:38 HNO_3(2)	7/1/93 22:38 HNO_3(3)	7/2/93 12:15 (combined)	7/2/93 21:00 (combined)
Cr	0.05	6.9	5.5	10.7	16	2	1.2	0.6	<0.05
U	0.05	<0.05	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tc	0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Cd	2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Hg	2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Pb	0.5	<0.5	0.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	0.15	0.7	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Ba	0.25	2	2.4	<0.25	2.7	35	0.5	1.2	0.8
F	100	<100	<100	<100	<100	<100	<100	<100	<100
Cl	100	<100	<100	<100	<100	<100	<100	<100	<100

Table 10.14
Emissions from Duramelter™ 100 (ppb)

Date/Time of sample	Concentration (ppb)									
	Cr	U	Tc	Cd	Hg	Pb	Th	Ba	F	Cl
7/1 - 16:40	1.5	<0.02	<0.05	<0.5	<0.5	0.1	<0.02	0.3	<25	<25
7/1 - 22:38	1.3	<0.01	<0.05	<0.5	<0.5	<0.1	<0.02	2.5	<25	<25
7/2 - 12:15	0.01	<0.01	<0.05	<0.5	<0.5	<0.1	<0.02	0.2	<25	<25
7/2 - 21:00	0.01	<0.01	<0.05	<0.5	<0.5	<0.1	<0.02	0.2	<25	<25

Table 10.15(a)
Mass Distribution of Metals and Radionuclides in Duramelter™ 100 Runs

Elements	Glass	Scrubber Solid	Scrubber Liquid	Baghouse	Off-Gas	Total (g)
	grams	milligrams				
Cr	10.18	600	2989.5	225.4	8	14.003
Ti	33.93	160	11.5	2	ND	34.104
Ni	11.20	240	ND	1.7	ND	11.442
Sr	6.79	40	ND	1.5	ND	6.832
U	67.87	80	73.75	0.6	ND	68.024
Ba	171.36	700	790	ND	10	172.860
Pb	31.73	ND	38.25	6.6	ND	31.775
Th	8.14	ND	5.5	0.0006	ND	8.146
Hg	0.017	ND	ND	0.006	ND	0.017
Tc	ND*	ND	ND	<0.05	ND	<0.05 (mg)
Cd	0.102	ND	2.75	1.9	ND	0.107

ND = Not Detected

*Note: Sample dilution factors (and therefore detection limits) are about 1000 times larger for glass analysis than for baghouse particulates.
Detection limits for ^{99}Tc by ICP-MS are high due to the presence of ^{99}Ru.

Table 10.15(b)
Percentage Distribution of Metals, Fluoride and Radionuclides

	Glass	Scrubber Solid	Scrubber Liquid	Baghouse	Off-Gas
Cr	72.7	4.3	21.4	1.6	0.06
Ti	99.3	0.5	0.03	0.006	<0.2
Ni	97.4	2.1	<0.001	0.02	<0.5
Sr	98.7	0.6	<0.02	0.02	<0.8
U	99.8	0.1	0.1	0.02	<0.01
Ba	99.1	0.40	0.5	<0.001	0.01
Pb	99.8	<0.03	0.1	0.02	<0.06
Th	99.8	<0.04	0.07	<0.001	<0.07

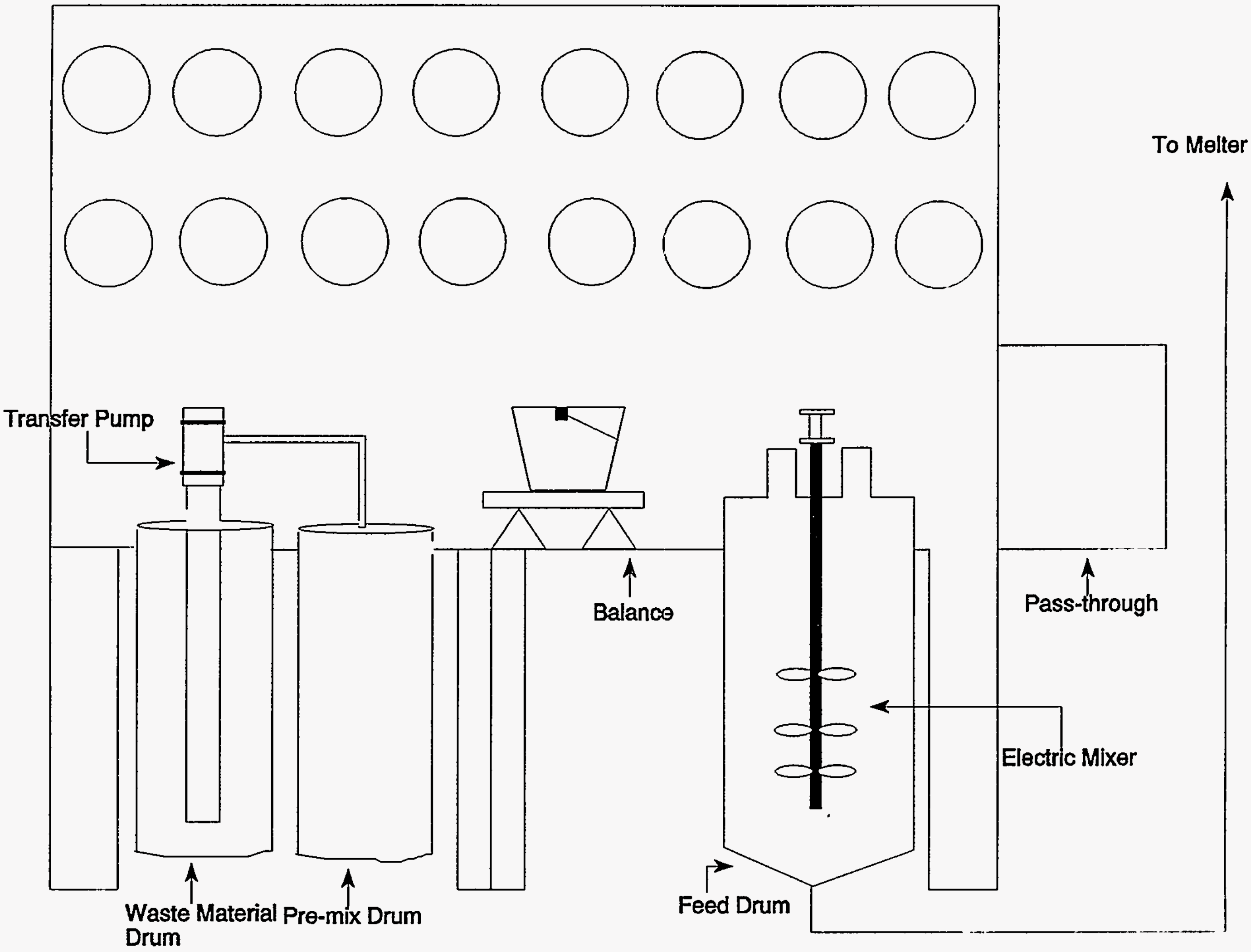


Figure 10.1a
Duramelter™ 100 Feed System

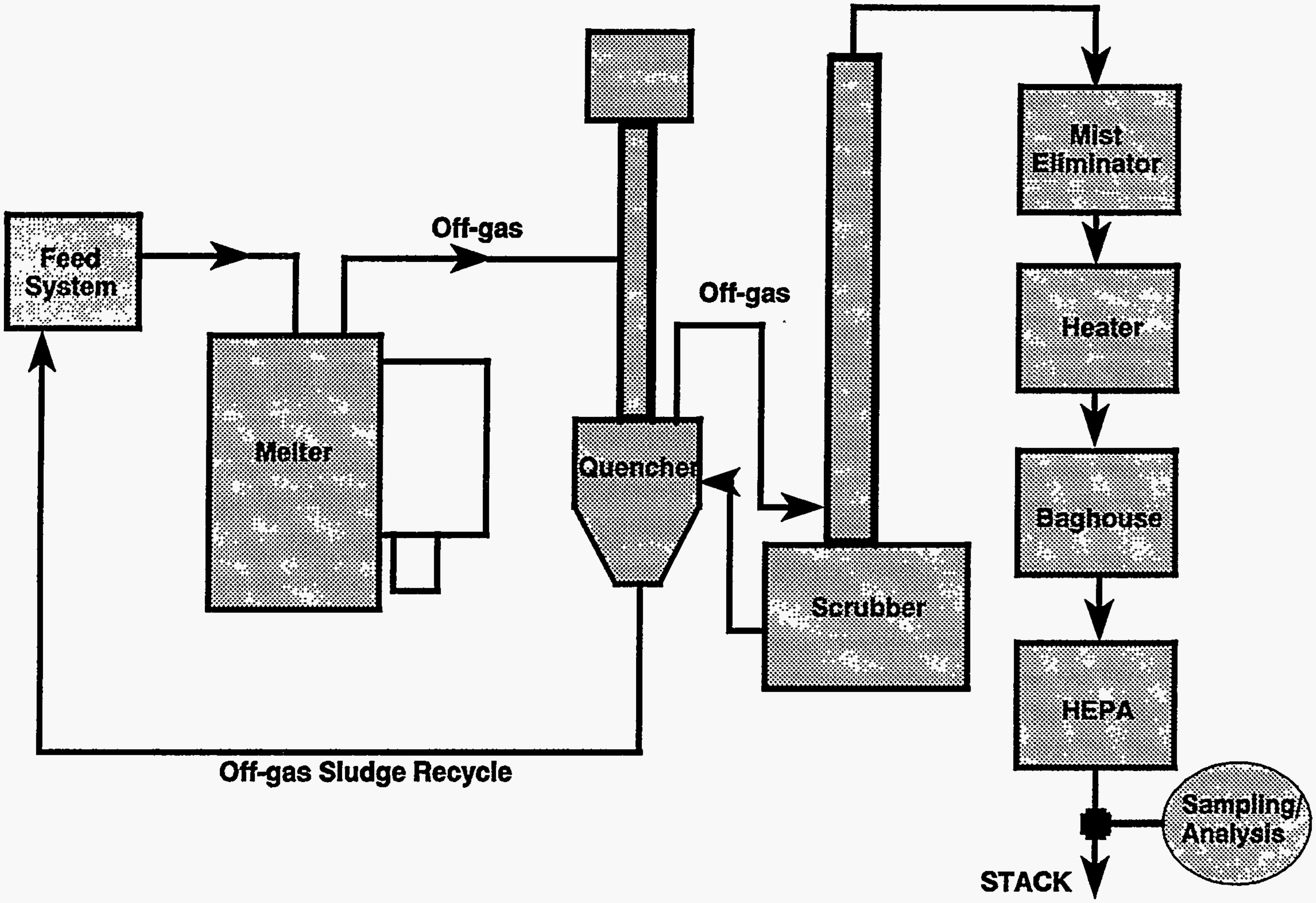


Figure 10.1b
Schematic of Duramelter™ 100 System

DURAMELTER™ 100

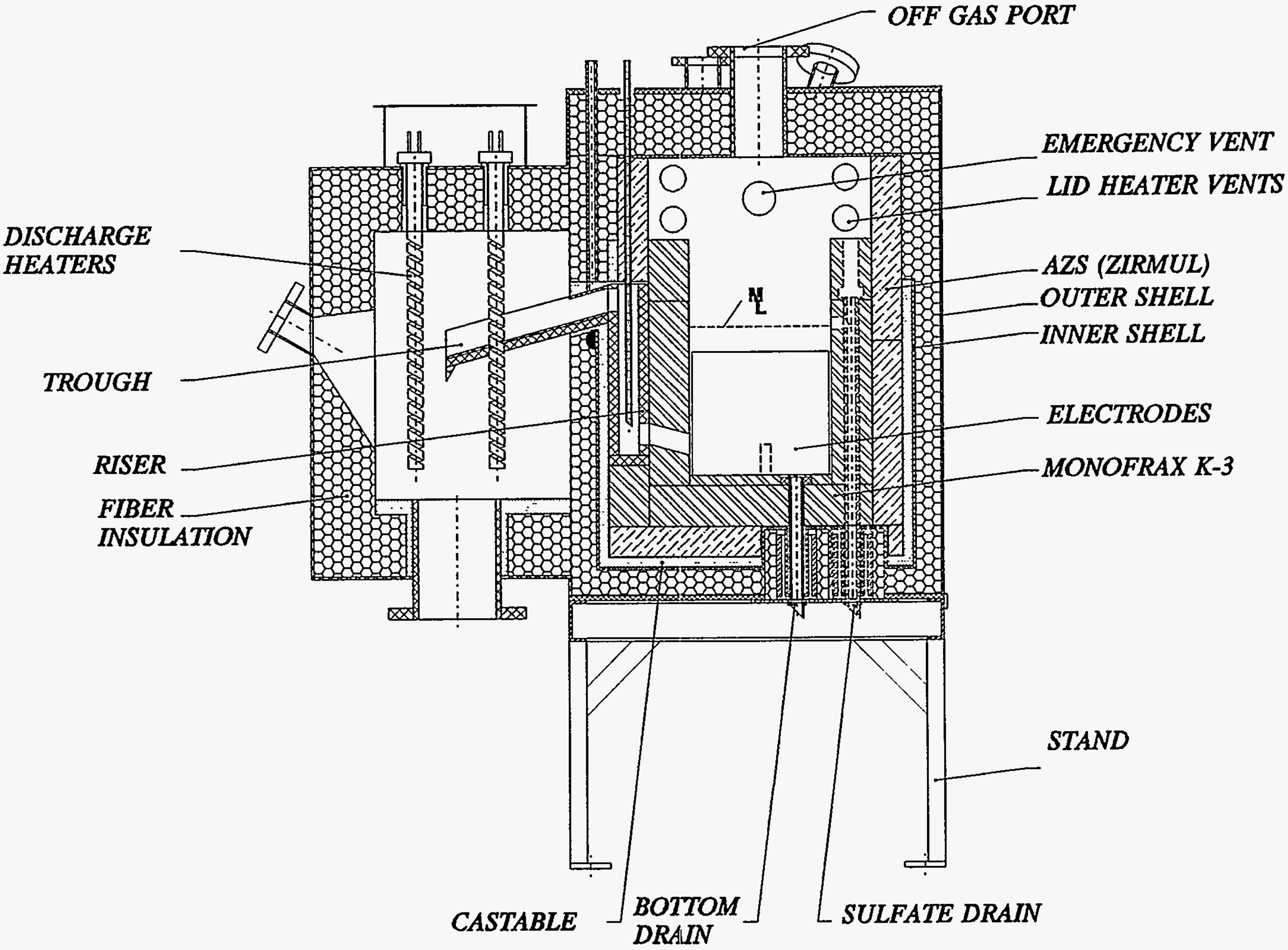


Figure 10.1c
Cross-section through the Duramelter™ 100 joule-heated melter.

Figure 10.2
Results from PCT tests on Duramelter™ 100 glasses compared to the high-level waste standard glass (SRL-EA) after 7 days

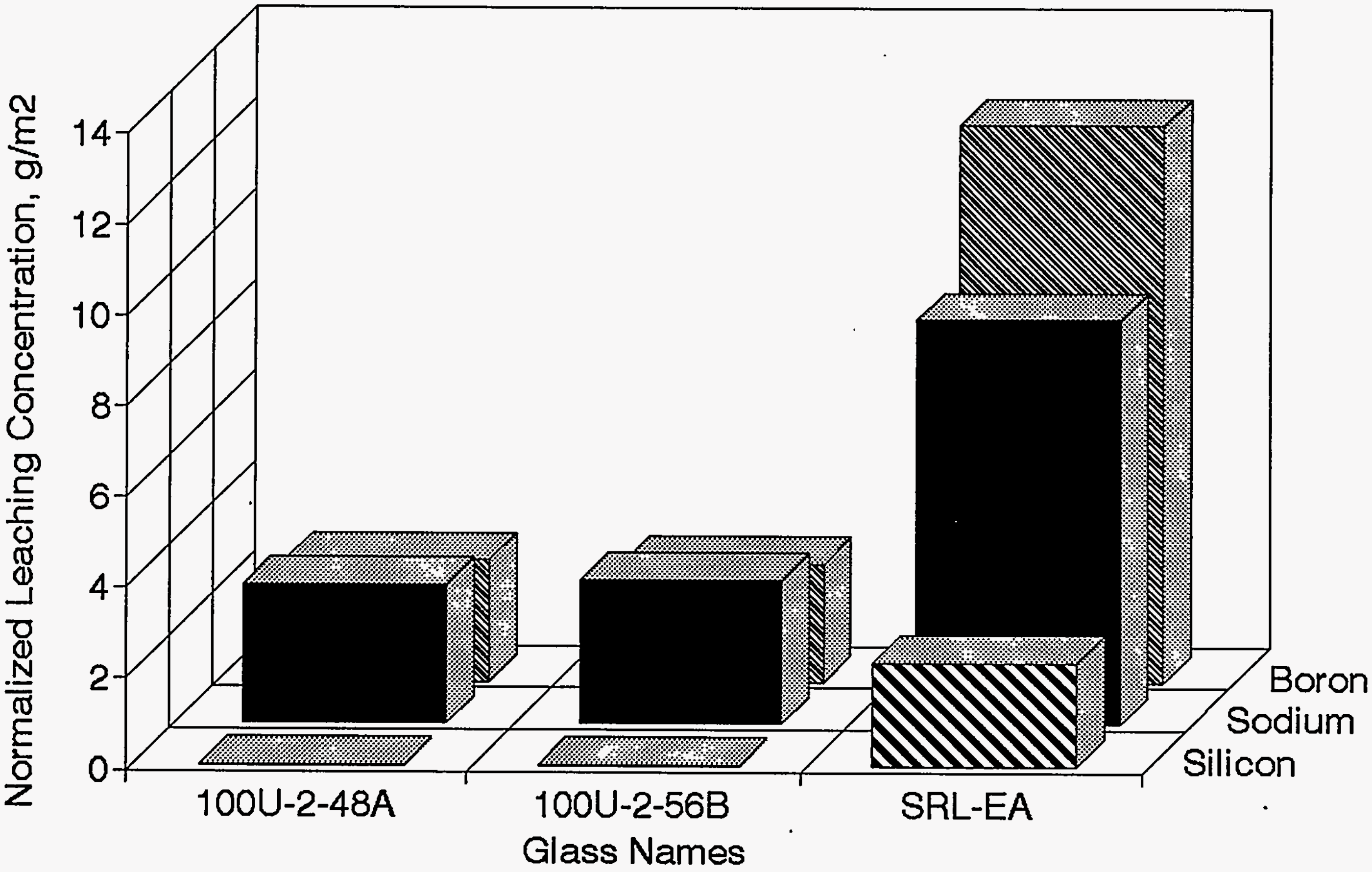


Figure 10.3
Concentration (ppm) of boron, potassium, and silica in scrubber solutions during continuous melter runs.

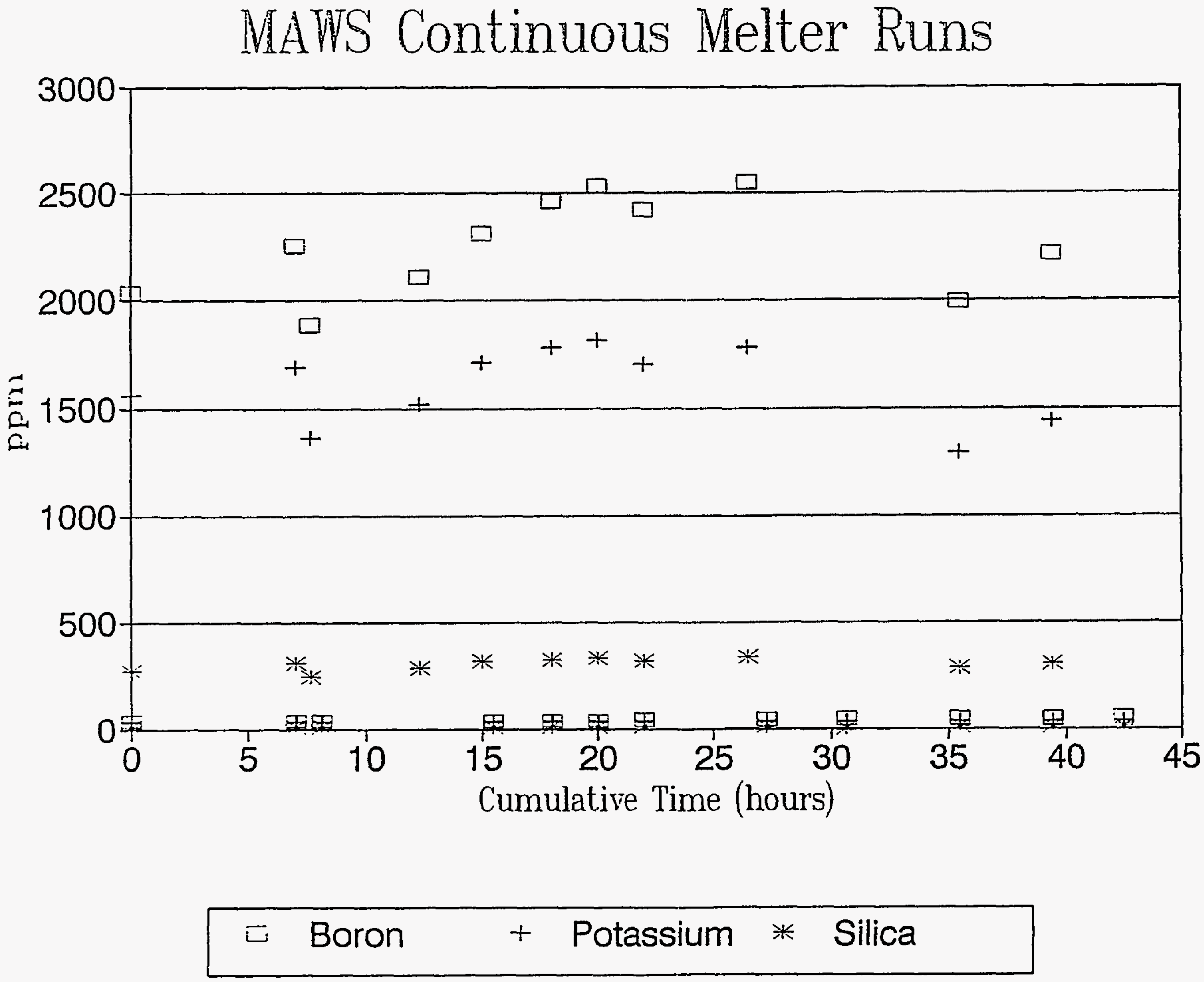


Figure 10.4

Concentrations of chromium, iron, aluminum, and magnesium in scrubber solutions during continuous melter runs.

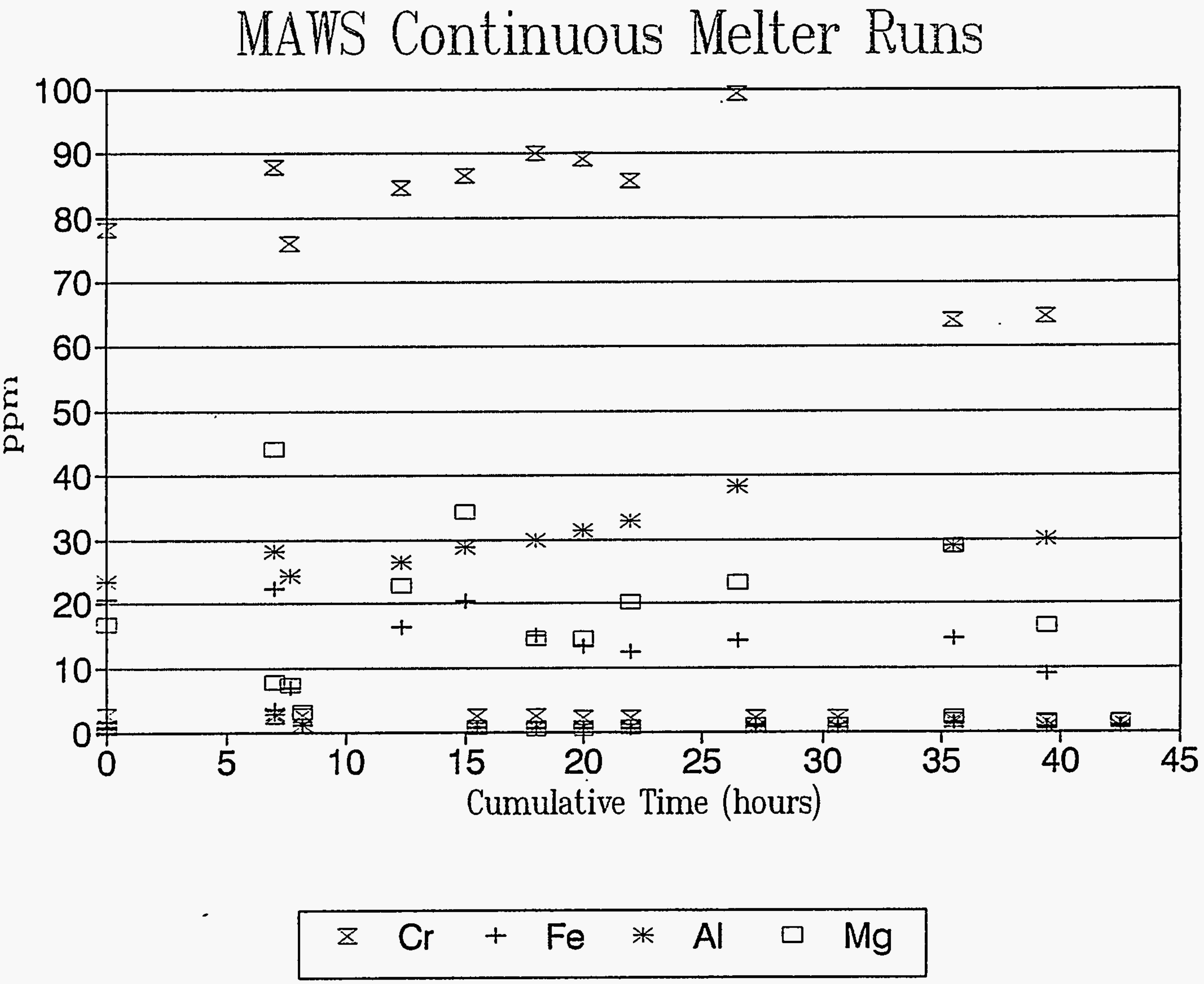


Figure 10.5
Concentrations of fluoride in scrubber solutions during continuous melter runs.

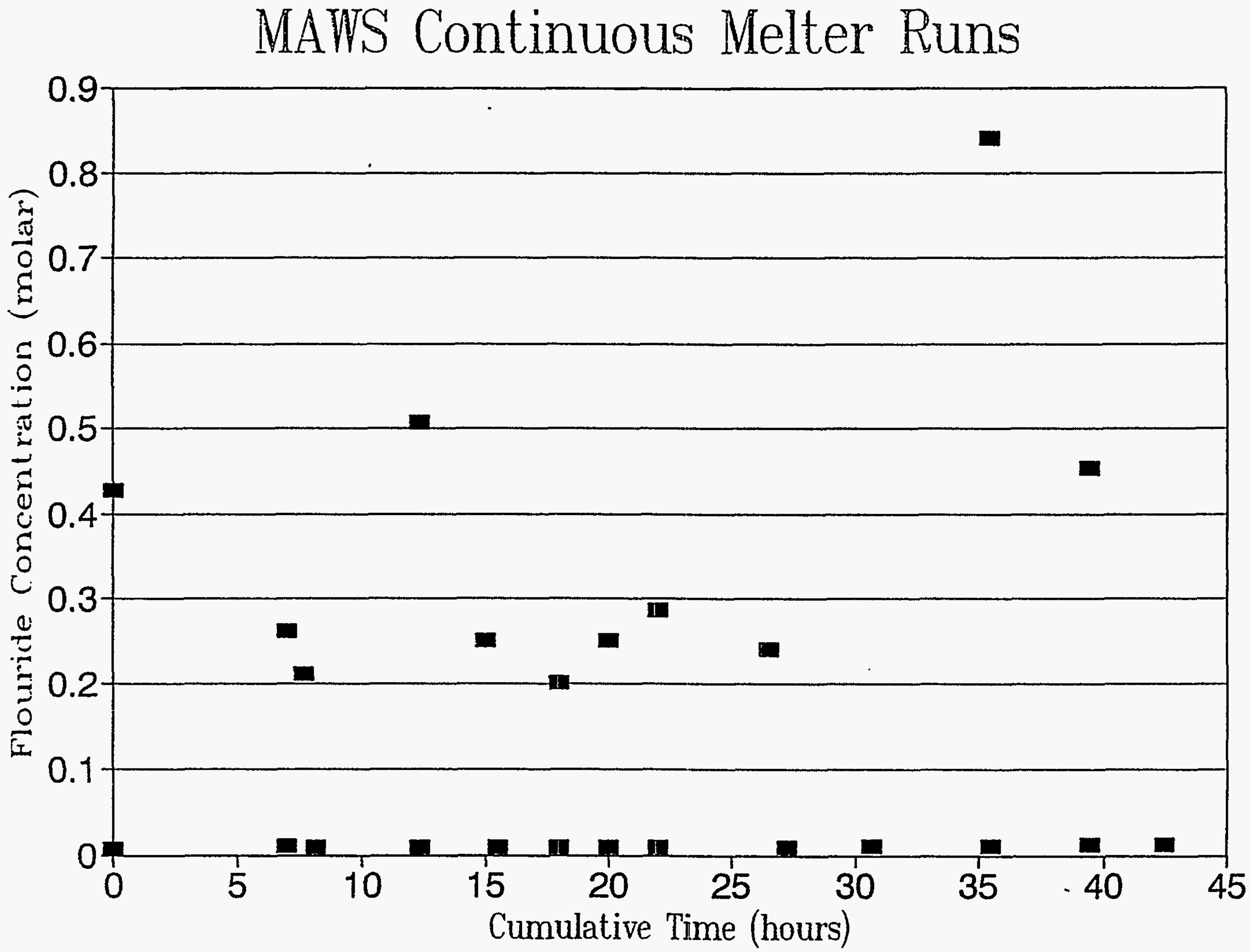
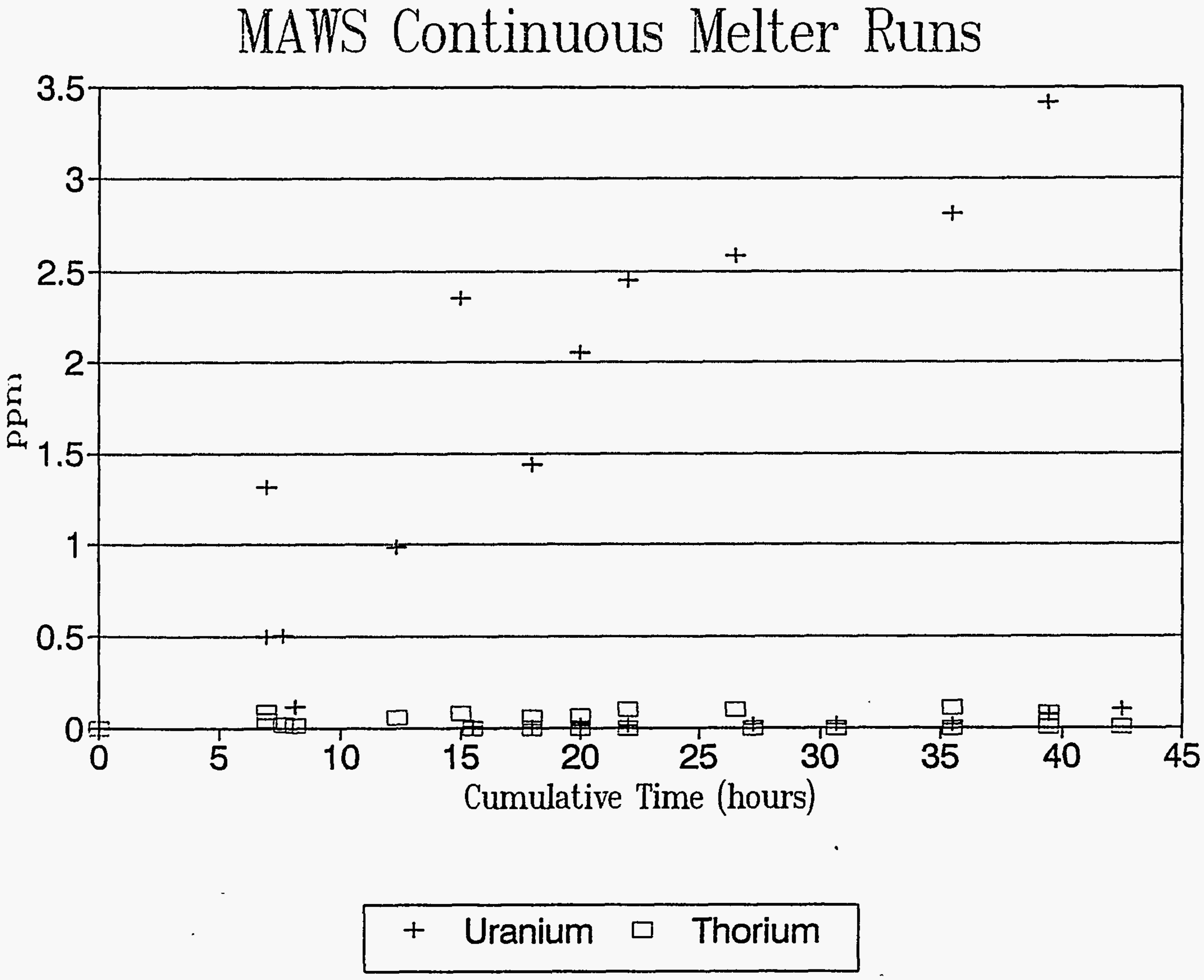


Figure 10.6

Concentrations of uranium and thorium in scrubber solutions during continuous melter runs.



SECTION 11.0
Duramelter™ 300 System Test at Fernald

11.1 The Duramelter™ 300 System

The Duramelter™ 300 system installed at the FEMP site is a slurry fed joule-heated melter with an off-gas system designed specifically for Fernald wastes. The melter is continuously fed and continuously or intermittently discharged. The glass can be discharged in bulk form into an appropriate container or into a "gem machine" to produce flattened marbles called "gems." The off-gas treatment system maintains negative pressure within the melter at all times and quenches and scrubs the gasses evolving from the melter. Each sub-system will be described below. A schematic diagram of the Duramelter™ 300 system is shown in Figure 11.1.

11.1.1 Melter

The Duramelter™ 300 (Figure 11.2) is a sealed joule-heated, rectangular tank straddled by two rectangular shaped electrodes that supply the main source of heat to the glass pool. Electrical conduction between the electrodes causes heat dissipation within the glass pool which provides the energy necessary to melt added waste feed. It is therefore essential to feed into the melter compositions that will produce glass with appropriate conductivities and viscosities. The science and technology that has been used to successfully operate the Duramelter™ 10 and Duramelter™ 100 have been fully utilized in the Duramelter™ 300 system.

Four lid heaters (protected in sheaths) span the length of the melter above the glass pool. The lid heaters are used during the initial heat-up of the system. Once the melter temperature is high enough (500-750°C), glass frit is fed through a port on top of the melter and the electrodes are activated. The lid heaters are also used to control the temperature in the plenum area of the melter to span the range from "hot-top" to "cold-top" operation.

The molten glass capacity of the melter is 35.1 gallons (133 liters). Three hundred kilograms per day is the nominal glass production rate. However, tests on smaller scale systems suggest that a rate of 900 kg/day should be possible (see Table 11.1 for melter characteristics and operating conditions). The molten pool of glass is contained by three types of refractories which are contained in an inner alloy shell. The inner shell is encased in fiberboard and fiber blanket insulation. An airlift discharge orifice exits the tank into a discharge trough. The airlift lance introduces air into the riser chamber which displaces the glass and causes it to flow down the discharge trough. The discharge trough is located inside the discharge chamber which has six heaters to facilitate draining. In addition to the air lift discharge, a bottom drain can be used to discharge all of the glass from the melter when modifications or maintenance to the melter must be made. When the feed system is activated, the slurry is pumped at a predetermined rate through a water-cooled feed tube passing through a port on top of the melter and onto the molten glass pool. Temperature is monitored at several locations in the melter and gem machine. A total of 33 type-K thermocouples are located at various points throughout the melter.

11.1.2 Feed System

The feed system for the melter consists of two 4000 gallon feeding/mixing tanks, two recirculation pumps, two propeller mixers, one main feed pump, and connecting piping and valves. The system allows for feed preparation in one tank while feeding from the other tank. The feed materials are mixed inside one feed/mix tank to form a slurry and recirculated constantly by a recirculation pump and are kept in suspension by an overhead propeller mixer. A portion of the slurry from the recirculation line is diverted to the main feed pump which pumps the feed slurry to the feed tube on the top of the melter.

11.1.3 Off-gas System

The off-gas treatment system has been designed to handle the high-fluoride wastes present at Fernald. The system consists of a quencher, a scrubber, mist eliminator, heaters, blowers, pre-filters, and HEPA filter. The hot gases, containing hydrogen fluoride, are drawn from the melter and enter the quencher where they are sprayed with a sodium hydroxide solution (2-3M) to react to form sodium fluoride. As the fluoride concentration in the quencher sump solution increases, the solubility limit of sodium fluoride is eventually exceeded (at about 1M) beyond which solid sodium fluoride is formed. This high-solid slurry from the quencher sump is then pumped to the separation tank and introduced at a later time into the feed batch. The scrubber uses a lower concentration of sodium hydroxide (solids are not formed) than the quencher to provide secondary cleaning of the off-gas stream. A mist eliminator is used to remove liquid droplets from the off-gas stream after the scrubber. An inline heater together with a side stream of heated dilution air reduce the relative humidity of the exhaust air prior to filtration through pre-filters followed by a HEPA filter. The total water volume in both units is kept constant by controlling the rate of water condensation in the liquid scrubber and evaporation in the quencher. The rate of condensation is controlled by adjusting the temperature of the liquid scrubber sump solution by use of a heat exchanger in the scrubber solution recirculation line. Negative pressure is controlled in the system by opening and closing several dampers which increase or decrease the volume of dilution air. The melter is equipped with an emergency vent line that automatically activates when the melter pressure differential (to atmospheric) is too low. A dilution air port is always used to provide quench air when the emergency vent line is operational. The off-gases, when run through the emergency vent line, are only treated by the pre-filters and HEPA filters. The emergency vent line is used during bakeout and during maintenance/modification of the components of the off-gas system.

There are 12 thermocouples located throughout the off-gas system. The thermocouples help to monitor the sump and recirculation temperatures of the quencher and scrubber and the temperature of the gas stream. The readouts for the thermocouples are located on the Off-Gas Control Console. The melter also has seven flow sensors that show their readings on the Off-Gas Control Console. The off-gas system is more sophisticated than the Duramelter™ 100 or Duramelter™ 10 systems. The indicators (temperature and flow) are tied into the Programmable Logic Controller (PLC) where alarm limits have been set. Located on the Off-Gas Control Console is a grid indicating many of the alarm conditions that may occur, such as "Quench Level High" or "Scrubber Low Flow." The operator can easily see the condition of the off-gas system and react to any situation. Also, the set-points, when reached, signal another piece of equipment to be energized. For instance, if the temperature indicator for the scrubber outlet reaches its low set-point, the scrubber heat exchanger will be automatically secured and provide heat to the off-gas stream until the high set-point is reached, in which case it will be automatically energized. The off-gas system has been designed to have these automatic features to aid in operations. It should be emphasized, however, that this does not take the place of the proper training that is necessary for a complex system such as this. All features can also be set to a "Hand" mode which is the manual mode for the system.

11.1.4 Gem Machine

The gem machine is attached to the bottom of the discharge chamber at the gate valve flange. Glass flows from the discharge chamber onto a horizontal gob cutting wheel which cuts the glass into small pieces. The molten glass pieces fall onto a horizontal, rotating wheel and cool as the wheel rotates. A graphite scraper bar sweeps the gems off of the wheel and directs them down a chute into a 30-gallon insulated drum. Throughout this operation, the air lift flow, temperature of the discharge chamber, gob cutter speed, and cooling wheel speed are all adjusted to maintain the optimum conditions for gem production.

11.2 Design, Construction, and Installation

Design of the Duramelter™ 300 system was performed by GTS Duratek and Catholic University, Vitreous State Laboratory personnel during Phase I of the MAWS program. Procurement of equipment and supplies proceeded as quickly as design activities permitted. GTS Duratek's Beltsville, Md facility was designated as the place to begin construction of the system in order to expedite the process of installation at Fernald. During this time, the Plant 9 facility at Fernald was being renovated and decontaminated in preparation for installation of the MAWS components. The melter body (inner shell, outer shell, bricks), bubbler bridge, and water treatment system were assembled and prewiring of electrical panels etc. was completed at the Beltsville plant during the first few months of 1993. The melter body and water treatment system were shipped to Fernald in March 1993. Once the melter was received at Fernald, other components of the system were installed as they became available, including the control room, the components of the off-gas system, the melter stand, the feed tanks, the gem machine, etc. Much of the construction of the system was contingent on the installation of a crane in Plant 9. During June, the crane was placed in Plant 9, but until installation was completed access to parts of the system (melter, control room) was limited.

Procedures for bakeout of the melter and operation of each sub-system (off-gas, feed system, temperature, power, and integrated operations) were under preparation as the system was being constructed. Numerous meetings and discussions between FEMP and GTS Duratek personnel concerning construction acceptance tests and the operational readiness review were held.

By the end of May, most of the major equipment (feed tanks, pumps, heaters, motors, valves, ion exchange media etc.) needed for operation had been shipped to Fernald. Installation of the plumbing and electrical wiring for the system then proceeded as quickly as possible. At the beginning of August, the construction acceptance test was reviewed and approved by FERMCO's QA/QC department allowing bakeout of the melter to commence on August 5, 1993. During bakeout, the emergency vent line was used while the construction of the off-gas system continued. Borosilicate glass frit melted in the Duramelter™ 100 at VSL was added to the melter to complete the bakeout procedure.

11.3 Test Run with Borosilicate Feed

The MAWS Phase I scope of work included a single test run with borosilicate feed to provide for a general checkout and debugging of the system. This run demonstrated that the nominal system glass production rate was easily achievable and provided the basic data necessary to identify system modifications that will be implemented prior to using fluoride and radioactive feeds. This section briefly describes the operations that were involved in the eight-hour run with a borosilicate feed composition.

Water had previously been run through the feed system so that any leaks could be identified. The water already present was used as part of the feed recipes. The ferric hydroxide sludge was pumped into the feed tank first using an air pump. The remaining chemicals were weighed and loaded onto pallets and lifted to the top of the feed tanks where operators wearing dust masks and harnesses carefully loaded them into the tank. Unfortunately, the recirculation pump's packing failed at this point but the mixing tank was filled to the height of the propeller in the mixing tank which allowed for the mixer to be activated in order to homogenize the feed. The propeller mixer kept the batch homogenized throughout the night. A spare diaphragm pump was installed in the feed system in order to continue preparations for the eight-hour borosilicate run. Further minor modifications to the feed system were also made at this point in order to improve operations. A temporary operating procedure was written to operate the modified system. The recirculation system for the feed worked very well when the air pump was energized.

The check list for the off-gas system was completed and the system was put into operation. Once the emergency vent valve was closed, the melter emissions were routed through the main off-gas system.

Feed system modifications were completed by September 30, 1993. The main off-gas system was put into operation with the quencher and scrubber recirculation pumps enabled. All systems were inspected and were found in good working order.

At 1404 hours, September 30, 1993, a safety meeting was held with everyone involved in the operation. The meeting addressed specific safety concerns associated with the new feed system. Melter operations, in general, were also addressed. Teams were established to work on the three main system components: feed, power, and off-gas. The purpose of the teams was to assign responsibility to the team leaders and establish lines of communication so that duplication of efforts would be minimized. Three engineers from the VSL were present to train operators and to provide technical advice during the run.

Feed rate was measured with the main feed pump set at 2, 3, 5, 10, and 50%, with the results shown in Table 11.2. The feed rate necessary to produce 300 kg/day of glass from this slurry feed is approximately 600 ml/min. Throughout the entire run, the feed system performed without any clogging events.

The initial readings of the off-gas system indicators (flows, pressures, temperatures) along with power settings for the heaters (lid and discharge) and the electrodes were collected and recorded. Samples of the quencher and scrubber sumps were also taken before feeding began.

The feed system was activated at 1507 hours on September 30, 1993. During the first two hours of the run, the main off-gas system was operating while feeding was intermittent. During the first hour of operation, attempts to increase the temperature of the glass pool were not successful due to the very high conductivity of the glass in the melt pool (a high-sodium starter frit had been used for the initial heat-up phase). Within about an hour and a half into the run, the conductivity had decreased sufficiently due to the compositional adjustment brought about by the new feed; by 1648 hours the temperature had risen to 1131°C, which was the average operating temperature for the run.

Power to the heaters in the discharge chamber was increased to attain a temperature appropriate for making gems (above 950°C). However, 790°C was the highest temperature that could be achieved with the main off-gas system operating. Air leaks into the gem machine were large enough that, with the melter under relatively large negative pressure, air was pulled through the gem machine into the discharge chamber. This increased air flow caused undesirable cooling of the discharge chamber. This leakage could be reduced, and a temperature greater than 900°C in the discharge chamber could be attained, by disabling the main off-gas system which activated a reduced flow through the emergency vent line. This temporary mode of operation was adopted in order to make gems during the run. Improved sealing of the gem machine was one of several recommended system modifications.

Forty-three kilograms of gems were produced during the two hours that the gem machine was activated. The gem machine is attached to the bottom of the discharge chamber at the gate valve flange. A chute is located at the scraper bar which directs the gems down the chute and into a 30-gallon insulated drum. Adjustments were made during the gem production (air lift flow, gob cutter speed, and cooling plate speed) to achieve gems that were cool by the time they reached the scraper. The gem machine functioned well and was easy to operate. Occasionally, stray gems were formed, but they did not hinder the overall operation of gem production. However, the mentioned modifications for sealing air leaks need to be made to the gem machine before it can operate simultaneously with the main off-gas system.

After two hours of operation, the gem machine was removed from the system and a 30-gallon stainless steel drum was aligned under the discharge chamber. An airtight seal between the drum and the drum flange was formed. The main off-gas system was activated and there was no trouble maintaining the temperature of 1000°C in the discharge chamber. The remainder of the eight-hour run was completed from 2244-0456 hours with the main off-gas system, feed system, and discharge system operational. Although the run was trouble free, conditions were identified that warrant additional design modifications. During the later part of the run, (at 0456 hrs) the differential pressure across the HEPA filters rose from 4.0" water to 5.5" water , which was high compared to the initial pressure reading of 1.5" water. This rate of pressure rise is unacceptable for long runs and therefore the off-gas system should be modified to prevent, or at least greatly reduce, build-up of pressure across the HEPA filters during operation. Water was condensing in the quencher during the run and had to be emptied into the holding tank several times; the system temperatures, pressures, and flow rates must be monitored and controlled in order to ensure that there is no net accumulation of water in the off-gas system over time. The run objectives established for the 8-hour run did not include balancing the water in the off-gas system. The objective of the run was to operate the system for eight hours to determine the operating conditions of the melter and to provide training for the operators. Development of these detailed control protocols will require extended testing on both the Duramelter™ 300 and the Duramelter™ 100 systems.

Samples of the quencher and scrubber liquid were taken approximately every two hours during normal operation. The total weight of the glass discharged in bulk was 136.3 kg. The main off-gas system was disabled at 0524 hrs and the run terminated at 0531 hrs. The system was set in idle mode (emergency vent line activated, bubbler set to 8 cfh, glass temperature set to 1050°C, discharge chamber to 750°C).

During the eight hour run, voltage and current readings on three of the heat sources, (the discharge chamber, lid heaters, and the electrodes) temperature readings at various locations throughout the system, melter and off-gas pressure, off-gas temperatures, feed rate, bubbling rate, and level of quencher and scrubber sumps were monitored and recorded every thirty minutes. A summary of these data is shown in Tables 11.3 and 11.4.

A brief description of the purpose of each reading is given below.

11.3.1 System Operating Parameter Readings

TI09: Temperature indicator 09 is located in a thermowell 6" from the melter floor. This temperature indicator is located in the center (approximately) of the glass pool. TI09 is the control thermocouple for the Dimension Controller. The temperature was set to 1130°C on the controller and this temperature was maintained, on average, from 1648-0430 without any difficulty.

TI11: Temperature indicator 11 is located in a thermowell 12" from the melter floor. This temperature is located at the interface (approximately) of the glass pool and the cold cap. When the feed system is activated, the temperature ranges from about 912 - 1100°C. During gem production, the temperature (at TI11) was about 1100°C.

TI17: Temperature indicator 17 is located in the discharge chamber. The discharge chamber was about 760°C during the initial feeding. The temperature was lower than expected due to air in-leakage through the gem machine. During the second feeding operation, a 30 gallon drum was connected and sealed to the discharge chamber. The temperature was then easily maintained at 1000°C.

TI25 and TI33: Temperature indicator 25 is located on a lid heater sheath and temperature indicator 33 is located in the air near the lid heaters. TI25 typically reads about 100°C higher than TI33. During feeding and while the main off-gas system was operational, the plenum area was cooler, ranging from about 650 - 700°C. When the feed system was disabled and the emergency vent line open, the temperature of the plenum was about 950°C.

Feed rate: The feed rate was calibrated (shown in Table 11.2) prior to the initial operation.

The feed system was activated during 1503-1730 hours and 2244-0430 hours. Throughout the feed operation, the feed rate was between 600-2000 ml/min and the average was estimated to be 750 ml/min.

Quench Inlet temp: The quench inlet temperature (in degrees celsius) is the temperature of the exhaust gases entering the quencher from the melter. While running the main off-gas system, the temperature of the exhaust gases is about 435°C.

Scrubber Inlet temperature: The scrubber inlet temperature (in degrees celsius) is the temperature of the gases as they exit the quencher and enter the scrubber. While running on the main off-gas system, the temperature is about 36°C. During the 8-hour run, quencher heat exchanger was activated. When quencher heat exchanger is secured, the exit temperature is normally about 80-90°C.

PIS9101 (Melter Pressure): The melter pressure is the absolute pressure of the melter with reference to atmospheric pressure. The melter pressure is established by opening and closing dampers located throughout the off-gas system to control air flow from the melter. It was decided to operate the melter at about -1.0" water while the main off-gas system was running. When the emergency vent line was operational, the melter pressure was about -0.2" water.

DPIS9106 (Differential Pressure across the Filter Housing): This pressure is measured across the filter housing to determine the efficiency of the filters. When the value of the differential pressure rises, the filters are becoming clogged with particulate matter. There is a general increase in the pressure of the filter housing from the beginning of the run. The differential pressure gradually rose from 1.5" water to 5.5" water.

PI9101 (Pressure Pre-Filter Housing): This pressure is measured across the pre-filter housing. The pressure in the line before entering the filter housing gradually decreased. signifying the decreasing ability of the main blower to pull the off-gases through the filter housing. This pressure gradually decreased from above 5" water to 3.5" water.

QLI (Quench Sump Level Indicator): This indicates the level of liquid inside the quench sump. The level of the quench sump increased while the feed system was activated. The water was transferred from the quench sump to the separator/holding tank four times. During the feed operation between 2244-0430, the quencher was emptied three times. The quench sump heat exchanger was on during the run.

SLI (Scrubber Sump Level Indicator): This indicates the level of liquid inside the scrubber sump. The level of liquid inside the scrubber sump is dependent on the rate of vapor condensation as compared to the rate of evaporation for the quencher. The most efficient operation is one in which the evaporation and condensation rates are balanced. Throughout the entire 8 hour borosilicate run, the level of the scrubber sump remained relatively constant because most of the water evaporated in the melter was condensed in the quencher.

Bubbling Rate: The bubbling rate is the rate at which air flows through the bubbler located in the glass pool inside the melter. The bubbling rate is controlled by a flow valve located on the Instrument and Utility Rack. During feeding, the bubbler was set to an average rate of about 17 scfh. The rate of bubbling was adjusted according to the need for a larger or smaller cold cap.

11.3.2 Run Results

The amount of each component used to prepare the borosilicate feed is shown in Table 11.5. More than enough feed was prepared for this run, because it was necessary to fill the feed tanks to a certain level so that the lowest impeller blade (36" from the bottom of the feed tank) could effectively mix the batch.

Compositional analyses in triplicate of the glass produced at the end of the 8-hour borosilicate run, along with the calculated target composition, are shown in Table 11.6. The three analyses of the glass are in very good agreement with each other. However, the data indicate that the glass contains more sodium and about half the iron of the target. This is due to incomplete change over of the glass composition that was in the melter at the beginning of the run. Initially, when the 300 kg/day melter was heated during bakeout, 200 kg of glass from the Duramelter™ 100 runs was used as a start up frit in combination with commercial glass frit. The overall composition of that blend was higher in sodium and lower in iron than the borosilicate feed. Since only 180 kg of glass was produced in the 300 kg/day borosilicate run, and the melt pool contains about 300 kg of glass, it is evident that a combination of the composition of the start-up frits and the target feed was produced, which then, as expected, shows a lower concentration of iron and a higher concentration of sodium than the target composition.

Both viscosity and conductivity were measured over a range of temperatures, with the results shown in Tables 11.7 and 11.8. The electrical conductivity data for each glass were fitted to Arrhenius equations and the melt viscosity to Vogel-Fulcher equations and interpolated to standard temperature for convenience of comparison. The viscosities and conductivities of the borosilicate melts are higher than the fluoride glasses we will use later in the melters. As the compositions of the two types of feed are so vastly different, it is not possible to obtain similar viscosity-conductivity curves for the two types of glasses. However, while this is desirable, it is not essential since the primary requirement is for a glass that is easy to work with and which exhibits processable viscosities and conductivities at 1100-1150°C. The purpose of using the borosilicate glass composition as a "starter" glass is that it is very easy to work with in that it does not crystallize easily and does not produce toxic emissions. It is therefore a natural choice for start-up testing and operator training.

Table 11.9 summarizes the production rate statistics for the borosilicate run; the 300 kg/d nominal glass production rate was easily exceeded, even in this first system test. Table 11.10 shows the results of analysis of the scrubber samples taken at various times during the run. There is a gradual increase of the concentrations of the glass constituents over time, as would be expected, but the concentrations remain generally low. The chromium build up is due to release from the melter components (refractories and possibly electrodes); this is frequently greatest early on and tends to stabilize as the system is operated for longer times.

11.4 Comparison of the Duramelter™ Systems

Table 11.11 summarizes some of the statistics for the three melters. The only parameter that is the same for all melters is the operating temperature which is 1050-1150°C. The quencher and scrubber sumps are the same size for the Duramelter™ 100 and 300. The other variables are roughly proportional to the size of the melter.

Following are summaries of each subsystem of the melter and the changes that were made in subsequent melters.

Melter: The Duramelters™ 10, 100, and 300 are all sealed joule-heated melters with one pair of electrodes used as the main source of heat for the molten glass pool. All melters have a bubbler, various thermocouples, lid heaters and controllers. The main differences between the systems, other than size, is the level of control of the various heating systems. The Duramelter™ 10 has a simple set-point controller for the electrodes based on a thermocouple located in the glass pool. The lid and discharge heater currents are manually controlled with a variac. The Duramelter™ 100 has a programmable controller that regulates the power to the electrodes based on a control thermocouple. This controller allows for alarm features to be programmed into it to warn the operators of conditions that warrant operator input. The lid and discharge heaters are controlled with a variac, as with the Duramelter™ 10. The Duramelter™ 300 has the programmable controller for the electrodes and a back-up controller if the control thermocouple fails. This prevents the system from losing power if the control thermocouple fails. The discharge heaters can be both manually or automatically controlled. The lid heaters are controlled by a potentiometer that regulates the voltage to the heaters. As the melters increase in size, the number of thermocouples also increase. The Duramelter™ 10 has six thermocouples located throughout the melter, while the Duramelter™ 100 has 14 and the Duramelter™ 300 has 28 thermocouples. The number of lid heaters also increases: the 10 has two, the 100 has four and the 300 has four during normal operation and has the capacity for four additional heaters (used during bakeout).

Discharge System: The Duramelter™ 10 used a bottom drain method to discharge glass. This proved very inconvenient in that it was difficult to start the molten glass flowing out of the melter and it was also difficult to stop the glass stream once it had started. The difficulties in starting the glass to drain were due to the large temperature gradient between the bottom drain area and the glass pool temperature. The glass would form crystals as it slowly cooled. To stop the glass from emptying completely, a plunger was utilized to plug the drain opening. However, it was found to be difficult to position the plunger in the correct spot. An airlift is used to discharge glass from the Duramelter™ 100. This method of intermittently discharging glass worked very well; however, there were a few instances when discharging the radioactive composition that the airlift became clogged. It is believed that the glass cooled around the airlift and formed crystals that were difficult to melt. As long as the temperature of the air lift is ≥ 1050°C, this will not occur. Thus far, the airlift on the Duramelter™ 300 has worked well.

Feed System: All three Duramelter™ feed systems have a feed tank, a method for mixing the feed tanks, a feed pump, piping, valves, and a water cooled feed tube. The feeding systems present different problems as the melters are scaled up. All systems experience problems with the settling of feed in the feed lines to some degree. The Duramelter™ 10 was constantly burdened by clogging in the feed tube and settling of feed in the feed lines. This resulted in intermittent feeding and constant monitoring during feeding into the melter. The Duramelter™ 300 has some settling in the line but has never experienced a clogged feed tube or severe enough settling in the feed lines to interfere with the operations. The feed rate for the Duramelter™ 300 is about three times faster than the 100. The feed system for the 300 also has a recirculation loop where the feed is recirculated and a portion of the feed is diverted to the main feed pump. This has turned out to be the best method for keeping the feed flowing in the feed lines and preventing clogging. As the melters are scaled up, the feed tanks were also scaled up. The Duramelter™ 10 has a feed tank of 10 gallons and all components of the feed are added to the tank and mixed using a simple propeller mixer set up on top of the feed tank. This equipment and operation takes place inside a glovebox. The feed system is a little more complex for the 100. All mixing of the feed components take place in a large glovebox. The Pit 5 sludge is mixed and transferred into a mixing drum using a drum pump. Soil-wash fractions, NaF, and additives are then mixed with the sludge. The feed mixture is screened as it is pumped into the 55-gallon feeding drum. The contents of the feed drum, as with the Duramelter™ 10, are also mixed with a propeller mixer mounted on top of the feed tank. The mixing/feeding tanks for the Duramelter™ 300 system are two 4000-gallon tanks. The feed chemicals are added directly to the feed tank where it is mixed by a double propeller mixer and a recirculation pump that pumps the feed slurry from the bottom of the tank to the top of the tank. The disadvantage to this system is the formation of a heel around the outside edges of the feed tank. The advantage is that once a feed tank is prepared, it will last about seven days of continuous feeding.

Off-gas System: It was found in the Duramelter™ 10 that sodium borate, potassium borate, sodium fluoride, and other solids form in the transition piece between the melter and the quencher. To aid in the removal of these solids, spray nozzles were added to the transition piece in the Duramelter™ 100 and Duramelter™ 300. The spray nozzles use scrubber liquid and spray such that the solids are forced into the quencher. The Duramelter™ 300 is set up to automatically spray scrubber liquid through the transition piece when the level of the quencher is low. The spraying at regular intervals of time helps to prevent large build-ups in the transition piece.

To aid in the removal of solids from the quencher, a mixer (or homogenizer) was added to the quencher sumps in the Duramelter™ 100 and Duramelter™ 300. The NaF solids in the quencher of the Duramelter™ 10 were removed manually via a bottom bucket. As the systems were scaled up, it became necessary to pump the solid NaF from the quencher to a holding tank for latter recycling into the feed. The sodium fluoride that is formed in the quencher is homogenized by a mixer. This allows the solids to be pumped out of the quencher, which removes one manual process and also distances the operator from the radioactive hazards.

11.5 Summary and Discussion

We have seen in this section that the final scale-up of the Duramelter™ systems has been put into operation at Fernald. Lessons learned from running the Duramelter™ 10 and Duramelter™ 100 have been used in the design and operation of the Duramelter™ 300. Initial start-up using borosilicate feed showed the Duramelter™ 300 to be operational. This completes the objectives of the MAWS Phase I program. Since then, a 72-hour surrogate run (fluoride feed) has been completed and the data are being analyzed to assess readiness for radioactive runs; results from this run will be presented in a subsequent report.

Table 11.1
Duramelter™ 300 Physical Characteristics and Operating Conditions

Total Surface	503.7 in^2
Tank Depth	24"
Melt Depth	~16"
Glass Volume	35.1 gallon (133 liters)
Glass Operating Temp.	1000-1150°C
Max. Glass Temp. (absolute limits)	1250°C
Plenum Temperature	400-1000°C
Discharge Chamber Temp.	600-1150°C
Melter Pressure (DPIS 9101)	negative 1" water minimum (range -1 to -5)
Production Rate	300-900 kg/day
Melter Turnover Time (3 volumes)	78 hours

Table 11.2
Feed Rate as a Function of Pump Setting

Pump Setting (%)	Rate (ml/min)
50	2556
10	1428
5	775
3	795
2	722

Table 11.3
300 kg/d Data Check Sheet for 8-hour Run (9/30/93-10/1/93)

Time	Lid heater		Electrodes		Discharge Htrs		TI09 glass pool °C	TI11 bottom + 12" °C	TI17 Discharge °C	TI25 lid heater sheath °C	TI33 plenum (air) °C
	amps	volts	amp	volts	amps	volts					
1408	72	50	590	49			1048	1020	655	850	815
1519	72	50	980	84			1039	945	748	770	689
1530	100	67									
1544	95	66	600	53			1047	981	741	800	713
1615	100	67	830	57			1112	1075	745	750	631
1648	115	83	760	48			1131	1097	783	793	668
1715	115	83	730	45			1132	1114	789	803	690
1753	110	83	1015	64			1125	1124	932	865	841
1900	90	67	850	53	78	113	1126	1114	966	921	822
1931	90	67	800	50			1130	1109	972	941	941
2000	90	67	790	50			1130	1113	990	955	952
2032	90	67	750	48			1131	1104	1104	963	960
2124	89	67	720	47	76	113	1131	1090	1015	972	968
2200	90	67	730	49			1131	1072	983	944	941
2237	88	67	620	42			1130	1086	1046	1008	982
2300	110	84	995	67	78	113	1133	980	987	955	854
2350	112	85	800	56	64	93	1118	961	998	884	768
0014	118	86	895	64			1131	1039	998	833	706
0100	120	87	660	49	60	87	1138	1051	998	773	645
0134	120	87	860	69	66	95	1125	1077	996	812	695
0205	119	87	960	69	63	93	1128	1045	1001	822	694
0233	120	87	830	60	66	96	1132	1061	996	806	689
0302	120	87	850	60							
0330	120	87	760	53			1135	912	998	791	647
0409	120	87	830	55			1134	991	1001	823	693
0456	110	81	520	39			1103	881	999	818	703

Table 11.3 (continued)
300 kg/d Data Check Sheet for 8-hour Run (9/30/93-10/1/93)

Time	Feed rate ml/min	QLI (Quencher Level Indicator)	SLI (Scrubber Level Indicator)	Bubbling Rate (scfh)
1480	0	1.25	1.73	2
1519	0	1.45	1.6	10
1544	750	1.5	1.65	10
1615	750	1.55	1.65	14
1648	750	1.55	1.65	13
1715	750	1.55	1.65	13
1753	0	1.55	1.65	2
1900	0	1.55	1.65	9
1931	0	1.55	1.65	10
2000	0	1.55	1.65	12
2032	0	1.55	1.7	12
2124	0	1.55	1.7	13
2200	0	1.55	1.65	6
2237	0	1.35	1.65	5
2300	750	1.40	1.65	14
2350	750	1.45	1.65	14
0014	750	1.40	1.65	15
0100	0	1.25	1.67	25
0134	0	1.35	1.67	25
0205	750	1.4	1.67	15
0233	750	1.2	1.67	22
0302	750	1.2	1.67	22
0330	0	1.4	1.67	20
0409	750	1.25	1.67	15
0456	0	1.35	1.67	8

Table 11.4a
Off-Gas System Data Check Sheet 9/30/93-10/1/93
From 1413 hrs to 2040 hrs

Location	Indicator	1413 hrs	1520 hrs	1550 hrs	1650 hrs	1746 hrs	1857 hrs	1944 hrs	2040 hrs
I & U Rack (em line)	PIS 9101 ("water)	-2.1	-2.2	-2.0	-1.0	-0.2	-0.2	-0.2	-0.2
(melter diff)	DPIS 9101("water)	0.3	0.4	0.4	0.2	0.1	0	0	0
(quench diff)	DPIS 9102 ("water)	0	0	0	0	<0	<0	<0	0
(scrubb diff)	DPIS 9103 ("water)	0.4	0.4	0.4	0.4	0.2	0	0	0
(mist elim)	DPIS 9104 ("water)	0	0	0	0	0	0	0	0
(pre-HEPA)	PI 9101 ("water)	5+	5+	5+	5+	4.5	4.0	4.0	3.8
(pre-HEPA)	DPIS 9105 ("water)	0	0	0	0	0	0	0	0
(HEPA diff)	DPIS 9106 ("water)	1.5	1.6	1.6	1.8	2.6	3.4	3.7	3.9
(off-gas discha)	PI 9102 ("water)	2.4	2.4	2.4	2.4	2.4	2.2	2.2	2.1
(gem)	PIS 9102 ("water)	—	-0.2	-0.2	-0.2	—	-0.2	-0.2	-0.2
Off-gas Control Console	Quench recir flow (gpm)	16.2	16.7	16.7	16.3	15.9	off	0	0
	Scrubber recir flow (gpm)	24.3	23.7	29.4	29.4	29.5	off	0	0
	Scrubber air flow (cfm)	184	161	157	203	208	190	197	200
	System air flow (cfm)	1145	1115	1110	1098	985	908	904	901
	Quench inlet temp (°C)	499	469	447	458	60	27	23	22
	Quench sump temp (°C)	36	43	43	36	31	28	27	26
	Quench recir temp (°C)	29	30	29	27	16	21	20	18
	Scrubber inlet temp (°C)	31	39	38	32	23	14	18	17
	Scrubber sump temp (°C)	31	32	32	29	27	28	28	28
	Scrubber recir temp (°C)	29	29	29	27	26	24	21	19
	Scrubber outlet temp (°C)	30	33	33	29	26	25	22	20
	Scrubber heater inlet temp (°C)	28	29	29	26	26	26	25	24
	Scrubber heater outlet temp (°C)	43	42	44	42	43	43	43	43
	HEPA heater outlet temp (°C)	37	38	38	39	42	43	42	41
						CD2 open	CD2 open	scrubr outlet heater on	
						CD3 open	CD3 open	HEPA heater "hand"	
						CD1 open	CD1 open	Scrubr ID fan "hand	
							em. vent on		
							gem making		

Table 11.4b

Off-Gas System Data Check Sheet 9/30/93-10/1/93

From 2245 hrs to 0532 hrs

Location	Indicator	2245 hrs	2400 hrs	0100 hrs	0200 hrs	0300 hrs	0400 hrs	0447 hrs	0532 hrs
I & U Rack (em line)	PIS 9101 (″water)	-1.0	-1.0	-1.0	-1.0	-0.8	-0.5	-0.8	-0.1
(melter diff)	DPIS 9101 (″water)	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0
(quench diff)	DPIS 9102 (″water)	0	0	0	0	0	0	0	0
(scrubb diff)	DPIS 9103 (″water)	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0
(mist elim)	DPIS 9104 (″water)	0	0	0	0	0	0	0	0
(pre-HEPA)	PI 9101 (″water)	4.3	4.2	4.3	4.2	4.0	3.5	3.5	2.9
(pre-HEPA diff)	DPIS 9105 (″water)	0	0	0	0	0	0	0	0
(HEPA diff)	DPIS 9106 (″water)	4.0	4.0	4.1	4.2	4.7	5.4	5.5	5.8
(off-gas disch)	PI 9102 (″water)	2.0	2.0	2.0	2.0	1.9	1.7	1.7	1.7
(gem)	PIS 9102 (″water)	---	---	---	---	---	---	---	---
Off-gas Control Console	Quench recir flow (gpm)	14.9	17.1	16.9	16.7	16.7	16.7	16.8	0
	Scrubber recir flow (gpm)	29.6	29.1	29.5	30.4	30.0	29.1	31.1	0
	Scrubber air flow (cfm)	192	172	168	174	137	139	126	87
	System air flow (cfm)	980	982	973	976	944	884	867	788
	Quench inlet temp (°F)	530	442	384	428	427	429	378	55
	Quench sump temp (°F)	34	47	44	43	46	43	39	34
	Quench recir temp (°F)	27	30	29	29	29	26	24	13
	Scrubber inlet temp (°F)	29	44	36	34	39	36	31	14
	Scrubber sump temp (°F)	29	34	32	32	32	29	27	26
	Scrubber recir temp (°F)	28	31	30	30	31	26	25	21
	Scrubber outlet temp (°F)	28	34	34	33	35	33	32	26
	Scrubber heater inlet temp (°F)	24	25	26	24	23	23	23	18
	Scrubber heater outlet temp (°F)	42	43	44	44	44	42	42	19
	HEPA heater outlet temp (°F)	39	40	40	39	40	42	43	45
		CD2 closed	CD2 closed	CD2 closed		CD1 open	CD1 open	feeding stopped	em. vent on
		CD1 open	CD1 open	CD1 open		CD2 closed	CD2 closed	no discharging	all systems off
		CD3 open	CD3 open	CD3 open		CD3 open	CD3 open		

Table 11.5
Composition of the Borosilicate Feed (300-BS-01-01)

Components	Target Weight (kg)
SiO_2	1021
Al_2O_3	72
H_3BO_3	844
Na_2CO_3	743
$Fe(OH)_3$ Sludge	1951
K_2CO_3	245
H_2O	1965

Table 11.6
Three DCP Analyses of the Glass Sample
from the End of the 8-hour Run

Component	Weight Percent			Target Composition (wt%)
Al_2O_3	4.47	4.65	4.54	3
B_2O_3	21.7	21.7	22.4	20
CaO	0.59	0.59	0.58	0
Fe_2O_3	6.37	6.42	6.41	12
K_2O	5.84	5.82	5.68	7
MgO	0.12	0.12	0.13	0
Na_2O	21.4	21.7	21.4	15
P_2O_5	0.34	0.34	0.33	0
SiO_2	36.9	37.1	37.8	43
Total	97.7	98.4	99.3	100

Table 11.7
Viscosity of the Glass from the 8 hr Run

Temperature (°C)	Viscosity (Poise)
1000	27.5
1050	17.5
1100	12.1
1150	8.9
1200	6.9

Table 11.8
Conductivity of the Glass from the 8 Hour Run

Temp (°C)	Conductivity (S/cm)
950	0.33
1000	0.45
1050	0.57
1100	0.69
1150	0.81
1200	0.92

Table 11.9
Statistics from the 8-Hour Run

Total Glass Produced	179.5 kg
Total Run Time	8.13 hours
Rate of Glass Produced	529.4 kg/day
Weight of Gems Produced	43.2 kg
Total Time of Gem Production	114 minutes
Rate of Gem Production	545.7 kg/day

Table 11.10a
DCP Analysis of Quencher Solution Samples from the 8 Hour Borosilicate Run (ppm)

Date/Time	Sample	Cr	P	B	Si	Ti	Mn	Fe	Al	Zr	K	Na	Li	Mg	Ca
9/30 2:21 pm	QS1421	2.80	8.21	9.77	4.70	0.03	0.06	0.87	0.30	0.01	18.2	36.8	0.28	17.4	51.8
9/30 5:21 pm	QS1721	1.14	0.30	5.17	2.67	0.00	0.07	0.02	0.03	0.00	9.00	13.7	0.07	10.4	13.4
10/1 0:32 am	QS0032	8.85	0.41	50.7	4.68	0.01	0.06	0.01	0.06	0.00	66.5	72.8	0.11	13.8	18.7
10/1 5:25 am	QS0525	8.55	0.10	128	7.40	0.01	0.01	0.17	0.04	0.00	130	143	0.08	7.84	9.88

Table 11.10b
DCP Analysis of Scrubber Solution Samples from the 8 Hour Borosilicate Run (ppm)

Date/Time	Sample	Cr	P	B	Si	Ti	Mn	Fe	Al	Zr	K	Na	Li	Mg	Ca
9/30 2:21 pm	SS1421	0.97	0.20	3.40	2.76	0.00	0.11	0.05	0.04	0.00	6.93	12.2	0.08	12.1	14.2
9/30 5:21 pm	SS1721	1.20	0.15	5.44	2.64	0.01	0.08	0.04	0.07	0.00	9.32	14.6	0.09	11.5	14.5
10/1 0:32 am	SS0032	1.46	0.27	7.31	2.70	0.00	0.09	0.01	0.04	0.00	10.8	15.3	0.07	10.6	13.4
10/1 5:25 am	SS0525	1.57	0.12	11.4	2.60	0.00	0.06	0.00	0.04	0.00	14.7	18.7	0.07	9.77	12.8

Table 11.11
Comparison of the Three Duramelter™ Vitrification Systems Used in the MAWS Program

	Duramelter™ 10	Duramelter™ 100	Duramelter™ 300
Glass mass	10 kg	100 kg	300 kg
Glass pool surface area (m^2)	1.61×10^{-4} m^2	$9.29 \times 10^{-4} m^2$	3.25×10^{-3} m^2
Electrode surface area	1.61×10^{-4} m^2	1.08×10^{-3} m^2	1.35×10^{-3} m^2
Avg power requirements during processing fluoride/radioactive	1.1-3.3 kW	40-45 kW	60-80 kW[*]
Operating temperature of glass pool	1050°C-1150°C	1050°C-1150°C	1050°C-1150°C
Quencher volume	15 l	284 l	284 l
Scrubber volume	45 l	757 l	757 l
Production rate	10-30 kg/day	100-300 kg/day	300-900 kg/day
Feed tank size	37.85 l	208.2 l	15,140 l
Feed rate	30-80 ml/min	230-290 ml/min	600-800 ml/min

[*] Processing of borosilicate glass

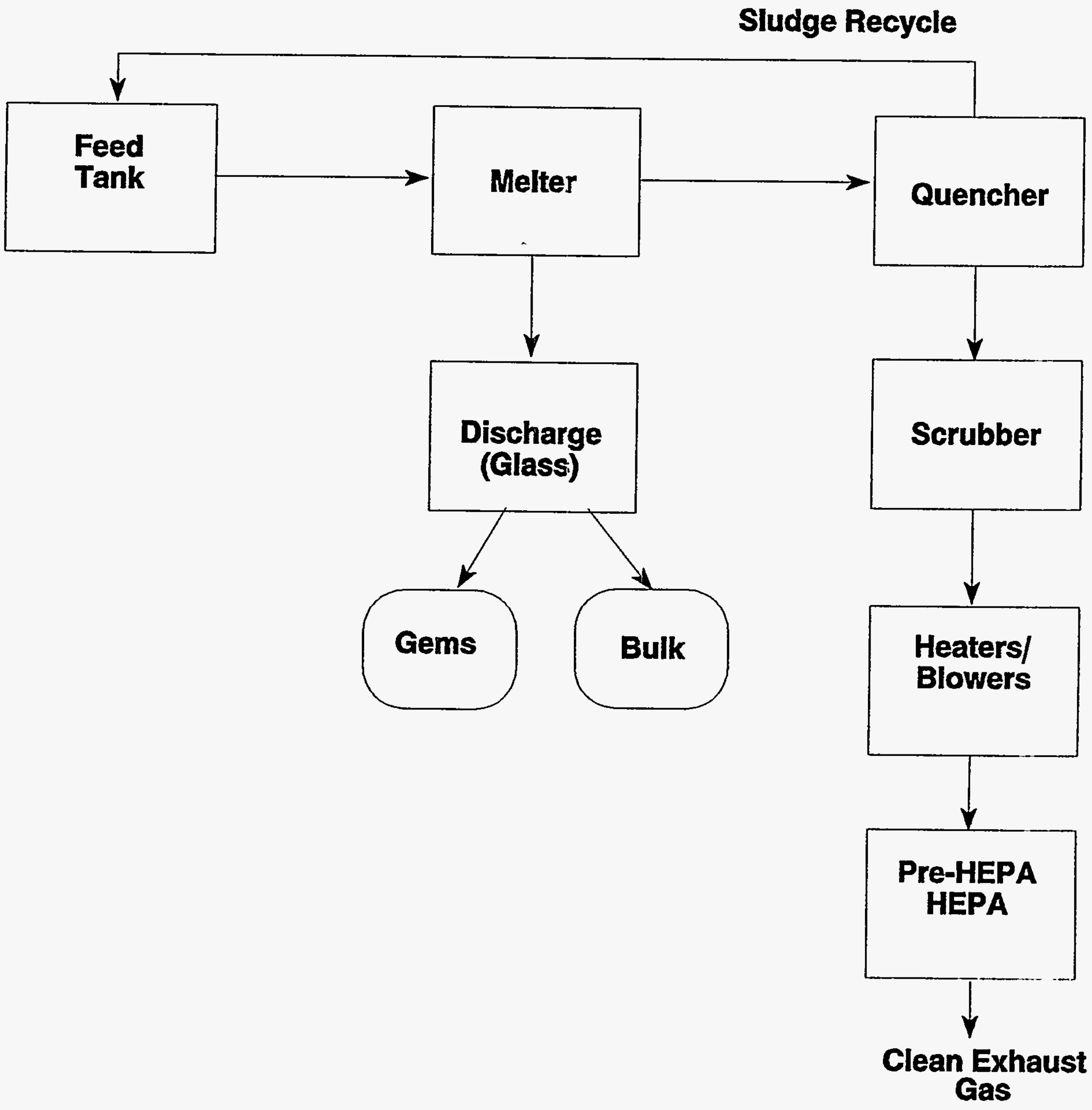


Figure 11.1
Duramelter™ 300 flow diagram

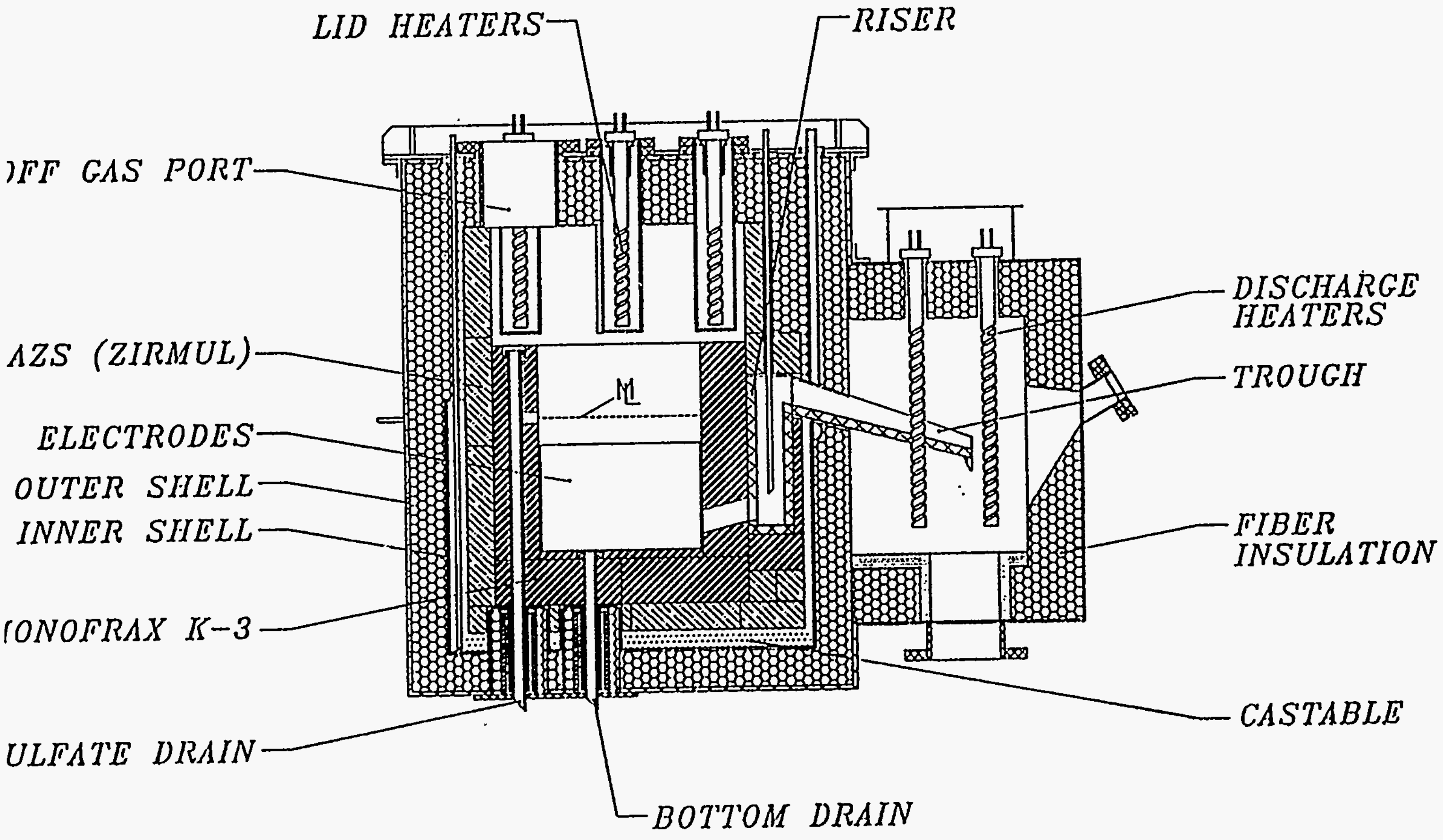


Figure 11.2. Cross-section through the Duramelter™ 300 joule-heated melter.

SECTION 12.0
Ion Exchange Testing

The MAWS system uses a soil washing process to reduce the volume of contaminated soils that are directed to the vitrification process and to provide a soil-sludge ratio in the feed which is suited to glass formation. The contaminated water that is generated in the soil washing process is treated in an ion exchange system which extracts the dissolved uranium before recycling the cleaned water back to the soil washing system. When the ion exchange columns are loaded with uranium, they are stripped to regenerate them and the uranium-containing stripping solution is directed to the feed for the vitrification system. A number of lab-scale tests were performed to demonstrate the viability of this approach and to obtain basic data relating to ion exchange system operation and performance. The results of these tests are presented in this section.

12.1 Ion Exchange Column Loading Tests

Ion exchange column loading tests were performed in Lockheed's soil laboratory. The solutions used were generated from lab-scale soil washing tests that were performed on radioactive soil from Fernald. Two tests were performed, the first using the soil-wash water directly and the second using the same solution with 40 ppm of a defoaming agent added. Lab-scale soil washing tests had shown that the defoaming agent was needed and therefore the second test was conducted to check for any adverse consequences on ion exchange performance. Both tests used columns packed with 25 ml of Dowex 21 K ion exchange resin. The set up used was similar to that shown in Figure 12.1. The flow rate was set at the equivalent of 0.5 gallons per minute per square foot (about 2 ml/min/cm^2). A total of 1100 ml of solution was fed in test 1 and 1146 ml in test 2. The effluents were collected in 200 ml samples which were then analyzed for uranium at Lockheed. The results are shown in Table 12.1 and Figure 12.2.

Samples of each of the influent and effluent solutions and both the loaded ion exchange columns were then shipped to VSL for further analysis. The solution samples were analyzed by ICP-MS at VSL as a check on inter-lab consistency; the results, shown in Table 12.2, compare very well with those in Table 12.1.

12.2 Ion Exchange Column Stripping Tests

The loaded ion exchange resin from the second loading test (UL-T2, including the defoaming agent) was used for stripping tests at VSL. All tests were conducted using the arrangement shown in Figure 12.1 with 2 ml of loaded media in each column. Two sets of tests were performed as follows; a summary of the run parameters is given in Table 12.3.

12.2.1 Stripping Solution Composition Tests

An ideal stripping solution would remove the great majority of the uranium from the ion exchange resin in a minimum volume of solution, using relatively rapid flow rates and low concentrations of inexpensive chemicals that are compatible with the vitrification process and which do not introduce any unnecessary additional hazards into the system. In view of these considerations, it is clear that some compromises are required. The stripping solutions that were selected for evaluation in the lab-scale tests were:

(A) 50 g/l NaCl + 15 g/l $NaHCO_3$
(B) 17.5 g/l NaF + 15 g/l $NaHCO_3$
(C) 1 M HNO_3
(D) 1 M H_3PO_4
(E) 1 M oxalic acid
(F) 1 M H_2SO_4

Solution (A) was used as a reference solution since it is the one recommended by Dow Chemicals for stripping uranium from Dowex 21K. However, the high chloride concentration makes it undesirable from a vitrification perspective. Solution (B) replaces the chloride by fluoride (the lower concentration is due to solubility limitations) which is compatible with the vitrification process.

Previous experience has shown nitric acid to be effective in stripping uranium from Dowex 21K and sulfuric acid was tested despite the preference for low sulfate levels for the vitrification process.

Each solution was used to elute a separate column containing 2 ml of the loaded Dowex 21K ion exchange resin (UL-T2) at a flow rate of 4 ml/hr, equivalent to a residence time of 30 minutes. The eluent was collected as 2 ml samples which were subsequently analyzed for uranium by ICP-MS. A total of 25 ml of solution was used in each test. The results are shown in Figure 12.3 as the cumulative amount of uranium removed from the column as a function of the number of column volumes of eluent. The results show clearly that solution (A) gives the best performance. Solution (C), however, comes closest to meeting the requirements listed above, particularly when compatibility with vitrification is considered. Further, tests were therefore conducted with a nitric acid stripping solution.

12.2.2 Stripping Solution Concentration Tests

These tests again used columns containing 2 ml of the loaded Dowex 21K ion exchange resin (UL-T2). The stripping solutions used were 1 molar, 2 molar, and 4 molar nitric acid solutions. In these tests, the flow rate was reduced by a factor of ten to 0.4 ml/hr to increase the residence time and, therefore, the stripping efficiency. The eluent solution was collected in 0.5 ml samples, each of which was analyzed for uranium by ICP-MS. About 40 samples were taken in each test. The results are shown in Figure 12.4 as the cumulative amount of uranium removed from the column versus column volumes of eluent. The limiting amount of uranium removed (Figure 12.4a) was significantly higher for the 1M HNO_3 solution but we suspect that this may be an artifact due to variations in the amount of uranium on each 2 ml subsample of the loaded ion exchange media used to prepare these columns. (The media from the original 25 ml loaded column was mixed before subsampling but a concentration gradation from the top to the bottom would be expected). A more appropriate comparison is therefore shown in Figure 12.4b which plots the cumulative fraction that is removed of the apparent total amount of uranium on each column. These results indicate that 2 M HNO_3 performs significantly better than does 1M HNO_3, but the benefits of increasing the concentration further appear to be small.

12.3 Activity of Regenerated Media

The ion exchange material that was stripped with solution (C) (1M HNO_3, Section 12.2.1) was used to check that the material was still active and capable of removing uranium from a fresh influent solution. The conditions were the same as those used for the loading tests described in Section 12.1 (test 2) except that since a 2 ml column was used instead of a 25 ml column, the flow rate was scaled down to 0.6 ml/min to maintain approximately the same residence time. The results, shown in Figure 12.5, demonstrate that the ion exchange media can be successfully regenerated by this process. At this point we have not performed tests with these soil-wash waters to determine the number of loading-regeneration cycles that can be performed while maintaining the activity of the media. However, past experience and vendor information suggests that Dowex 21K could be regenerated up to five times.

12.4 Stripping Solution for Vitrification Tests

The second 25 ml column of loaded ion exchange resin that was received from Lockheed was used to generate strip solution for vitrification testing. The material was stripped into 90 ml of 2 M HNO_3 and the resulting solution (ULT122) was used as part of the feed batch in preparing glass crucible melt number F5-68, described in Section 4.

12.5 Discussion and Conclusions

The results presented in this section demonstrate that Dowex 21K ion exchange resin is effective in removing uranium from the soil-wash waters that are generated in the Lockheed TRUclean process developed for Fernald soils. Several stripping solutions were tested for regeneration of the uranium-loaded resins with the conclusion that 2M HNO_3 was best suited to the MAWS process in which the uranium-containing stripping solution is directed to the vitrification process. These tests also demonstrated that, after stripping, the ion exchange resin has indeed regained its capacity to capture uranium. These test results were used in determining the design and operating parameters for the water treatment system installed at the Fernald site as part of the MAWS system. Similar data should become available from the field operations to confirm the laboratory data presented here.

Table 12.1
Uranium Concentrations in Effluents from Column Loading Tests as Measured at Lockheed.

ppm	Influent	Effluent from Test 1 (Lockheed ID Nos.)						Effluent from Test 2 (Lockheed ID Nos.)					
	EF-T1	E1-T1	E2-T1	E3-T1	E4-T1	E5-T1	E6-T1	E1-T2	E2-T2	E3-T2	E4-T2	E5-T2	E6-T2
Uranium (total)	1190	42	94	121	251	384	412	41	94	138	232	269	382

Table 12.2
Uranium Concentrations in Effluents from Column Loading Tests Measured by ICP-MS at VSL

	Influent	Effluent from Test 1 (VSL ID Nos.)						Effluent from Test 2 (VSL ID Nos.)					
Radionuclides (ppm)	FEINF	FE19E1	FE19E2	FE19E3	FE19E4	FE19E5	FE19E6	FE20E1	FE20E2	FE20E3	FE20E4	FE20E5	FE20E6
U-233	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U-234	0.04	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
U-235	6.1	0.2	0.5	0.7	1.3	2	2	0.2	0.5	0.7	1.2	1.4	2.1
U-236	0.3	<0.01	<0.01	0.02	<0.01	0.03	0.03	<0.01	<0.01	0.02	0.01	0.02	0.03
U-238	1.1X10^3	33	83	125	289	338	363	31	84	131	258	302	351

Table 12.3
Summary of Ion Exchange Column Stripping Tests

VSL Run #	Column Packing Material	Influent	Nominal Flow Rate
First Test			
240	2 mL UL-T2	1M HNO_3	4 mL/h
241	2 mL UL-T2	1M H_3PO_4	4 mL/h
242	2 mL UL-T2	1M H_2SO_4	4 mL/h
243	2 mL UL-T2	50 g/l NaCl + 15 g/L $NaHCO_3$	4 mL/h
244	2 mL UL-T2	17.5 g/l NaF + 15 g/l $NaHCO_3$	4 mL/h
245	2 mL UL-T2	1M Oxalic Acid	4 mL/h
Second Test			
247	2 mL UL-T2	1M HNO_3	0.4 mL/h
248	2 mL UL-T2	2M HNO_3	0.4 mL/h
249	2 mL UL-T2	4M HNO_3	0.4 mL/h

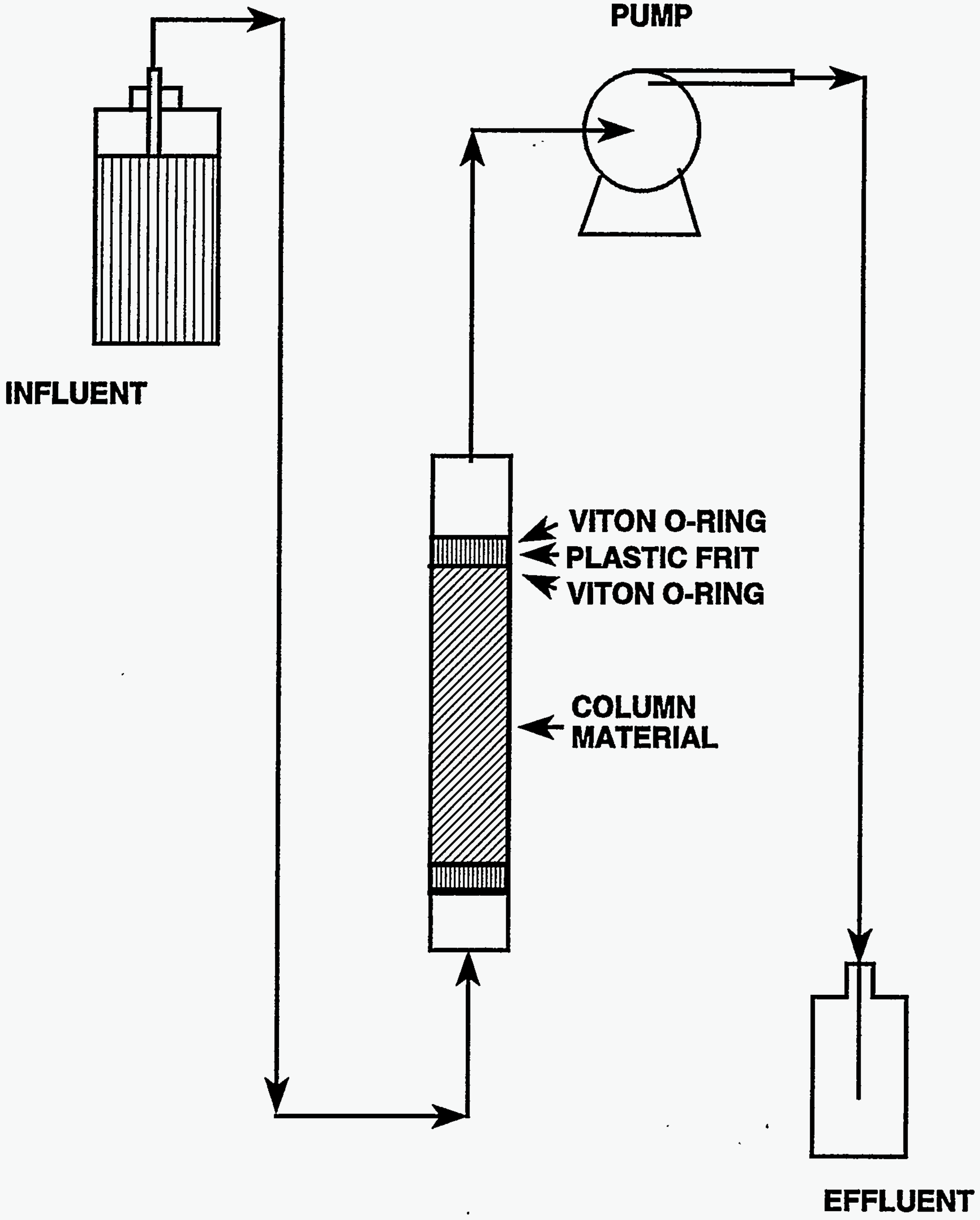


Figure 12.1
Schematic diagram of ion exchange media stripping experiments

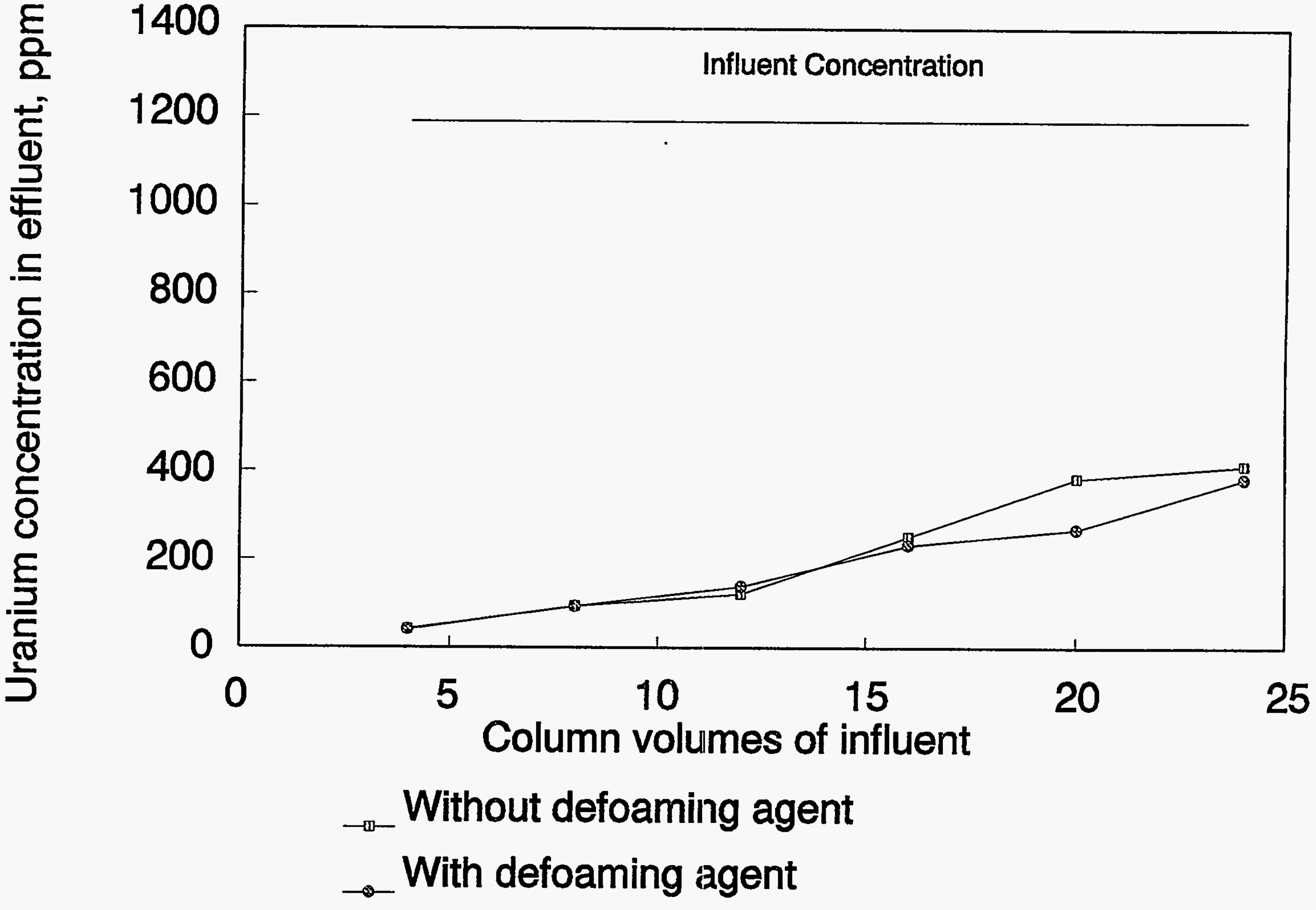


Figure 12.2
Results from ion exchange column loading experiments using uranium-contaminated water from soil-washing tests.

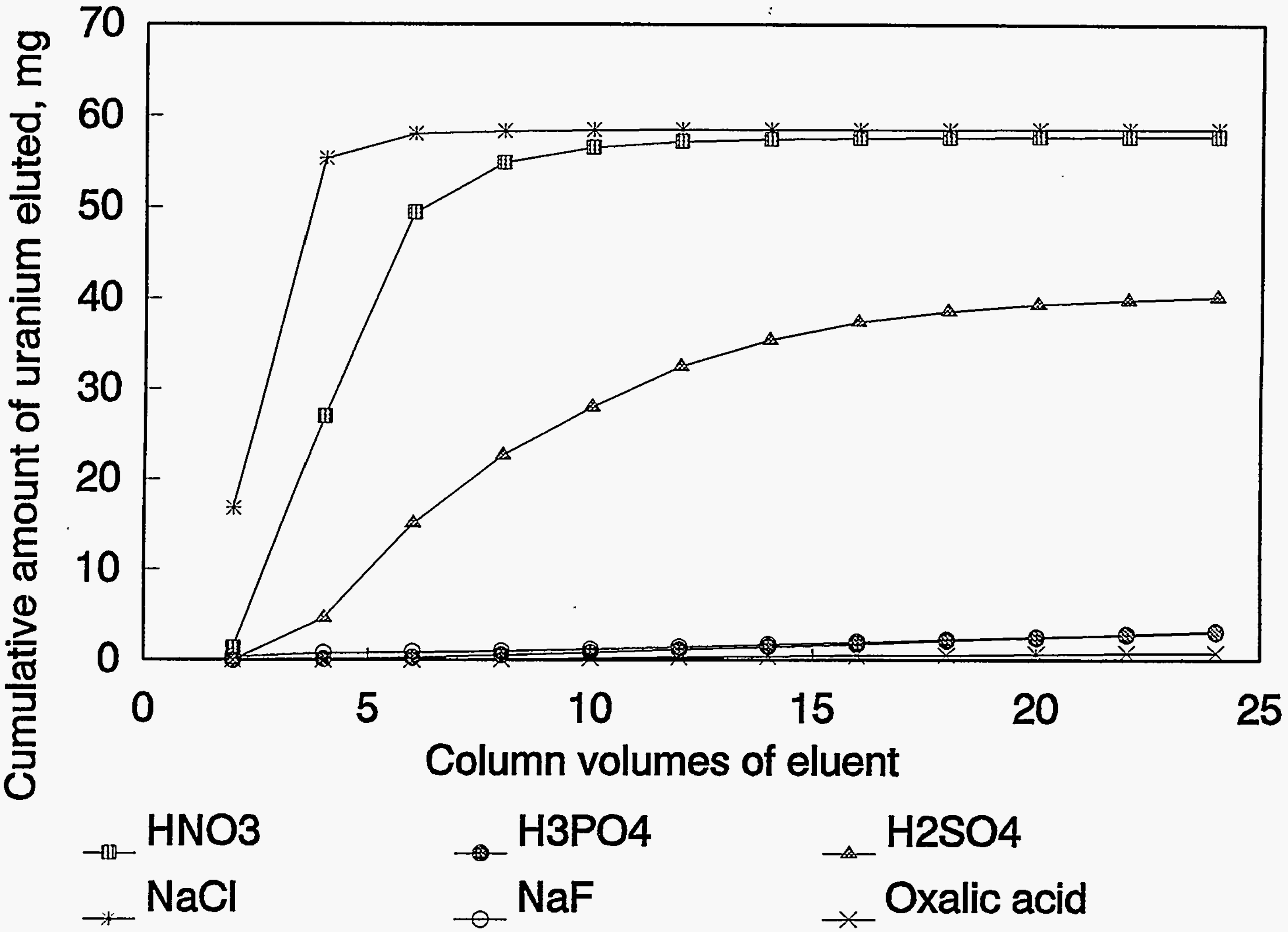


Figure 12.3
Results from ion exchange column stripping experiments using various stripping solutions.

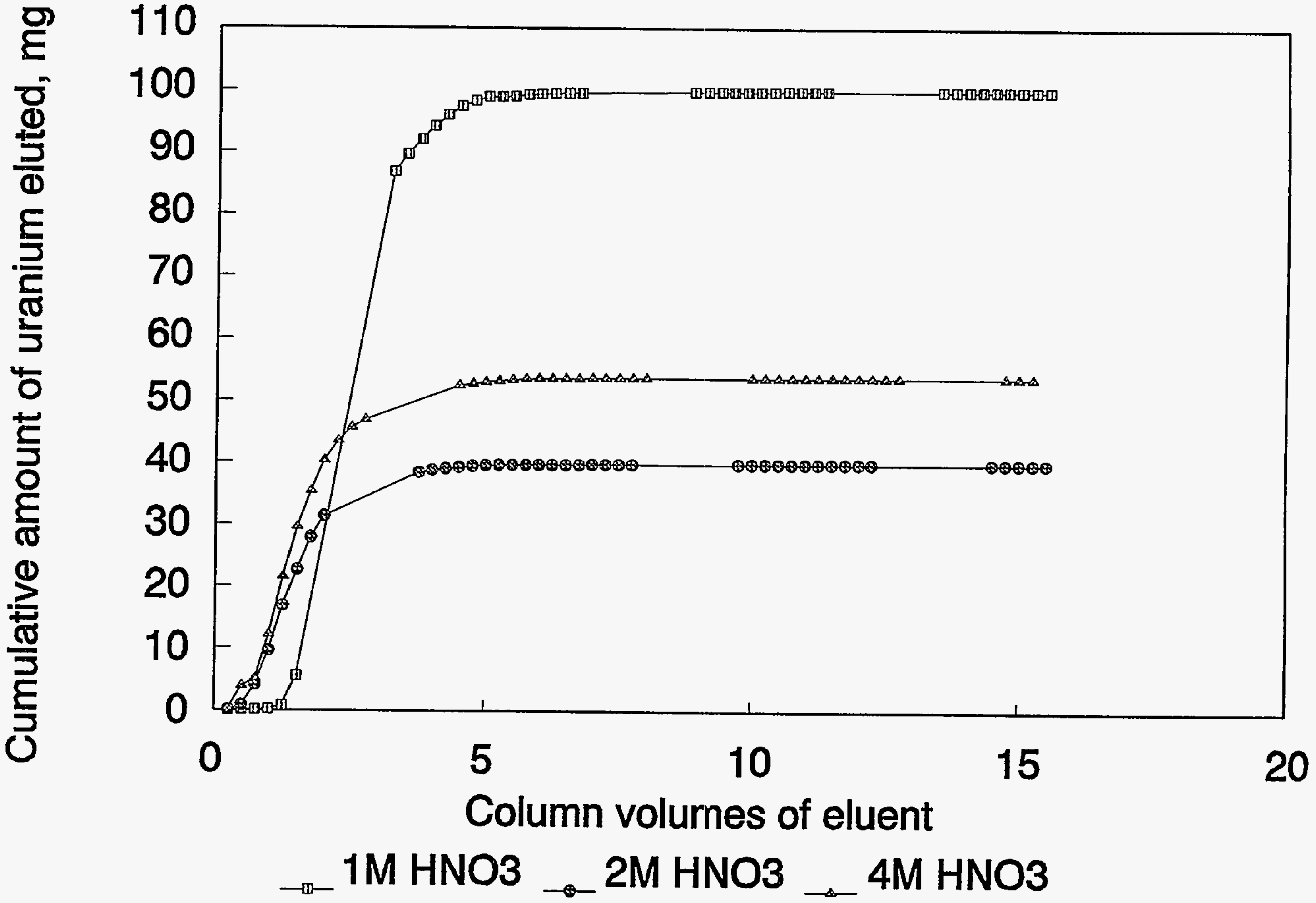


Figure 12.4a
Results from ion exchange stripping experiments showing effect of nitric acid concentration on cumulative amount of uranium removed.

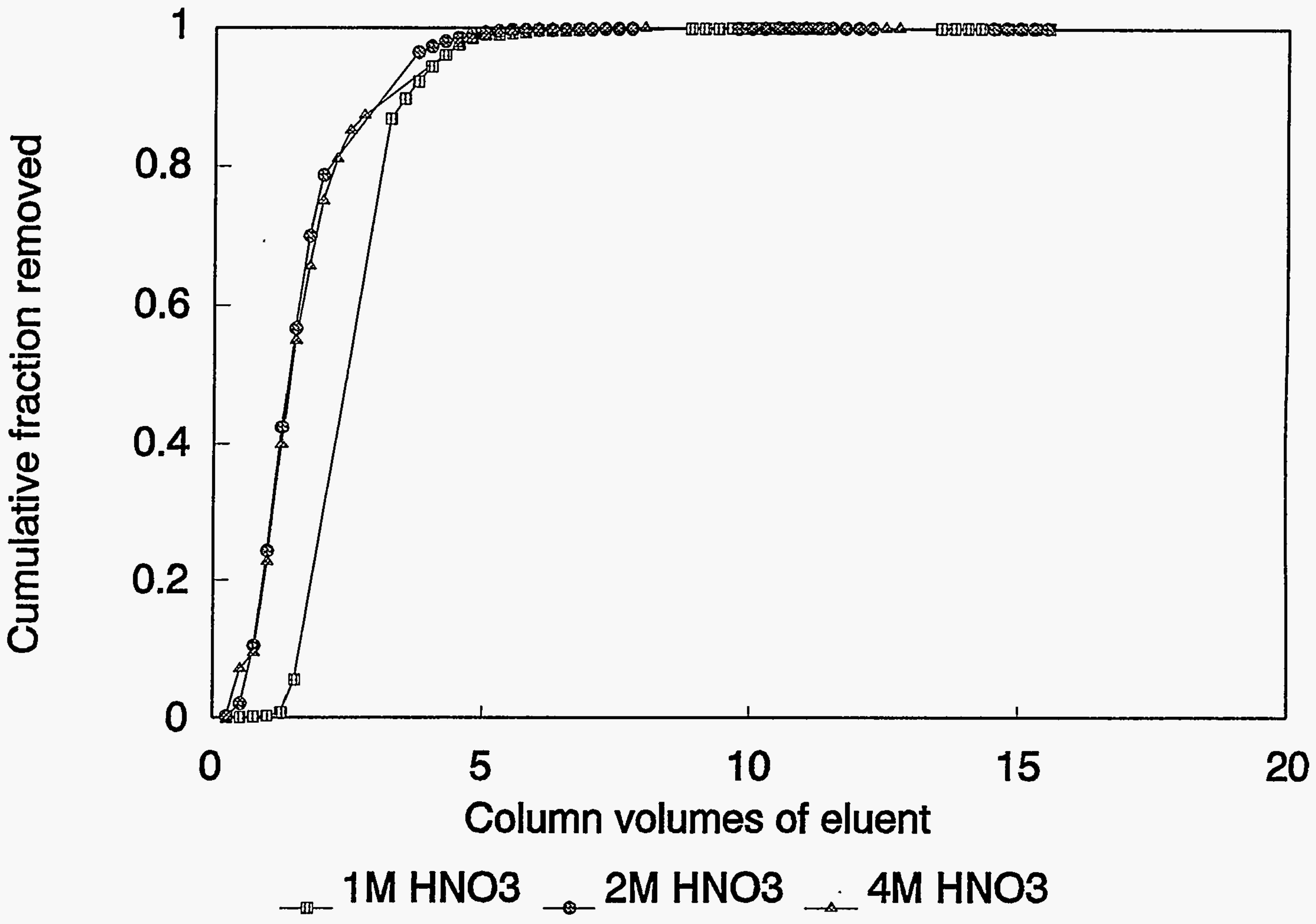


Figure 12.4b
Results from ion exchange column stripping experiments showing effect of nitric acid concentration on cumulative fraction of uranium removed.

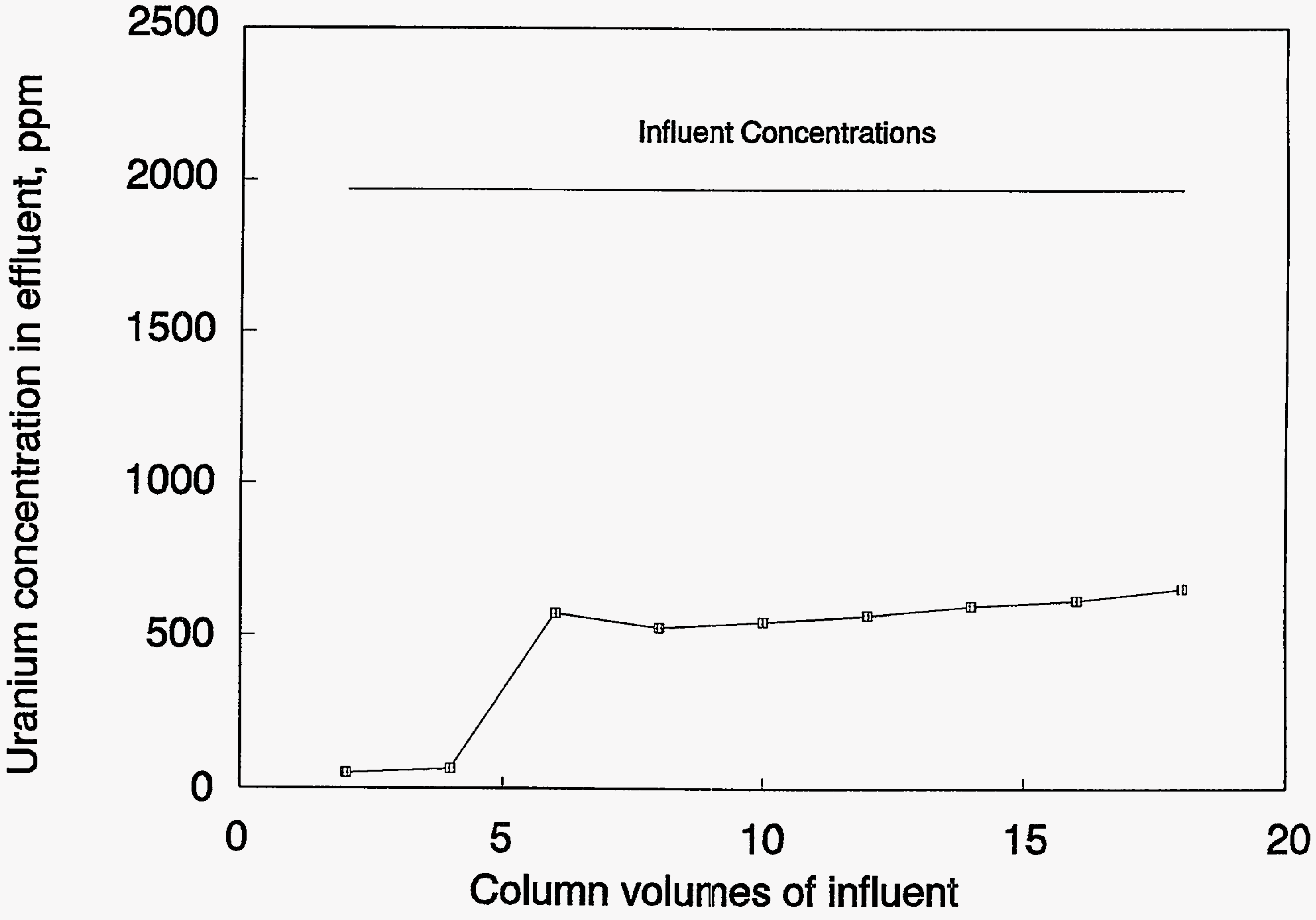


Figure 12.5
Results from ion exchange column loading experiments after one stripping cycle showing that media has been regenerated.

SECTION 13.0
Discussion and Conclusions

Significant progress has been made in Phase I of the MAWS development and demonstration program for the Fernald site. In the area of general support, the Work Plan has been prepared, reviewed by EPA, and responses to comments have been provided; modifications to the FEMP Plant 9 facility have been completed; operational safety assessments have been completed for the MAWS system components and similar preparations for on-site radioactive vitrification runs are in progress; a variety of system test runs have already been successfully performed. Waste form development activities have led to formulations with up to 96% waste loadings which produce a processable high-quality wasteform; the data obtained for this purpose provide a solid foundation for the incorporation of other waste streams into the process. Glasses have been prepared from various combinations of FEMP Pit 5 waste and soil-wash concentrates (our previous studies have demonstrated similar success with blends of Pit 5 sludge, Fernald soil, and Fernald fly ash). All of the objectives of Phase I of the MAWS program, presented in the Introduction, have been met.

Extensive characterization data (chemical and radionuclide composition, particle size distributions, water content, density, etc.) have been collected for several 55-gallon drum samples of Fernald Pit 5 sludge and a variety of soil-wash fractions generated from lab-scale soil washing tests on contaminated Fernald soils. Six 55-gallon drum samples of Pit 5 waste were selected by FEMP personnel and shipped to the Vitreous State Laboratory over the course of Phase I of this work. Due to delays in shipping subsequent drums, much of the development work was performed on Pit 5 material from the homogenized contents of the first 55-gallon drum that was received. Later samples showed lower contents of magnesium fluoride and greater contents of sulfates than did the first samples. Discussions with FEMP personnel concerning process knowledge of the generation of the Pit 5 material indicated that the overall sulfate content of Pit 5 was expected to be low (below 0.1 wt%) and consequently the Phase I studies have concentrated on the low-sulfate material. By the end of Phase I, however, three of the six drums received showed sulfate contents of 10-13 wt% on a dry basis. Phase II work will therefore address further the variability in the Pit 5 sludge composition, an important factor for any treatment technology, as well as broadening the compositional envelope of acceptable glass formulations accordingly.

A total of 31 crucible melts were made from six different samples of Pit 5 sludge and seven different soil-wash fractions. Characterization of the resulting glasses included determination of the melt viscosity and electrical conductivity as functions of temperature; determination of their phase stability including the amounts and types of secondary phases that are produced on heat treatment and estimated liquidus temperatures; and measurement of their leach resistance by the EPA TCLP procedure and the high-level nuclear waste glass Product Consistency Test (PCT). These results were used to select the optimal formulation for continuous melter tests using the requirements for processability, leach resistance, and economics (primarily waste loading and cost of additives).

The majority of the glasses produced, covering a wide range of compositions, show very good leach resistance on the EPA TCLP test; most show below 20% of the regulatory limit for concentrations of the RCRA metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se) in the leachate. In addition, the data indicate that these glasses can meet the required release limits (with respect to the presently available information on ARAR standards for FEMP) for ^{99}Tc, ^{232}Th, and ^{238}U. In terms of the overall leach resistance of the glass wasteform it is useful to examine the release of major glass matrix components into solution under more aggressive conditions than those of the TCLP test. The Product Consistency Test (PCT) that was developed for the high-level waste vitrification program is useful in this respect since there already exists a large database to provide a benchmark for comparison. The PCT procedure uses a higher temperature (90°C vs. 22°C), a longer time period (at least 7 days vs. 18 hrs), and a larger ratio of glass surface area to the volume of leachant (2000 m^{-1} (i.e. 10 g of 75-150μm powder in 100 ml of leachant) vs. about 20 m^{-1} (i.e. 100 g of material passing 3/8" sieve in 2000 ml of leachant)) than does the TCLP procedure. Both the PCT normalized leachate concentrations and normalized leach rates for typical glasses prepared from FEMP wastes compare very well with the corresponding values for the present standard glass for high-level waste acceptance (Savannah River Laboratory Environmental Assessment (SRL-EA) glass). Thus, these studies have demonstrated that it is possible to produce high-waste loading, processable glasses from FEMP low-level and mixed wastes that would meet the leach resistance requirements for treatment of high-level nuclear waste. Furthermore, as discussed in the Appendix, there is good evidence that this waste form option would be considerably less expensive than cement stabilization.

A step-wise approach was used for the continuous melter tests, progressing from tests on 10 kg/day and 100 kg/day laboratory Duramelter systems up to the on-site 300 kg/day system. Each step provides more realistic information and approaches more closely the process that would occur in a production-scale system. The continuous melter tests provide information, such as off-gas emissions and processing rates, that cannot be obtained from crucible melts. Information learned in the small-scale melter tests provides an important basis for the design and selection of larger, production-scale systems.

Data collected in these tests included production rates, power requirements, off-gas composition, distribution of chemical components between various parts of the system (glass, off-gas scrubber solution and sludge, filtered particulates, and off-gas emissions), off-gas sludge recycle, and characteristics of the resulting glass product.

Several formulations have been tested using actual FEMP wastes in a 10 kg/day Duramelter vitrification system at VSL to obtain such processing information. This system has been operated for six months using high-fluoride feeds. The off-gas system is able to remove fluorides from the off gas stream to emission standards and 100% recycle of the off-gas scrubber sludge to the melter feed has been demonstrated. The glasses produced in the tests using this vitrification system also pass the TCLP leach test.

The larger scale 100 kg/day Duramelter system installed at the VSL has been operated for 16 weeks, processing over 1300 gallons of fluoride and non-fluoride feeds; glass production rates of over 250 kg/day were achieved in these tests. The melter has been successfully drained and restarted and corrosion checks have revealed no degradation of the electrodes or refractories. Minor system and procedural modifications were made as a result of these tests prior to radioactive operations. In the radioactive runs 410 kg of Fernald Pit 5 sludge was processed with 63 kg of Fernald soil-wash concentrates and small amounts of additives; a second run processed 100 kg of simulated Pit 5 sludge spiked with uranium, thorium, and RCRA metals, with 49 kg of soil-wash concentrates and additives. The feed system permits 55 gallon drums of waste to be opened in a glove box where the contents are mixed and blended with other feed components and slurry pumped to the melter. The glasses produced in these runs passed the TCLP test and showed the expected good performance on the PCT test. Off-gas emissions were consistently low for the radionuclides and RCRA metals, including below 25 ppb F, and below 20 ppt Tc, U, and Th.

The 300 kg/day Duramelter vitrification system has been installed in the modified Plant 9 facility at the Fernald site and is now fully operational. The basic system components are similar to those for the 100 kg/day system with the exception of the feed system which is considerably larger; the 300 kg/day Duramelter feed system is composed of two 4000 gallon feed tanks fitted with agitators, slurry pumps and recirculation pumps. A number of test runs have been performed since October 1993 using slurry feeds to produce borosilicate glass, primarily for system and operating procedure debugging and operator training. Several hundred kilograms of glass were produced in these runs at rates of up to 550 kg/day. This system also incorporates a "Gem Machine" which is fed by the molten glass stream and produces approximately hemispherical beads ("Gems") of glass about 1-2 cm in diameter. This form offers several advantages: the rapid quenching prevents crystallization and therefore permits higher waste loadings; this shape packs more efficiently than marbles; the cost of containers can be reduced or eliminated; and this form is easily transportable. In January 1994, a 75 hr run was completed with a fluoride-containing feed; over 1000 kg of glass was produced at slurry feed rates of about 0.8 liters/min (nearly 1500 kg per 24 hr day). The results of these test runs are being evaluated and will be reported separately; any necessary system or procedural modifications will be made prior to commencing radioactive operations with actual Fernald Pit 5 wastes in Phase II of the MAWS program.

Laboratory soil washing studies at LESC have resulted in the development of a viable system configuration that uses a combination of physical and chemical processes to achieve decontamination levels of below 35 pCi/g. Up to 80% volume reductions are obtained while producing a contaminant-enriched fraction that is depleted in calcium and enriched in silicon. Over 1700 kg of FEMP soil have been processed in these lab tests which also made use of an integrated GTS Duratek ion exchange water treatment system. About 350 kg of soil wash concentrates were shipped to VSL for vitrification studies.

Laboratory tests have demonstrated the viability of regenerating the uranium-loaded ion exchange media by acid stripping and the subsequent vitrification of the stripping solutions in blends with Pit 5 sludge and soil wash fractions.

Construction of the on-site TRUclean soil washing system has been completed and the supporting on-site water treatment system was delivered to the FEMP Plant 9 Facility in mid-March, 1993. System tests with water and with non-radioactive soil have been completed and evaluated. Operations with radioactive soil commenced in December 1993 and successfully processed approximately 100 yd^3 of soil in these tests. Results from soil washing tests will be reported separately.

The results obtained to date provide strong support for the viability of the MAWS approach, as outlined above, for the treatment of Fernald waste streams. Extremely high waste loadings (up to 96%) in the feed formulations were obtained and these feeds were successfully processed in continuous melter systems using actual Fernald wastes. The resulting glasses pass the TCLP test and exhibit performance comparable to high-level waste glasses on the PCT test. While the continuous melter tests performed to date have been relatively short, the overall performance of the systems has been very good and showed no indications of any major problems which might preclude scale-up to production-scale systems. The very large volume reductions obtained by this approach (over seven-fold, see Appendix), as compared to a volume increase of about a factor of three on cement stabilization, coupled with the large volume-based disposal costs results in very large potential cost savings (about 56% by independent estimates made by Fernald site personnel) in the treatment and disposal of these wastes.

In conclusion, some of the potential benefits of an integrated, multiple-technology, blended-waste-stream treatment system for a site such as FEMP have been discussed. We have demonstrated that glass-based wasteforms can be designed for low-level and mixed wastes that show excellent leach resistance, are processable using improved JHCM technology, and can achieve very high waste loadings. Furthermore, the very large volume reductions that have been demonstrated make vitrification a very much more economical option than cement stabilization, particularly when life-cycle costs are considered. The synergism possible between appropriately selected and optimized system components also serve to further increase waste loading, decrease additive requirements, and improve volume reductions. Many of the general MAWS concepts are applicable in a variety of alternative system configurations to suit available waste stream combinations characteristic of any given site. Thus, this approach should have wide applicability across the DOE complex and offer the potential of substantial reductions in remediation costs as well as improved performance of the final waste form.

Recommendations that can be made on the basis of Phase I testing results include the following: Continue the phased scale-up of the testing activities from laboratory tests to on-site system tests; conduct significantly longer system test runs under steady-state conditions; conduct test runs on laboratory and on-site systems to better define the system operational envelope (limits for key operating parameters) for these wastes; conduct test runs to confirm the extent of the compositional envelope identified by crucible studies; evaluate other FEMP waste streams to broaden the MAWS waste stream blend and maximize the benefits of this approach; evaluate the variability of Pit 5 sludge composition, particularly with regard to sulfate and particularly on the feed-batch scale (presently, a few thousand gallons); expand the compositional envelope as appropriate to whatever additional characterization data suggest is the "mean" Pit 5 sludge composition and variability; batch-by-batch analysis is clearly necessary for process control and therefore alternative analytical methods with rapid turnaround times should be evaluated; the long-term effects of FEMP melts (especially with respect to the high fluoride content and low viscosities) on melter components should be evaluated.

APPENDIX
Effect of Volume Reduction on Economics

Technologies that produce "enhanced" final waste forms, i.e. waste forms that are highly leach resistant, are often perceived as expensive with respect to alternatives that produce satisfactory, but often much more leachable waste forms. However, when volume reduction differences and the volume-based cost of disposal of the final waste form is taken into consideration together with the cost of actual treatment, technologies that produce enhanced final waste forms can actually become economically preferable. This is a very important principle that is incorporated into the general MAWS approach and, more specifically, into the selection of stabilization by vitrification. It is therefore instructive to review some of our conclusions with respect to volume reduction obtained with MAWS glasses in comparison to other technologies; for definiteness, we will use cement stabilization as a baseline. Table 13.1 defines the terminology that is used in the remainder of the discussion. Table 13.2 summarizes specific values of these parameters for MAWS glasses; the two glasses selected satisfy the processability and leach resistance requirements and span a wide range of both the Pit 5 waste loadings and the water contents of the various Pit 5 samples received. The calculated values of f_g of 0.047 and 0.147 correspond to very large volume reduction (by factors of 21 and 6.8, respectively).

The total cost (T_g or T_c, for glass and cement, respectively) of treatment plus disposal, per unit volume of waste that is treated and disposed, is then:

$$T_c = (P_c + d)f_c$$

and

$$T_g = (P_g + d)\, f_g$$

The breakeven disposal cost $\bar{d}$ can then be found by setting $T_c - T_g = 0$ to give

$$\bar{d} = \frac{(P_c f_c - P_g f_g)}{(f_g - f_c)} \quad ;$$

vitrification will be cheaper than cementation for any disposal cost below this value. It is instructive to consider the case in which $\bar{d}$ drops below zero (mathematically) since in that case vitrification is always cheaper than cementation, regardless of disposal cost. The condition for

$\bar{d} < 0$ yields (assuming $f_g < f_c$)

$$\frac{P_c}{P_g} < \frac{f_g}{f_c}$$

or alternatively, $P_c < (f_g/f_c)\ P_g$.

Treatability studies for cementation of Pit 5 sludge have yielded $f_c \simeq 3.7$ and values above 2 are typical for most wastes. Using the values in Table 13.2 for our MAWS glasses we obtain the range $f_g/f_c \simeq 0.013 - 0.074$. Thus, even in the most favorable scenario (for cementation) and using a very unlikely disposal cost of zero, the processing cost for cementation would have to be less than 8% of the processing cost for vitrification in order to make cementation to be the cheaper option, a very unlikely situation. When the additional effects of the typically large disposal costs are also included, the economics tip even further in favor of a volume-reducing technology such as vitrification (see, for example, Minimum Additive Waste Stabilization (MAWS) Technology Summary, DOE/EM-0124P, Feb. 1994).

Note that the above discussion has deliberately focussed on volume reduction with respect to Pit 5 sludge alone. In the MAWS approach, additives are replaced, to the fullest extent possible, by other waste streams and thus, overall waste loadings are correspondingly higher. In the particular examples above, no credit has been taken for the soil-wash concentrates that are converted to a leach resistant glass waste the form in the course of treating the Pit 5 sludge. Clearly, this will further improve the economics and reduce overall remediation costs.

Table A.1
Definition of Symbols used in the Discussion

Pit 5 Sludge	
L_1	Weight loss from as-received to 450°C
L_2	Weight loss from 450°C to 1150°C
W_s	Weight fraction of Pit 5 sludge (dried at 450°C) in the feed batch
ρ_s	Density of Pit 5 sludge as-received
Glass	
ρ_g	Density
G	Packing fraction of gems
f_g	Ratio of volume of glass produced to volume of sludge treated
P_g	Processing cost per unit volume of product
Cement	
ρ_c	Density
f_c	Ratio of volume of stabilized material produced to volume of sludge treated
P_c	Processing cost per unit volume of product
Disposal	
d	Disposal cost per unit volume of waste form disposed

Table A.2
Values of Parameters Defined in Table 13.1 for MAWS Glasses, Pit 5 Sludge, and a Cement-Stabilized Waste Form

Crucible Melt	F5-52B	F5-47
Pit 5 Sample Used	FE15	FE1
L_1 L_2 W_s	0.903 0.186 0.681	0.706 0.231 0.422
f_g	0.047	0.147

ρ_s	1.2 g cm^{-3}
ρ_g	2.7 g cm^{-3}
G	0.8
ρ_c	2.7 g cm^{-3}
f_c	2-4 typically