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DEVELOPMENT OF A COMBINED SOIL-WASH/IN-FURNACE VITRIFICATION SYSTEM FOR SOIL REMEDIATION AT DOE SITES

—

Final Report

Contract No. 02112414

By

Ian L. Pegg, David C. Grant, Yuning Guo, Edward J. Lahoda,
Shan-Tao Lai, Isabelle S. Muller, and Jacqueline Ruller

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PREFACE

Currently available technology is not adequate to assess environmental contamination at Department of Energy (DOE) sites, take permanent remedial action, and eliminate or minimize the environmental impact of future operations. Technical resources to address these shortcomings exist within the DOE community and the private sector, but the involvement of the private sector in attaining permanent and cost-effective solutions has been limited.

During 1990, on behalf of DOE's Office of Technology Development, Argonne National Laboratory (ANL) conducted a competitive procurement of research and development projects addressing soil remediation, groundwater remediation, site characterization, and contaminant containment. Fifteen contracts were negotiated in these areas.

This report documents work performed as part of the Private Sector Research and Development Program sponsored by the DOE's Office of Technology Development within the Environmental Restoration and Waste Management Program. The research and development work described herein was conducted under contract to ANL.

On behalf of DOE and ANL, I wish to thank the performing contractor and especially the report authors for their cooperation and their contribution to development of new processes for characterization and remediation of DOE's environmental problems. We anticipate that the R&D investment described here will be repaid many-fold in the application of better, faster, safer, and cheaper technologies.

Details of the procurement process and status reports for all 15 of the contractors performing under this program can be found in "Applied Research and Development Private Sector Accomplishments - Interim Report" (Report No. DOE/CH-9216) by Nicholas J. Beskid, Jas S. Devgun, Mitchell D. Erickson and Margaret M. Zielke.

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ABSTRACT

This report addresses research and development of technologies for treatment of radioactive and hazardous waste streams at DOE sites. Weldon Spring raffinate sludges were used in a direct vitrification study to investigate their use as fluxing agents in glass formulations when blended with site soil. Storm sewer sediments from the Oak Ridge, TN, Y-12 facility were used for soil washing followed by vitrification of the concentrates. Both waste streams were extensively characterized. Testing showed that both mercury and uranium could be removed from the Y-12 soil by chemical extraction resulting in an 80% volume reduction. Thermal desorption was used on the contaminant-enriched minority fraction to separate the mercury from the uranium. Vitrification tests demonstrated that high waste loading glasses could be produced from the radioactive stream and from the Weldon Spring wastes which showed very good leach resistance, and viscosities and electrical conductivities in the range suitable for joule-heated ceramic melter (JHCM) processing. The conceptual process described combines soil washing, thermal desorption, and vitrification to produce clean soil (about 90% of the input waste stream), non-radioactive mercury, and a glass wasteform; the estimated processing costs for that system are about \$260 - \$400/yd^3. Results from continuous melter tests performed using Duratek's advanced JHCM (Duramelter) system are also presented. Since life cycle cost estimates are driven largely by volume reduction considerations, the large volume reductions possible with these multi-technology, blended waste stream approaches can produce a more leach resistant wasteform at a lower overall cost than alternative technologies such as cementation.

Executive Summary

This report addresses research and development of specific technologies in the area of remediation of soils at DOE sites contaminated with radionuclides, heavy metals, inorganic ions, organics and/or nitrates. The novel system approach described is a combination of soil washing and in-furnace vitrification technologies which provides several important advantages over existing technologies.

The benefits of vitrification over other technologies are briefly reviewed and various approaches to vitrification are summarized. For a variety of reasons, including economics, *in-situ* vitrification (ISV) techniques are not applicable at many sites. Thus, alternate vitrification approaches should be demonstrated. This project focused on soils from two such sites: Weldon Spring, MO, and Oak Ridge, TN. Weldon Spring raffinate sludges were used in a direct vitrification study to investigate their use as fluxing agents in glass formulations. Storm sewer sediments from the Oak Ridge, TN, Y-12 facility were used to develop the approach of soil washing followed by the vitrification of the concentrates.

A mercury/uranium contaminated soil from Oak Ridge was used to investigate the feasibility of producing a clean soil and a concentrated waste stream compatible with stabilization by vitrification. The testing showed that both mercury and uranium could be removed from the soil by chemical extraction. In addition, segregation of the highly contaminated fines was an effective means for concentrating a large fraction of the contamination. In bench-scale testing studies the soil washing process contributed an 80% volume reduction for this waste stream. However, the large amounts of highly volatile mercury present in the contaminant-enriched minority fraction produced by the soil washing process posed significant problems for subsequent stabilization by vitrification. It was found that by combining thermal desorption with soil washing, the hazardous component (mercury) could be effectively segregated from the radioactive component (uranium) of the waste. This unique combination of the two technologies resulted in over 80% of soil being recovered as clean, and produced non-mixed waste concentrate streams, and a uranium concentrate that was a viable candidate for vitrification. Vitrification tests demonstrated that high waste loading glasses could be produced from this material. These glasses showed very good leach resistance as determined by both TCLP and PCT testing and viscosities and electrical conductivities in the range suitable for joule-heated melter processing. A conceptual process is described which combines soil washing, thermal desorption, and vitrification to produce clean soil (about 90% of the input waste stream), non-radioactive mercury, and a glass waste form. The estimated processing costs for such a system are in the range of \$260 - \$400/yd^3.

Samples of soils and raffinate sludges from the Weldon Spring site have also been extensively characterized in this study. An important finding was that previous analyses of the raffinate sludges grossly underestimated anion concentrations (especially sulfates and fluorides), a result that impacts both of the present baseline technologies (vitrification and cementation) at Weldon Spring. The characterization data have been used to formulate a range of soil-sludge blends that have been vitrified with and without additives. The resulting glasses show excellent

leach resistance: all pass the EPA TCLP test and most show performance comparable with high-level nuclear waste glasses using the SRL PCT leach procedure. Melt viscosities and electrical conductivities have been determined over a range of temperatures since these are critical processing parameters. Raffinate sludge loadings of up to 70% with 30% site soil (i.e. zero additives) produce melts with acceptable viscosities for processing at temperatures that are low enough (about 1150°C) to keep off-gas problems to a minimum. Due to the low alkali contents of these melts their electrical conductivities are lower than would be needed for direct application of existing joule-heated ceramic melter technology (JHCM) such as has been developed for the high-level nuclear waste program. However, Duratek's advanced JHCM (Durameter) is able to process these formulations with little or no additives. Due to the unexpectedly high content of sulfates in these sludges about 10% of each melt separated into an immiscible sulfate layer on the top of the melt. This soluble alkali sulfate phase incorporates some of the hazardous constituents but the great majority of the radioactive components remain in the glass phase. Several process options have been considered, the two most promising of which involve either (a) production of a wasteform composed of a dispersed calcium sulfate phase in a glass matrix using a melting system, such as the Duramelter, which can accommodate low-conductivity alkali-free feed formulations, or (b) separation of the alkali sulfate phase, dissolution and ion exchange followed by recycle of the contaminants to the melter feed stream.

The large volume reductions that are possible with these multi-technology, blended waste stream approaches can produce a highly leach resistant glass waste form at a lower overall cost than alternative technologies such as stabilization by cementation. Life cycle cost estimates, which include disposal and long-term monitoring costs, are driven largely by volume reduction considerations. Using typical estimates for treatment and disposal costs and the laboratory data obtained in this study, the large volume reduction upon vitrification of Weldon Spring sludges (compared to a volume increase on cementation) results in a 70% lower treatment and disposal cost estimate for vitrification compared to cementation.

1.0 INTRODUCTION

This report summarizes results obtained from the research and development of specific technologies for remediation of soils and sludges at DOE sites that are contaminated with radionuclides, heavy metals, inorganic ions, and/or organics. The novel system approach under development, a combination of soil washing and in-furnace vitrification, provides several important advantages over existing technologies. In particular, due to the large volume reductions obtained the approach is both economically preferable to cementation and provides a waste form with superior leach resistance. Contaminated storm sewer sediments from Oak Ridge, TN, Y-12 facility, were used to develop the approach of soil washing followed by vitrification of the concentrates, while raffinate pit sludges from the Weldon Spring site, MO, were used to develop a direct vitrification process. Duratek's subcontractors, The Vitreous State Laboratory of The Catholic University of America (VSL) and Westinghouse Science and Technology Center (WSTC), bring considerable expertise in vitrification and soil washing technologies.

1.1 Technology Scope

Contamination of ground and surface waters at DOE sites within the Weapons Complex is widespread while contaminated soils and sediments are estimated to total billions of cubic meters; future investigations will surely uncover additional problems (US Congress OTA, OTA-0-485). A further indication of the magnitude of the problem is given in The DOE Five-Year Plan, first issued in 1990 (DOE, 1990), which describes DOE's goals, strategies, and specific programs for assessment and cleanup of contaminated sites and facilities, and calls for expenditures totaling over $30 billion on environmental restoration and waste management activities for fiscal years 1992-1996. Clearly, progress towards any such goal will depend greatly on the identification of applicable existing technologies as well as concerted efforts towards the development of new remediation technologies.

Remediation technologies for contaminated soils and sludges ultimately rest on some form of stabilization of the hazardous and radioactive contaminants into a solid, and therefore immobile, waste form that is stable and highly resistant to aqueous corrosion and any other form of degradation (such as biological) that would serve to release the contaminants entrapped therein. Also central to an effective remediation system is the ability to concentrate the contaminants into the minimum possible volume since this reduces disposal and monitoring costs. The ideal stabilization technology would therefore concentrate and immobilize all contaminants and render them chemically non-reactive. In what follows we discuss the potential roles of vitrification and soil washing in remediation systems.

1.1.1 Vitrification

Stabilization by vitrification rests primarily on the following factors:

(i) The powerful solvating properties of silicate glass melts and their ability to incorporate a wide range and large amounts of hazardous and radioactive components;

(ii) Well-developed processing technologies from both the commercial glass industry and, most recently, from high-level nuclear waste stabilization research and development efforts;

(iii) Thermal processing that effects the essentially complete destruction of hazardous organic compounds;

(iv) A stable homogeneous wasteform that can be made highly resistant to aqueous corrosion;

(v) A material that is very similar to many natural minerals whose long-term corrosion resistance has been demonstrated by the geological record; and

(vi) Relatively high density and therefore large volume reduction.

Some qualifications of these points are in order. Firstly, while alkaliborosilicate glass has been selected both in the U. S. and internationally as the principal stabilization technology for high-level nuclear waste from reprocessing operations, other types of glasses, such as lead-iron-phosphate (LIP) (Lutze and Ewing, 1988), have also been evaluated. However, the wealth of information presently available on alkaliborosilicate glasses makes these formulations the most promising for mixed, low-level, and TRU-waste stabilization problems in the near future. Secondly, while glass is, in fact, thermodynamically metastable with respect to the corresponding crystalline phase assemblage, the temperatures that the wasteform would experience in service are so far below the glass transition temperature (typically about 500°C) that the rate of this transformation is so extraordinarily slow as to make it essentially irrelevant (Boulos et al., 1980).

The energy intensive nature of vitrification and the capital equipment investment involved make the processing cost relatively high as compared to many alternative approaches for non-high-level waste, such as cement- or lime-based or thermoplastic and organic polymer technologies. However, in general, none of these alternative technologies enjoys all of the above listed benefits to the extent that does vitrification, as is reflected in the selection of vitrification for high-level nuclear waste stabilization (Hench et al., 1984) and the recent U. S. Environmental Protection Agency determination of vitrification as the BDAT (Best Developed Available Technology) for that problem (US Federal Register, 1990).

The superior corrosion resistance of a glass wasteform can ensure delisting of mixed and hazardous wastes while, as we argue below, the volume reduction (as compared to volume increase with most alternative technologies) can more than offset the higher processing costs for any reasonable disposal cost.

Vitrification processing is usually performed by using either fossil fuels or electric processing techniques. The latter include electric arcs using consumable carbon electrodes, plasma torch melting, and submerged electrode melting; all are based on well-developed electric furnace technologies from commercial metal and glass melting. The joule-heated ceramic melter (JHCM) technology developed by Batelle's Pacific Northwest Laboratory uses a ceramic-lined melter with large submerged plate electrodes (typically of Inconel 690) and relies on the conductivity of the molten glass to produce the joule heating effect. In most cases the waste is introduced onto the melt pool as an aqueous slurry but could also be fed dry. The JHCM approach has been selected for stabilization of high-level nuclear wastes at the Savannah River, Hanford, and West Valley sites and, as a result, this technology has benefitted from considerable research and development efforts in recent years. Duratek's Duramelter JHCM vitrification system includes several proprietary modifications to this base technology in order to more appropriately address the needs of large-volume mixed and low-level waste streams; several tests were conducted with such a system in this study.

1.1.2 Soil Washing

The objective of a soil washing process is to decontaminate as large a fraction of the input soil as possible such that the remaining levels of hazardous and radioactive contaminants fall below the corresponding regulatory limits and therefore that fraction of the material can be safely returned to the site or otherwise reused. In the process, the minor fraction becomes enriched in the contaminants and in this way a concentration or waste volume reduction is achieved. Much of the equipment and methods involved are well established in the mining and mineral processing industries. The basic processes involved are physical separation by density and particle size, and aggressive agitation and chemical extraction. The basis for the success of the process is the fact that most of the contaminating species are present only on the surface of the soil particles. Thus, it is then clear that (i) the concentration of contaminants will be greatest for the smallest particle size fraction, and (ii) the surface contamination on the larger particles can, in principle, be removed by a combination of abrasion and chemical extraction. Thus, optimization of the soil washing parameters involves determination of the optimum particle size fraction on which to base the segregation as well as the most appropriate combination of physical abrasion and chemical extraction and type of extractant. The extraction process is ideally operated in a closed-cycle regenerative mode so that little, if any, side-stream liquid waste is generated.

Volume reductions well in excess of 80% can be achieved by such soil washing techniques alone, while producing a significant enrichment of the contaminants in the minor fraction. Thus, a complete remediation process must also address the stabilization of that minor fraction. The approach we are presently developing involves combining the benefits of soil washing and vitrification technologies by feeding the soil washing concentrates to an in-furnace vitrification system. The objective is then to demonstrate that contaminated soils that are classified as mixed waste can be treated in such a way that the major fraction is decontaminated while the concentrates are vitrified to produce a highly leach-resistant wasteform that is no longer hazardous.

1.2 Waste Materials Selected for Study

1.2.1 Oak Ridge Site

A contaminated storm sewer sediment from the Y-12 Facility of the Oak Ridge, TN, site was identified as a suitable material upon which to develop and demonstrate the combined soil wash/in-furnace vitrification technique that we are developing. Large quantities of this material (about 500,000 tons) were collected during vacuum cleaning of site storm sewers. The gravelly material, presently stored in dumpsters at the Oak Ridge K-25 facility, is contaminated with between 0.2-75,000 ppm mercury, 1-21,000 ppm uranium, 0-280 ppm thorium, and 0.5-180 ppm PCBs. The particular batch selected for this study averages 4000 ppm mercury, 630 ppm uranium, 1.2 ppm thorium, and 24 ppm PCBs.

1.2.2 Weldon Spring Site

DOE now has responsibility for the Weldon Spring site in Missouri. During the 1940s and 1950s the site operated as an Army ordinance works until it was acquired by the Atomic Energy Commission who operated it as the Weldon Spring Uranium Feed Materials Plant processing about 16,000 tons of uranium, and some thorium materials, per year between 1957 and 1966. The liquid wastes were neutralized with lime and stored in four raffinate pits covering a 25-acre area on the site. The precipitates formed the estimated 200,000 yd^3 of raffinate sludge which must now be stabilized. In addition to the sludges, there are contaminated clay pit liner materials and contaminated surrounding soils to be addressed. There is some contamination from nitroaromatics from ordinance activities but the bulk of the remediation problem is the mixed waste sludges. The four pits differ somewhat in composition but typical levels of key contaminants are 32 ppm antimony, 400 ppm arsenic, 5 ppm beryllium, 5 ppm cadmium, 20 ppm chromium, 100 ppm lead, and up to 30 nCi/g from uranium, thorium, and radium, the bulk of which is due to ^{230}Th.

The Weldon Spring material was included in this study to demonstrate the development of a direct in-furnace vitrification approach. The material was selected since it is not amenable to either soil washing or *in situ* vitrification techniques. Soil washing is not likely to be a viable remediation approach when insoluble contaminants are distributed throughout the bulk of each particle, as is the case with the precipitates that form the raffinate sludges, rather than surface contamination. Furthermore, since the silica content is very low the sludge itself is not vitrifiable. In addition, the surface soils at the site form only a shallow covering over the limestone bedrock at the site. PNL (Koegler et al, 1989) concluded that application of ISV to the Weldon Spring sludges would require exhumation and blending of the sludges, clay liner, and soils to reach a vitrifiable composition, with the consequent loss of most of the major benefits of ISV.

1.3 Technology Programmatic Requirements

There is a clear need to treat contaminated soil and sludges in a manner that effectively protects public health, public safety, and the environment. Principal factors to be considered here include both provision for removing contaminants from the original site and assuring that the contaminants are locked irreversibly into a stable matrix.

Many years of research on high-level nuclear waste problems have conclusively demonstrated that vitrification provides one of the safest means of long-term stabilization of hazardous materials. The major issue addressed in this study is whether, through appropriate research and development, the process can be made economically competitive for the two specific sites studied.

1.4 Economic Considerations

While the costs associated with waste treatment are important components in a comparison of treatment technologies they in fact represent only a part of the total costs involved in site remediation. A life-cycle approach would also consider the costs associated with waste stream characterization activities and with disposal of the waste form as well as the necessary long-term monitoring involved. We contend that what are superficially perceived to be "expensive" treatment technologies, such as vitrification, can, from a life-cycle perspective, turn out to be the most economical approaches. This is so because of the relatively high and volume-driven costs associated with disposal. Furthermore, a waste form with higher leach resistance is likely to require less expensive disposal site preparation and subsequent long-term monitoring than one that is inherently more leachable.

To illustrate the key role of volume reduction in determining overall remediation costs, we will compare direct in-furnace vitrification and combined soil wash/in-furnace vitrification with one of the cheapest reference treatment technologies which is encapsulation in cement or grout. While the unit cost of vitrification is typically a factor of 3-6 times that of cementation, the former process produces a waste form of between about one-fourth to one-seventh the volume of the latter. Thus, when life-cycle costs are considered - that is, the cost of ultimate disposal, as well as the cost of treatment itself - disposal costs can dominate the selection of the most cost-effective treatment technology. For quite conservative unit costs ($400/ton and $70/ton, respectively) and volume reductions (or increases) for vitrification and cementation, a break-even point is reached at disposal costs of about $1.80/ft^3 for the 70% sludge formulations that we have developed for Weldon Spring wastes; for disposal costs lower than this, cementation is cheaper, whereas for disposal costs above this, vitrification is cheaper. A reduction of the unit cost of vitrification to $250/ton (probably more realistic for large volume remediation problems) reduces this figure to $0.03/ft^3. Even at $400/ton a typical disposal cost of $30/ft^3 makes vitrification about 75% cheaper than cementation. Note that despite these already gross differences we still have not included the cost savings that would be associated with the superior leach resistance of the vitreous wasteform arising from reduced disposal site preparation costs and subsequent monitoring costs.

2.0 METHODOLOGY AND APPROACH

The objectives of the present laboratory and bench-scale study include development and demonstration of the major principles on which the approach is based, and the accumulation of process and product characterization data which are necessary for development of conceptual process designs and evaluation of the suitability of the approach for larger-scale demonstration. A schematic diagram of the study is shown in Figure 2-1.

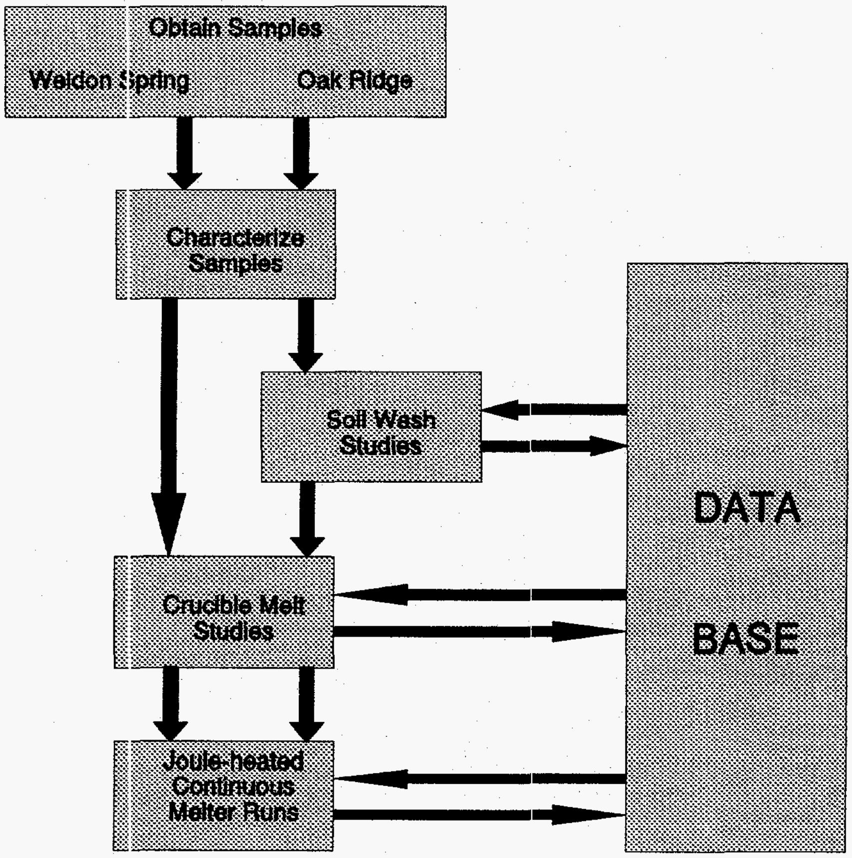


Figure 2-1. A schematic diagram of the study.

Soil and sludges from the Weldon Spring site were used for the direct vitrification study while storm sewer sediments from the Oak Ridge site were used for the combined soil wash/vitrification study. Since extensive delays in obtaining samples were encountered (up to 15 months in one case) a small amount of work was done on surrogate materials; the bulk of the study was performed on actual waste materials, however. All samples were characterized to obtain the necessary chemical composition and physical property data needed for application of the treatment technologies. In the case of the direct vitrification approach for Weldon Spring materials, various formulations of soil-sludge blends with chemical additives were used in a

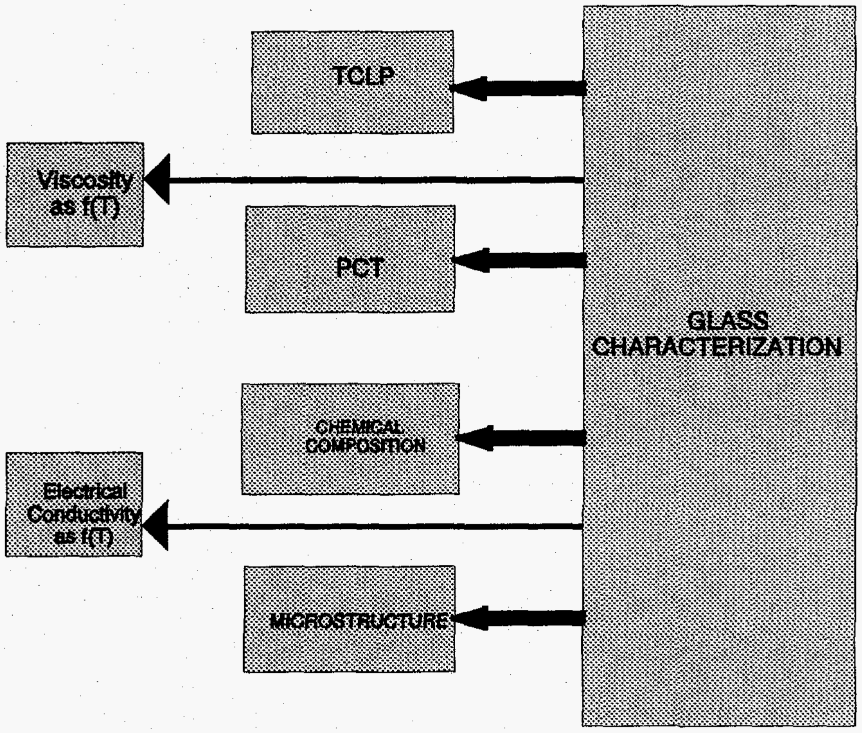


Figure 2-2. A schematic diagram of glass characterization activities.

composition study based on crucible melts of about 400 g each. The glasses produced were 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 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 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 Product Consistency Test (PCT) (Jantzen and Bibler, 1989), which is the present standard for high-level nuclear waste glasses, was also employed. This is a seven-day test at 90°C using 75-150 μm glass powder and is therefore 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, and the cost of the chemical additives that are used in the formulation.

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 application of known principles from glass chemistry and the use of composition-property modelling.

Several compositions were also tested in a small-scale Duramelter continuous joule-heated vitrification system using a slurry feed. The system had a typical glass production rate of about 20 kg/day. Such studies provide processing data that are not obtainable by simple crucible melts.

Samples from the Oak Ridge Y-12 facility were used for the study on treatment by a combination of soil washing and vitrification. The material was subjected to physical and chemical characterization to provide the data needed to design the soil washing study appropriately. Handling of this material was complicated by the unexpectedly high rate of mercury vapor generation from the sample, contrary to experience with previous samples. The original intention of the study was to use the contaminated fraction from the soil washing process directly in the vitrification study. In principle, the mercury would be volatilized in the vitrification system and captured in the off-gas system. However, after review of the data and considering the very high levels of mercury involved, the introduction of a thermal desorption step to strip out the mercury was also investigated. This approach was determined to be the preferred option based on our evaluation of alternative conceptual design options. A sample of the soil-wash contaminant-enriched fraction was treated by thermal desorption to remove the mercury and subsequently used to develop suitable vitrification formulations. The general approach was similar, but on a smaller scale, to that described above for the Weldon Spring materials. The glasses that were prepared were subjected to a similar characterization matrix to provide the requisite data.

2.1 Facilities, Equipment, and Experimental Methods

The major operations performed at VSL included glass melting, standard leach tests on the vitrified product, analysis of the materials and leachates, and product characterization. Standard glass characterization techniques including viscosity, conductivity and microstructure determination using scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX), were performed at VSL.

The major operations performed at Westinghouse Science and Technology Center included characterization (bulk density, moisture content, particle size distribution) of the contaminated soil, wet sieving, extraction testing, and mineral jig testing. This study also necessitated the demonstration of a thermal desorption process to remove mercury prior to vitrification testing. The specific techniques used are summarized below.

Glass Melting: The glasses were made using reagent grade powdered chemicals and the dried waste materials and were batched to yield about 400 g of glass. They were melted for 3 hrs at typically 1100°C in platinum or clay crucibles. The melts were quenched by pouring into a graphite mold. The glasses were annealed for one hour at ~ 500°C at which point the furnace was turned off and the samples were allowed to cool overnight. Larger scale tests were conducted in a 10 kg/day (nominal) continuous Duramelter vitrification system. The Duramelter vitrification system is a modification of the conventional joule-heated ceramic melter systems that have been selected for high-level nuclear waste vitrification. A variety of ceramic refractories are used for glass contact and backing insulation and these form a cavity inside an outer steel shell. Inconel plate electrodes are submerged below the glass pool and maintain the glass temperature by the joule-heating effect. Radiant heaters in the head space are used for initial melting of the starter glass to render it conducting. A slurry feed system pumps the waste blend (at typically 40 wt% solids) directly onto the glass pool where it first dries and then reacts and melts into the pool. Throughput of the system is enhanced by use of active stirring of the melt pool by means of an air sparger near the bottom of the pool. A number of proprietary design features extend the operating range of the system as discussed in Section 3.1.3. An air lift and botton drain provide alternate means of discharge. The melter system is maintained at slightly negative pressure by a multistage off-gas system consisting of wet scrubbers, mist eliminator, roughing filter, and HEPA filter.

Viscosity Measurement: The viscosity was calculated from measurements of the torque and rotation speed of a calibrated spindle of a Brookfield viscometer. Measurements were made at a range of temperatures. The estimated standard deviation of the measurements is 10%.

Conductivity Measurement: The 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. The estimated standard deviation of the measurement is 10%.

TCLP Test: The TCLP leach test (US Federal Register, 1990) was used to determine the leachability of arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver by measuring the leachate concentrations obtained after 18 hours at 22°C in a sodium acetate buffer solution. The estimated standard deviation of the measurements is 20%.

PCT Test: The PCT (Product Consistency Test) procedure (Jantzen and Bibler, 1989) evaluates the relative chemical durability of both homogeneous and devitrified 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. The estimated standard deviation of the measurements is 15%.

Scanning Electron Microscopy: Scanning electron microscopy was used to characterize the microstructure of the glasses by analyzing the glassy and crystalline phases using energy dispersive x-ray spectrometry. This permits determination of the volume fractions and compositions of crystalline phases in both as-melted and heat treated glasses.

Solution Analyses: 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 estimated standard deviations of the solution analyses themselves are 5%, 20%, 5%, and 10%, respectively.

Mineral Jig Testing: Mineral jig testing can be used to segregate soil by size or density, and can be used to displace contaminated extractant from clean solids. The soil is processed in an attrition scrubber first and then fed into a jig with desired settings so that the necessary stroke length, stroke frequency, bedding characteristics, and upflow solution rate can be determined.

Thermal Desorption: Thermal desorption is used to separate contaminants from soil. The soil is placed into a furnace and heated so that the volatile contaminants in the soil will vaporize. The vapor is led from the furnace and condensed in a cooled chamber leaving the soil essentially free of volatile contaminants. This technique was used to remove mercury in this study.

Wet Sieving: Wet sieving is used to determine the particle size distribution of the soil and the contaminant distribution as a function of particle size. A series of sieves of decreasing size are stacked and the soil is placed on top of the stack. Water is sprayed down through the sieves carrying the appropriate sized soil particles with it, thus separating the soil into groups by size.

Extraction Testing: Extraction testing is used to determine the optimum conditions for removing the contaminants from the soil of interest. The soil sample is combined with the appropriate chemical extractant and placed in an attrition scrubber. The sample is then sieved, washed, dried and analyzed for the contaminants of interest.

2.2 Quality Assurance

A Quality Assurance program is in effect at the Vitreous State Laboratory and a project-specific QA program was developed for operations at Westinghouse in order to ensure the reliability, verifiability and traceability of data obtained. The programs established at VSL and Westinghouse comply with the applicable quality assurance program requirements for nuclear facilities outlined in document ANSI/ASME NQA-1. A quality assurance program plan and quality assurance manual detail the implementation of these programs.

Technical procedures were employed for all operations performed in this project. Each procedure was prepared in order to ensure that data produced in the project are obtained with a known degree of statistical precision and accuracy and may easily be verified on repeating the procedure. All experimental data were recorded immediately and reviewed by qualified personnel.

3.0 RESULTS AND DISCUSSION

3.1 Weldon Spring

Due to delays in identification and shipment of suitable samples of sludge and liner materials from the Weldon Spring site, some preliminary testing was conducted with surrogate materials. Five test melts were made on the basis of available compositional data (DOE, 1989a, DOE 1989b, Koegler et al., 1989) as shown in Table 3-1. These melts were simplified surrogate compositions using only the major components. The qualitative data obtained from these glasses included approximate melting temperatures and viscosities (as estimated by "pourability") as well as visual determination of crystallization or secondary phase formation. Some evidence of the formation of a sulfate phase was found in glass number 5. These observations served to expedite the composition study performed with actual waste materials discussed below.

3.1.1 Sample Characterization

Six samples of sludge were received from the Weldon Spring site and were identified by the sample designations SWS-1 through SWS-6. Each five-gallon container was thoroughly mixed after opening to ensure homogeneity before removing subsamples for analysis. The solids content was measured by drying samples at 450°C for 4 hrs and determining the weight loss. Samples were also dried at 1100°C for 4 hrs prior to chemical analysis since this is the relevant basis for vitrification (i.e. carbonates, hydroxides, etc. are decomposed to the corresponding oxides). Small amounts of these samples were completely dissolved in HF/HNO_3 mixtures prior to elemental analysis by DCP spectroscopy. The sulfate content of these solutions was measured by ion chromatography. The results were converted to an oxide basis and are listed in Table 3-2. The six samples fell into two distinct compositional groups which differed most significantly in their levels of CaO, Fe_2O_3, and MgO. Table 3-2 also shows the ratios obtained from γ-spectroscopy for $^{212}Pb/^{214}Pb$ decays which reflect the differences in radionuclide compositions; with the exception of SWS-6 these data also support such a grouping.

Table 3-1. Glass Compositions for the Five Weldon Spring Surrogate Glasses (wt%)

	Glass 1	Glass 2	Glass 3	Glass 4	Glass 5
	50% sludge + 50% liner	90% Glass 1 + 10 Na_2O	80% Glass 1 + 20 Na_2O	Glass 1 + P_2O_5 + SO_3	80% Glass 4 + 20% Na_2O
Oxide	1	2	3	4	4
Al_2O_3	10.89	9.8	8.71	10.12	8.09
CaO	19.45	17.51	15.56	18.06	14.45
Fe_2O_3	6.71	6.04	5.37	6.23	4.98
K_2O	1.04	0.94	0.83	0.96	.77
MgO	6.62	5.96	5.30	6.15	4.92
MnO_2	3.18	2.86	2.54	2.95	2.36
Na_2O	1.71	11.54	21.37	1.59	21.27
SiO_2	50.41	45.37	40.33	46.82	37.46
P_2O_5	0	0	0	2.07	1.66
SO_3	0	0	0	5.05	4.04
TOTAL	100	100	100	100	100

The sulfate levels in all of the samples are very much larger than those previously reported (DOE 1989a, DOE 1989b) (which may have actually determined only leachable sulfate) and also somewhat higher than those obtained by Koegler et al. (1989). These results create particular problems for vitrification due to the limited solubility of sulfates in silicate glasses. As our study progressed the behavior of the glass melts led us to suspect the presence of significant amounts of fluoride in these samples. Dried samples of sludges SWS-1 and SWS-6 were extracted in a large excess (2 g in 200 ml of 1 M acid) of nitric acid or hydrochloric acid solutions with agitation over a 2 day period. The solutions were then analyzed for fluoride by ion chromatography. These measurements suggested fluoride contents of 10 wt% and 1 wt% in the samples of SWS-6 and SWS-1 (both dried at 450°C), respectively. The measurement was later repeated on SWS-6 using a two step $NaOH/HNO_3$ microwave dissolution followed by analysis for fluoride by ion selective electrode, a procedure which is now routine in our laboratory. This procedure yields fluoride contents of 13.5 and 13.0 wt% on two separate samples of SWS-6.

Table 3-2. Analysis of Weldon Spring Sludges (wt%)

	Group 1		Group 2			
Oxide	SWS-1	SWS-4	SWS-6	SWS-5	SWS-2	SWS-3
Al_2O_3	4.76	4.87	2.63	2.75	2.60	3.11
As_2O_5	0.36	0.34	0.31	0.31	0.33	0.33
B_2O_3	0.07	0.03	0.28	0.08	0.03	0.02
BaO	0.04	0.03	0.04	0.03	0.04	0.03
CaO	25.13	25.72	40.02	40.30	40.30	38.90
CoO	0.02	0.02	0.02	0.02	0.02	0.01
Cr_2O_3	0.03	0.03	0.05	0.04	0.03	0.02
CuO	0.14	0.14	0.09	0.09	0.10	0.10
Fe_2O_3	9.04	9.93	6.00	5.86	6.23	6.23
HgO	0.03	0.05	0.04	0.04	0.03	0.04
K_2O	0.28	0.26	0.39	0.25	0.15	0.18
Li_2O	0.16	0.13	0.36	0.24	0.23	0.18
MgO	9.29	9.78	5.80	5.77	5.84	6.14
MnO_2	0.98	0.77	0.37	0.30	0.34	0.30
MoO_2	0.65	0.68	0.92	0.92	0.92	0.92
Na_2O	4.75	4.88	2.23	2.06	1.70	2.23
NiO	0.35	0.03	0.06	0.05	0.04	0.03
P_2O_5	2.23	1.87	1.82	1.50	1.70	1.42
PbO	0.15	0.15	0.13	0.13	0.13	0.13
SiO_2	11.77	11.68	9.03	9.37	8.09	9.84
SrO	0.02	0.02	0.03	0.03	0.03	0.02
TiO_2	0.34	0.34	0.23	0.22	0.22	0.24
V_2O_5	2.96	2.96	4.75	4.57	4.86	4.57
ZnO	0.10	0.10	0.12	0.13	0.13	0.12
ZrO_2	0.06	0.05	0.09	0.08	0.08	0.07
TOTAL	73.67	74.85	75.81	75.13	74.16	75.20
SO_4^{2-}	21.5	18.9	17.5	16.6	18.0	18.0
% solids	32.0	33.4	30.5	31.2	31.7	30.5
γ decays $^{212}Pb/^{214}Pb$	1.53	1.37	2.08	5.72	5.88	5.53

Samples of Weldon Spring pit liner material were analyzed after drying at 1100°C by the same dissolution procedure followed by DCP spectroscopy. The results are shown on an oxide basis in Table 3-3.

3.1.2 Glass Melting

A series of crucible melts were made from blends of dried sludge and liner material with a variety of additives. The blends were melted in platinum or clay crucibles usually for 2 hrs at 1150°C with continuous stirring. However, for comparison purposes the WS-14 glass (same composition as the WS-7 glass) was melted for 25 hours. (The difference in the characterization data obtained on these two glasses probably reflects the greater loss of fluorides and sulfates from WS-14 due to volatilization.) Higher temperatures were used as necessary if the batch failed to melt.

All glass melts (Table 3-4) up to and including WS-18 were made from sludge SWS-6; the last two melts, WS-19 and WS-20, were made from sludge SWS-1 in order to confirm the vitrifiability of the other compositional group. In WS-19, additional CaO was added to bring the CaO level close to that of the corresponding glass made from sludge SWS-6, however, the behavior of these glasses was quite different. WS-19 proved to be quite refractory and solidified at temperatures below 1250°C; our viscosity data for that glass therefore cover only 1250-1300°C. We believe that these differences are due to different levels of fluoride in the sludge samples, as shown in Table 3-5. Fluoride acts as a strong fluxing agent in glass making and hence reduces melt viscosity and increases electrical conductivity. Since the SWS-6 sludge contains about 13 wt% fluoride and glasses WS-12 and WS-13 contain 40% sludge and 60% sludge, respectively, the expected fluoride content of these glasses is 5.3 and 8.0 wt%, respectively. The analyzed values are slightly lower, probably as a result of volatilization during melting. The lower fluoride content of the WS-20 glass is a result of the use of SWS-1 sludge and as a consequence both WS-20 and WS-19 would be expected to be much more refractory.

After preparation, the glasses were analyzed by total dissolution and DCP spectroscopy, ion chromatography and, in selected cases, fluoride analysis. The results are presented in Table 3-6.

Table 3-3
Chemical Analysis of Weldon Spring Pit Liner Material
(Dried at 1100°C)

Oxide	Wt%	Oxide	Wt%
Al_2O_3	12.88	Na_2O	1.29
B_2O_3	0.04	NiO	0
CaO	0.98	P_2O_5	1.67
Cr_2O_3	0.01	SiO_2	75.19
Fe_2O_3	5.24	SrO	0.02
K_2O	2.15	TiO_2	0.74
Li_2O	0.02	U_3O_8	0.01
MgO	1.05	V_2O_5	0.05
MnO_2	0.17	ZrO_2	0.01

Table 3-4
Weldon Spring Crucible Melt Batch Formulations

Sludge SWS-6	
Glass #	(Sludge:liner) : % additive*
WS-1	(50:50):30 Na_2O
WS-2	(50:50):20 Na_2O
WS-3	(50:50):10 Na_2O
WS-4	(70:30):10 Na_2O
WS-5	(50:50):10 Li_2O
WS-6	(80:20):10 R_2O mixed (20% Li_2O - 80% Na_2O)
WS-7	(70:30)
WS-8	(50:50):10 R_2O mixed (40% Li_2O - 60 Na_2O)
WS-9	(50:50):10 R_2O mixed (20 Li_2O - 80 Na_2O)
WS-10	(60:40):10 Na_2O
WS-11	(50:50):10 Na_2O + 10 CaO
WS-12	(50:50):10 Na_2O + 10 B_2O_3
WS-13	(60:40)
WS-14	(70:30)
WS-15	(60:40):5 Na_2O
WS-16	(60:40): 5.75% Fe_2O_3
WS-17	(65:35)
WS-18	(80:20)
Sludge SWS-1	
WS-19	(70:30):20 CaO
WS-20	(70:30)

* The notation used is as follows: (50:50):30 Na_2O indicates a formulation composed of 30 wt% Na_2O and 70 wt% of a blend of equal proportions (i.e. 50:50) of dried sludge and liner material.

Table 3-5
Fluoride Analysis of Sludge SWS-6 (dried at 450°C) and of Three Weldon Spring Glasses

	Wt% F
Sludge SWS-6	13.25%
WS-12	3.78%
WS-13B	5.98%
WS-20	0.82%

The composition study was designed to establish a database that permits the optimization of the waste form composition with respect to (i) viscosity (ii) conductivity (iii) durability (iv) phase stability (v) cost of additives, and (vi) waste loading. Waste loading has the largest potential impact on the overall remediation cost. The overwhelming majority of the hazardous and radioactive components are contained in the sludge and these components have apparently migrated through only a small fraction of the thickness of the liner, which is otherwise essentially uncontaminated. For these reasons we have included in our study compositions that are directed towards maximization of waste loading with respect to sludge, as opposed to total waste. The overall waste stream composition will clearly be directly impacted by the decision that is made at the site regarding the fraction of the liner material that would be treated. We concentrated our studies on sludge:liner ratios between 50:50 and 80:20, which correspond to treatment of 31% and 8% of the total liner material respectively.

Table 3-6
Results of Chemical Analysis of Weldon Spring Glasses (wt%)
(Note: The compositions of WS-3 and WS-7 are calculated)

	WS1	WS2	WS3	WS4	WS5	WS6	WS7	WS8	WS9	WS10
Al_2O_3	8.26	8.57	8.54	8.5	10.44	13.42	16.11	8.82	8.69	8.14
B_2O_3	0.15	0.07	0.13	0	0.09	0	0.19	0	0	0.02
BaO	0.05	0.05		0.05	0.05	0.04		0.05	0.05	0.05
CaO	13.31	18.32	17.69	26.88	20.55	26.86	23.78	22.18	22.74	26.94
Cr_2O_3	0.36	0.04	0.13	0.06	0.08	0.04	0.03	0.07	0.06	0.05
Fe_2O_3	6.19	6.02	6.84	6.68	5.8	5.84	6.49	6.56	6.47	6.7
K_2O	0.7	0.73	0.94	0.84	1.05	0.56	0.9	0.93	0.93	0.77
Li_2O	0.24	0.15	0.14	0.19	9.76	2.02	0.27	4.43	2.38	0.25
MgO	3.53	3.99	3.5	4.4	3.41	4.43	4.37	3.93	3.96	4.52
MnO_2	0.38	0.37	0.27	0.31	0.24	0.28	0.17	0.27	0.27	0.3
Na_2O	28.17	18.78	10.29	10.8	1.48	6.9	0.93	6.82	8.75	10.53
NiO	0.12	0.03	0.08	0.07	0.06	0.04	0.04	0.06	0.05	0.05
P_2O_5	0.88	0.57	0.25	1.02	0.9	1.3	0.72	0.6	1.02	1.22
SiO_2	37.05	41.7	48.32	39.56	45.36	37.36	42.18	44.58	43.95	39.79
SrO	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.02	0.03	0.03
TiO_2	0.54	0.54	0.56	0.54	0.66	0.8	0.88	0.6	0.58	0.56
ZrO_2	0.06	0.05	0.07	0.08	0.07	0.08	0.09	0.07	0.06	0.08
TOTAL	100	100	97.77	100	100	100	97.19	100	100	100
F^-										
SO_3	1.39	0.33		0	0	0		0.06	0.33	2.42

	WS11	WS12	WS13	WS14	WS15	WS16	WS17	WS18	WS19	WS20
Al_2O_3	7.99	8.15	8.45	9.46	10.19	9.44	10.34	7.4	10.25	10.75
B_2O_3	0.05	10.1	1.82	0.01	0.03	0.03	0.02	0.25	0.04	0.02
BaO	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.03	0.05
CaO	31.82	21.13	27.49	32.74	24.4	25.99	21.27	38.36	33.04	20.71
Cr_2O_3	0.1	0.07	0.04	0.02	0.02	0.01	0.02	0.06	0.05	0.04
Fe_2O_3	6.13	5.71	9.67	7.3	6.12	11.55	8.55	7.49	7.68	9.45
K_2O	0.65	0.96	0.97	0.91	1.06	1.02	1.2	0.63	0.38	0.86
Li_2O	0.23	0.17	0.23	0.24	0.19	0.18	0.15	0.29	0.24	0.17
MgO	3.67	3.49	4.68	5.36	4.06	4.43	3.87	6.78	7.08	7.94
MnO_2	0.26	0.25	0.34	0.35	0.26	0.28	0.28	0.42	0.76	0.91
Na_2O	9.49	10.21	2.16	1.67	6.2	1.59	1.25	1.59	1.96	3.44
NiO	0.1	0.04	0.05	0.04	0.03	0.03	0.04	0.12	0.05	0.04
P_2O_5	0.97	0.71	1.05	1.51	0.94	0.96	1.16	1.81	1.72	2.03
SiO_2	37.87	38.32	42.32	39.57	45.6	43.71	50.96	34.02	35.97	42.76
SrO	0.03	0.02	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03
TiO_2	0.53	0.54	0.56	0.61	0.71	0.59	0.73	0.49	0.67	0.73
ZrO_2	0.07	0.08	0.1	0.1	0.09	0.08	0.08	0.19	0.06	0.08
TOTAL	100	100	100	100	100	100	100	100	100	100
F^-		3.78	5.98							0.82
SO_3	0.58	0.05	1.73	2.08	2.2	1.1	0.47	5.86	1.91	0.92

The lower limit on liner content is determined by the amount of SiO_2 that is necessary to produce a homogeneous glass rather than a polycrystalline material. The high-sludge glasses foamed considerably when melted. The appearance of some of the glasses suggested partial devitrification which was confirmed by microstructural examinations. Melt WS-4 had a sludge:liner ratio of 70:30 and only 10 wt% added flux; this composition produced a good vitreous product after melting at 1150°C. This glass has a 90% overall waste loading and a 63% waste loading with respect to sludge.

An important consequence of high waste loading with respect to sludge, which contains large amounts of sulfates (about 15 wt% as SO_3), is the separation of an immiscible sulfate phase from the rest of the glass melt. In many of the glass melts, approximately 10% of the product was a sulfate phase. The distribution of hazardous and radioactive components between these two phases was investigated and the results indicate that the great majority of the radioactive components remain in the non-sulfate phase. An analysis of the sulfate phase is shown in Table 3-7.

The sulfate phases that are formed consist mainly of alkali sulfates, most of which melt below 900°C, and which therefore form a very fluid, high-conductivity phase which floats on top of the glass melt. Several melts were made without addition of alkali in order to reduce this effect. In these glasses, the sulfate (which is still insoluble in the silicate phase) forms a solid calcium sulfate phase (melting point = 1450°C as the pure material) which is present as a fine particulate ($< 1\ \mu m$) dispersion in the glass phase. Analyses of the as-melted glasses by SEM-EDX suggest that the small size of these particles gives rise to a stable suspension in the glass phase with little tendency to sediment. Since the main purpose of the alkali additions is to increase melt conductivity, one possible way of addressing the sulfate problem is to use a melter that can tolerate low-conductivity melts (as can the Duramelter, see Fig. 3-1) and use a feed formulation that does not use alkalies. This would produce a waste form consisting of a calcium sulfate phase that is dispersed in a glass matrix; such material can have very good leach resistance, as shown in Section 3.1.4.

The 80:20 sludge:liner melt, which also had 10 wt% of mixed alkali oxide additive, produced a highly devitrified product when melted at 1150°C. Remelting and higher temperature did not improve the homogeneity of the product and at 1500°C excessive foaming, probably as a result of volatilization of alkali sulfates, was observed. From a sludge waste loading perspective our 70:30 melts which produced homogeneous glassy products were the most promising.

Table 3-7
Composition of Sulfate Phase Formed from Weldon Spring Glass Melts

	Total Concentration in Sulfate Phase % or ppm			Percent of Element Added to Melt Batch that is Present in Sulfate Phase		
	WS2	WS3	WS4	WS2	WS3	WS4
Ca	2.6%	19.4%	24.2%	2%	14%	17%
Mg	0.2%	1.0%	1.8%	1%	6%	10%
Mo	1.9%	2.1%	2.4%	63%	71%	81%
V	1.2%	1.5%	2.3%	9%	11%	17%
Th-232	10	27	56	0.00%	0.01%	0.02%
U-238	44	359	1004	0.04%	0.29%	0.80%
Ag	3	3	3			
As	2250	2860	2860	22%	24%	28%
Ba	490	1140	1140	27%	61%	62%
Cd	6	0	0			
Cr	380	510	510	24%	20%	32%
Hg	1	0	0	0%	0%	0%
Pb	0	0	0	0%	0%	0%
Se	0	170	170			

The immiscible sulfate phase which formed on each of these melts has both a higher aqueous solubility and electrical conductivity than the glass phase; it is therefore essential to effectively separate the two phases before determining these properties or the sulfate phase would dominate the measurement. For this reason, a remelting procedure was used for all of the melts prepared. The sulfate phase was allowed to rise to the surface of the melt at 1200°C for 1 hour and as much as possible of the low-viscosity sulfate phase was then poured off and retained for separate characterization. Any remaining sulfate on the glass surface was evaporated by heating at 1450°C for 1.5 hours.

3.1.3 Viscosity and Conductivity

Both conductivity and viscosity were measured at typically five temperatures to span the range of likely processing parameters. The electrical conductivity data for each glass were fitted to Arhenius equations and the melt viscosity data to Vogel-Fulcher equations (Arhenius equation with allowance for the rapid rise in viscosity on approach to the glass transition temperature). For convenience, these equations were used to calculate the viscosity and conductivity at standard temperatures, which facilitates comparisons between glasses; these results are shown in Tables 3-8 and 3-9.

Table 3-8. Viscosity (Poise) of Weldon Spring Glasses at Standard Temperatures

Temp°C	WS2	WS3	WS4	WS5	WS6	WS7	WS8	WS9	WS10	WS11	WS12
1150	28.2	41.4	12.3	7.86	15.5	13.8	14.9	20.8	13.8	16.9	13.2
1100	47.2	72.8	20.9	11.8	26.3	26.8	23.3	34.0	21.2	67.3	20.7
1050	85.4	150	39.4	18.6	48.6	63.3	38.8	58.9	40.2	1790	35.3
1000	170	395	85.1	31.9	100	201	69.7	109	115		66.9
950	380	1530	221	60.0	236	1020	138	222	866		147

Temp°C	WS13B	WS14M2	WS15	WS16	WS17	WS18	WS19	WS20
1350	11.7	11.3	11.0	4.72	13.5	1.65	7.38	10.7
1300	13.6	13.3	14.6	6.50	21.1	1.87	8.52	17.2
1250	16.5	16.2	20.5	9.41	34.7	2.22	13.3	29.3
1200	21.1	21.1	30.6	14.5	60.7	2.83	Solid	52.7
1150	29.3	30.3	49.5	24.1	114	4.09	Solid	101
1100	47.0	51.2	89.5	44.3	233	7.72	Solid	212
1050	97.0	118	188	92.9	528	9.7	Solid	484
1000	341	546	492	234	1360	3630	Solid	1240
950	5190	22500	1790	763	4140	--	Solid	3680

Table 3-9. Electrical Conductivity (S/cm) of Weldon Spring Glasses at Standard Temperatures

Temp (°C)	WS2	WS3	WS4	WS5	WS6	WS7	WS8	WS9	WS10
950	0.166	0.033	0.042	0.274	0.027	0.007	0.102	0.067	0.053
1000	0.212	0.052	0.067	0.336	0.060	0.015	0.150	0.106	0.081
1050	0.264	0.078	0.101	0.403	0.107	0.030	0.208	0.154	0.120
1100	0.322	0.112	0.145	0.476	0.167	0.053	0.278	0.209	0.170
1150	0.387	0.156	0.200	0.554	0.239	0.087	0.359	0.270	0.234
1200	0.457	0.209	0.267	0.636	0.320	0.135	0.450	0.337	0.313

Temp (°C)	WS11	WS12	WS-13B	WS-14M2	WS-15	WS-16	WS-17	WS-18
950	0.17	0.041	0.005	0.000	0.006	0.004	0.001	0.030
1000	0.035	0.065	0.015	0.003	0.015	0.011	0.003	0.059
1050	0.065	0.096	0.036	0.015	0.029	0.023	0.007	0.103
1100	0.109	0.133	0.071	0.033	0.048	0.042	0.014	0.165
1150	0.172	0.175	0.126	0.052	0.072	0.066	0.024	0.247
1200	0.253	0.223	0.205	0.069	0.101	0.095	0.038	0.349

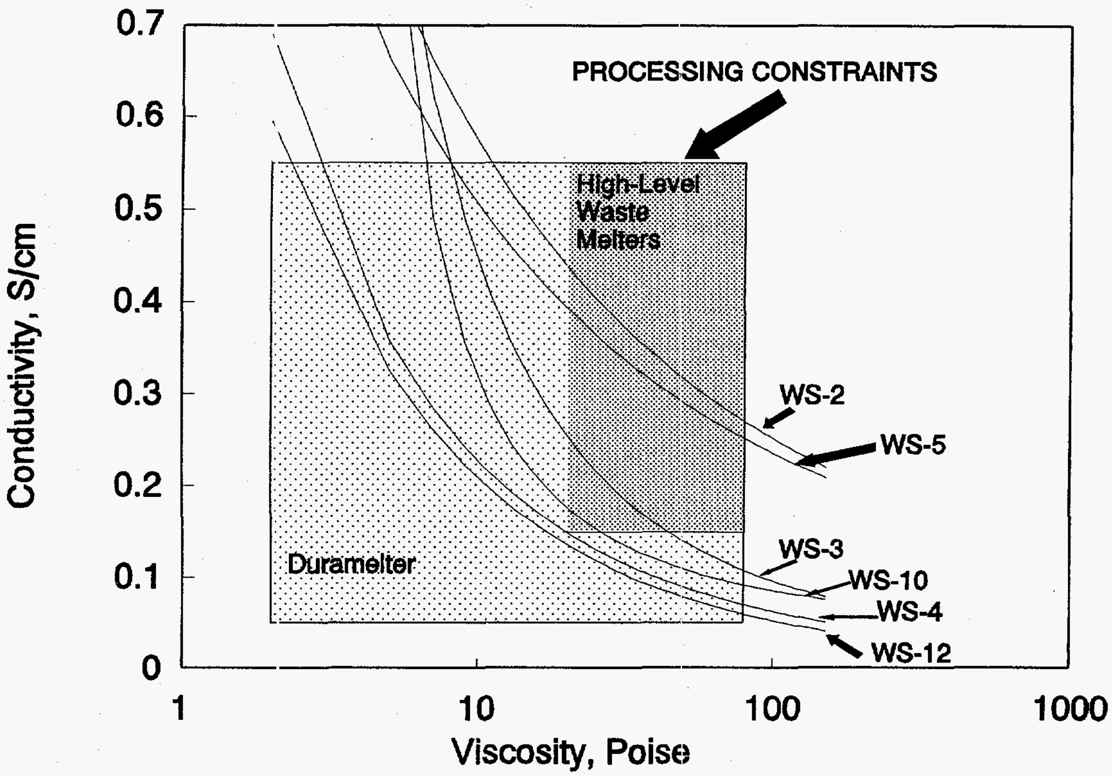


Figure 3-1. **Conductivity-viscosity behavior of Weldon Spring Glasses in relation to melter processing constraints.**

Typical constraints used for Joule-heated ceramic melter processing of high-level nuclear waste are 20 P ≤ viscosity ≤ 80 P and 0.14 S/cm ≤ conductivity ≤ 0.55 S/cm. The viscosity bounds represent increased corrosion (< 20 P) and slow throughput (> 80 P) and limitation due to the conductivity of the melter lining itself (< 0.15 S/cm) and due to current density limitations of the electrodes (≥ 0.55 S/cm). Figure 3-1 shows how the glasses WS-2, 3, 4, 5, 10, and 12 compare with these requirements; the lines are obtained from the fitted equations for each glass by eliminating the temperature (which increases to the left of the figure). Figures 3-2 and 3-3 show how the range of processing temperatures that meets these processability constraints varies with the raffinate sludge content of the glass and the additive content for both Na_2O and Li_2O additives ("V" and "C" denote viscosity and conductivity limits, respectively). Together these data indicate that glasses with high waste loadings can be produced that meet the key processing constraints of viscosity and conductivity. It is worth noting that Duratek has independently researched advanced joule-heated melter designs that expand these traditional limits used in high-level nuclear waste applications. The performance characteristics of Duratek's DURAMELTER vitrification system are also shown on Figure 3-1. Higher waste loading glasses which require reduced amounts of chemical additives can be processed with this system.

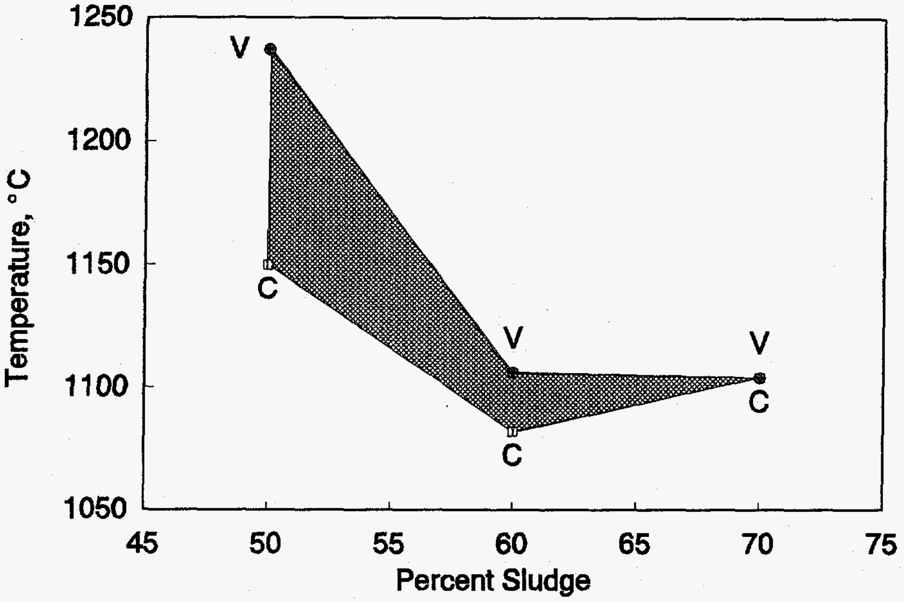


Figure 3-2. Temperature range over which Weldon Spring glasses (10% Na_2O additive) meet viscosity and electrical conductivity constraints used for joule-heated melter processing of high-level nuclear waste glasses as a function of sludge content

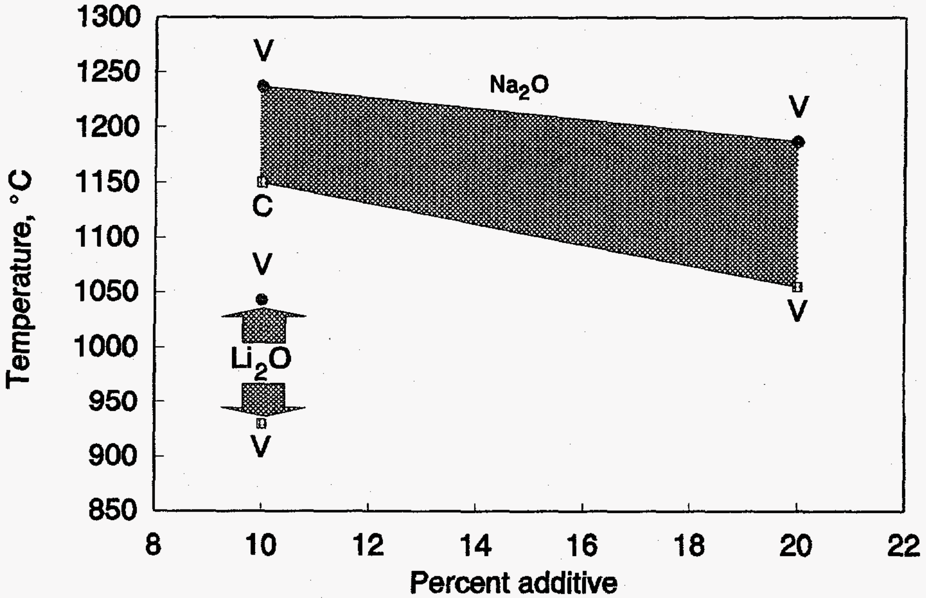


Figure 3-3. Temperature range over which Weldon Spring glasses (50% sludge) meet viscosity and electrical conductivity constraints used for joule-heated melter processing of high-level nuclear waste glasses as a function of additive content.

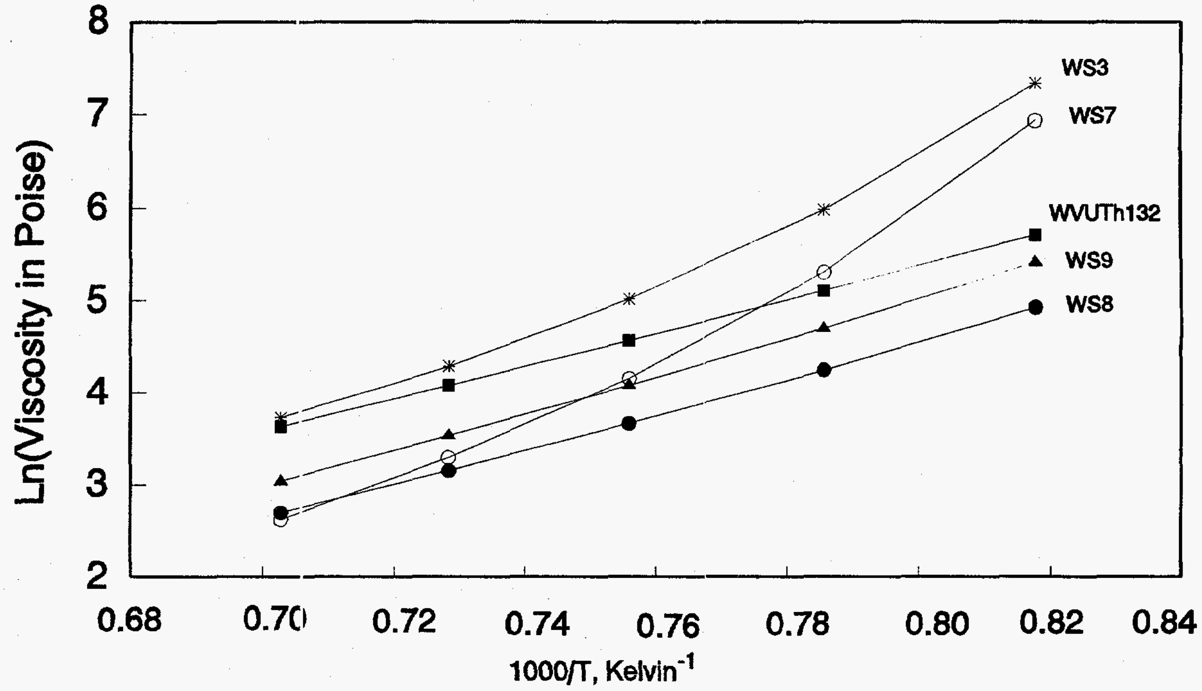


Figure 3-4. **Behavior of melt viscosity with temperature. Effect of alkali and mixed-alkali additives on Weldon Spring glasses.**

Glass	Composition
WVUTh132	High-level nuclear waste mixed-alkali borosilicate
WS-7	(70:30)
WS-3	(50:50):10Na_2O
WS-9	(50:50):10 R_2O with R_2O = 20% Li_2O + 80% Na_2O
WS-8	(50:50):10 R_2O with R_2O = 40% Li_2O + 60% Na_2O

Figure 3-4 shows the logarithm of the viscosity versus the reciprocal of the absolute temperature for various glass compositions. In such a plot, a simple activated process would yield straight lines with the slope proportional to the activation energy. This is the case for all of the glasses with mixed alkali (i.e. more than one alkali) additives (the high-level waste glass and WS-8 and WS-9). WS-7 and WS-3, which have no additives, and only Na_2O additive, respectively, show distinct curvature on these plots. Benefit can be taken of this "mixed alkali" effect in order to reduce the rate of rise of viscosity at low temperatures without increasing the amount of additives. Thus, while Li_2O is considerably more expensive than Na_2O, the nonlinear mixture effect on viscosity means that addition of a small amount of Li_2O can actually reduce the total additive requirements from a viscosity perspective and, consequently, may be cost effective in some situations.

There is, of course, a general downward displacement of these lines with increasing Li_2O content at fixed total R_2O on a weight percent basis due to the molecular weight difference which means that total R_2O is actually increasing on a molar basis.

3.1.4 Leach Testing

Weldon Spring glasses WS-1 through WS-12 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 in a sodium acetate buffer solution for 18 hrs at 22°C. The leachate solutions were analyzed for the eight listed metals using inductively coupled plasma-mass spectrometry (ICP-MS) with sample spiking as required in the EPA TCLP test procedure (US Federal Register, 1990). The results are listed in Table 3-10 together with the EPA regulatory limits. All of the glasses passed this test, in most cases by a wide margin. Due to difficulties in the selenium analyses by ICP-MS, numbers are not reported for this element for glasses WS-1 through WS-4. However, comparison of the directly measured and spiked sample results leads us to believe that these concentrations were below the regulatory limit in all cases.

The Savannah River Product Consistency Test (PCT) leaching procedure (Jantzen and Bibler, 1989) was conducted on twelve of the glasses produced from Weldon Spring raffinate sludges. The leachate sampling schedule used for this test was 7, 28, 56, and 180 days and every 180 days thereafter. While all of the glasses passed the EPA TCLP test and therefore constituted non-mixed waste forms, that procedure is not the best measure of long-term glass durability. The main reasons for this are that (i) the TCLP test is conducted under acidic conditions in which glasses generally perform very well; (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 (around 20 m^{-1}). The PCT test is conducted at 90°C for at least 7 days and with $S/V = 2000\ m^{-1}$ (10 g of 75-150 μm powder in 100 ml water) and under these conditions the natural pH-rise due to leaching of alkalies is accentuated. These high-pH conditions increase the silicic acid saturation concentration and promote the major dissolution mechanism for the 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.

Table 3-10
TCLP Results for the Weldon Spring Glasses (ppb)

Glass	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
WS1	6	25	520	18	0	0	0	pass
WS2	2	13	910	12	0	14	0	pass
WS3	8	42	95	12	130	0	14	pass
WS4	0	210	880	25	0	0	37	pass
WS5	0	84	750	3	0	0	41	300
WS6	0	59	320	0	0	0	22	600
WS7	0	110	330	4	0	0	0	0
WS8	0	93	280	0	0	0	20	22
WS9	0	23	120	0	0	0	4	42
WS10	4	870	690	13	0	16	0	0
WS11	36	94	260	6	172	2	0	0
WS12	5	130	790	0	61	0	0	620
EPA TCLP Limit	5000	5000	100000	1000	5000	200	5000	1000

Figure 3-5 compares the PCT normalized leachate concentrations (i.e. solution concentration normalized to that in the glass (Jantzen and Bibler, 1989)) of six Weldon Spring glasses (WS-2, WS-3, WS-4, WS-8, WS-10, and WS-12) with the present reference glass for West Valley (Ref 5) and glasses spanning the expected range of variability at Savannah River (DWRG and SRL131) after a 7 day sampling schedule. The SRL131 is significant since its performance is close to that of the DWPF EA glass that is the current standard for acceptability as detailed in the waste acceptance preliminary specifications (WAPS). The present WAPS requires reporting of boron, lithium, and sodium since these elements generally bound the normalized release of all other components. Figure 3-5 shows that all of the Weldon Spring glasses compare very favorably with the high-level nuclear waste glasses. It is worth noting that these glasses are of very different types of compositions in that the high-level nuclear waste glasses are low-calcium, mixed-alkali, borosilicate glasses, while the Weldon Spring glasses are high-calcium, low-boron, sodium silicate glasses.

Figure 3-5 shows similar data for the releases of silica and aluminum which are major matrix components. Again, the Weldon Spring glasses perform surprisingly well. Also shown in Figure 3-5 is the release of calcium and uranium; note that SRL131 contains no uranium and

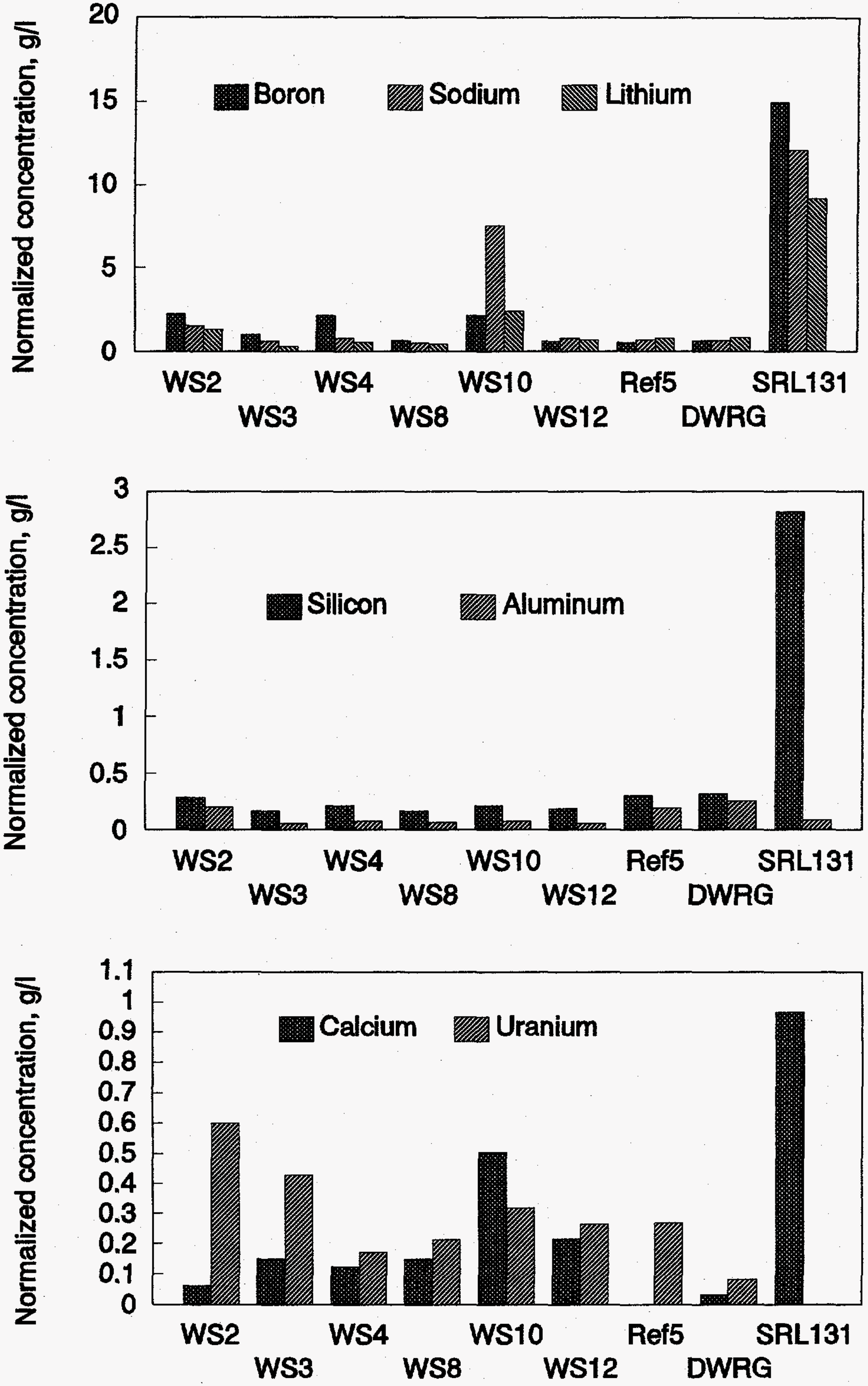


Figure 3-5. Comparison of 7-Day PCT leach test results of Weldon Spring glasses with high-level nuclear waste glasses.

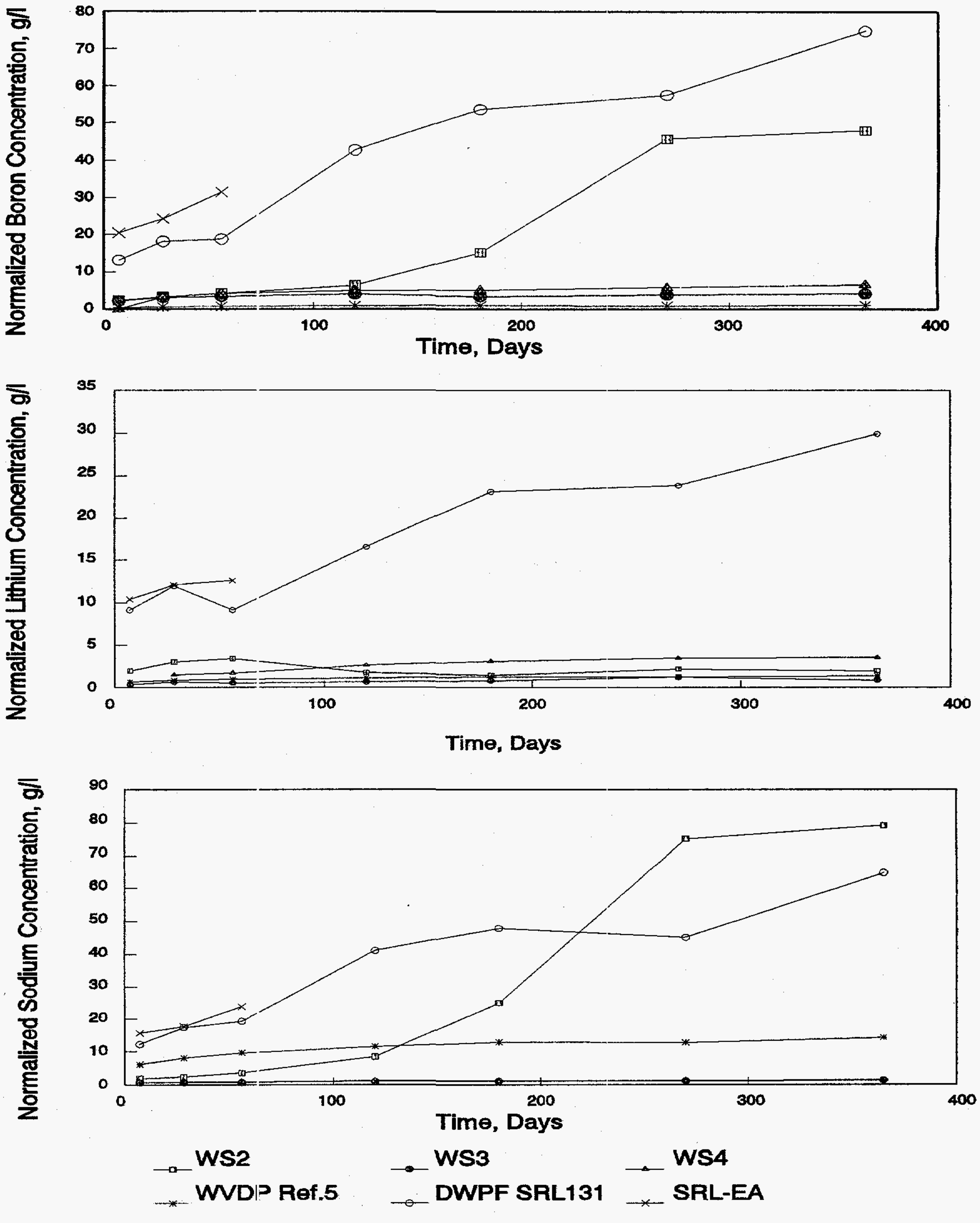


Figure 3-6. Results of PCT leach testing of Weldon Spring glasses (WS2, WS3, and WS4) compared with three high-level nuclear waste glasses.

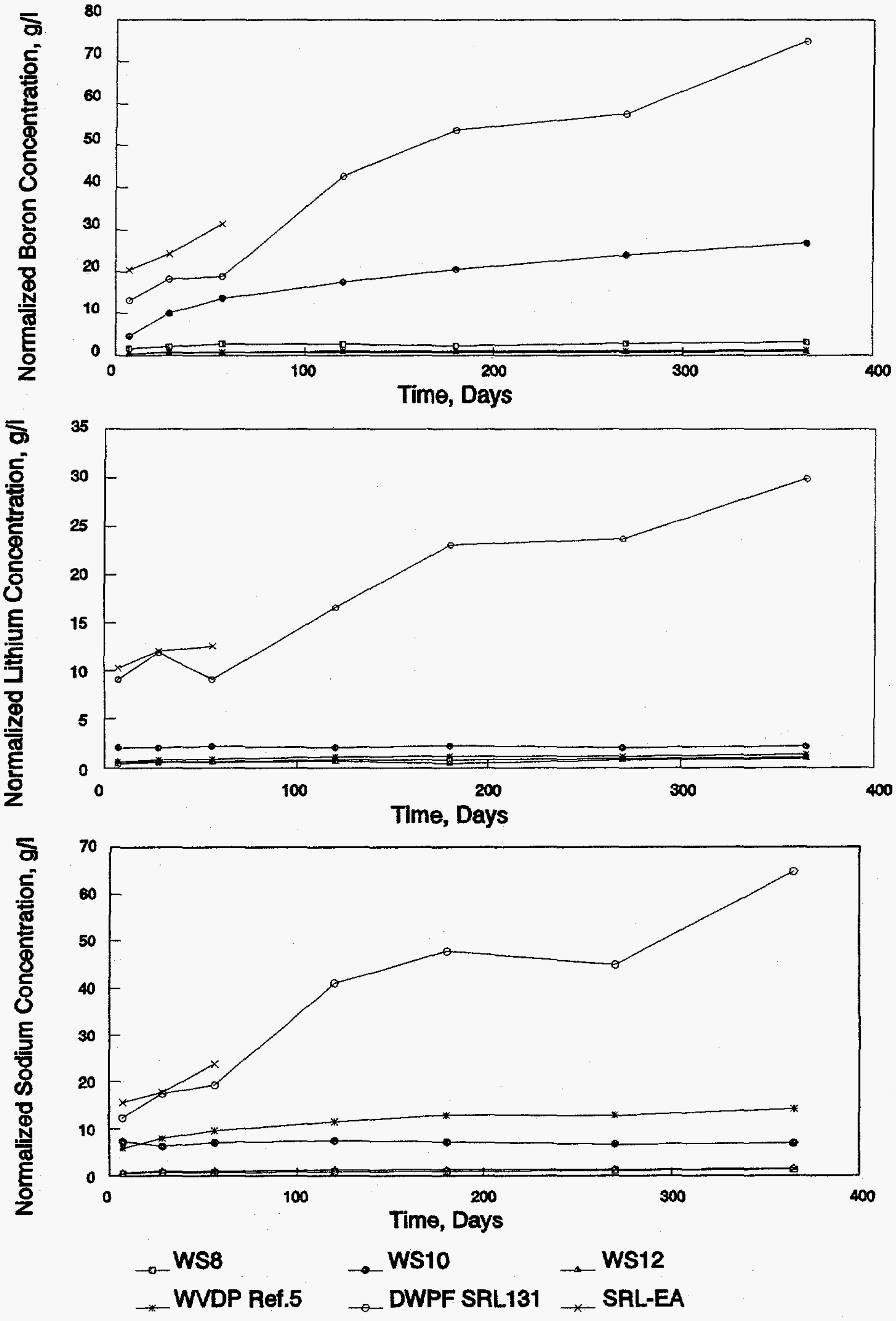


Figure 3-7. **Results of PCT leach testing of Weldon Spring glasses (WS8, WS10, and WS12) compared with three high-level nuclear waste glasses.**

Ref 5 contains only a trace of calcium. In making these comparisons it should also be recognized that radioactive decay heating is an important factor for high-level nuclear waste glasses, and therefore a test at 90°C is sensibly conservative, whereas it is highly unlikely that the Weldon Spring glasses would experience temperatures above about 20°C in a disposal facility.

Figures 3-6 and 3-7 show the PCT leach test data at 90°C for these same glasses as a function of leach test duration for exposures of over 360 days. In general, all of the Weldon Spring glasses compare very favorably with the high-level nuclear waste glasses, even over these extended periods of time. Glasses WS-3, WS-4, WS-8, and WS-12 show the best performance, which is comparable to that of the Ref. 5 glass in terms of normalized lithium and boron concentrations and actually somewhat better than Ref. 5 in terms of normalized sodium concentrations. WS-3, WS-8, and WS-12 have 50:50 sludge:liner ratios whereas WS-4 appears to be exceptional in that it has a 70:30 ratio. WS-2 shows the poorest performance of the Weldon Spring glasses, especially in terms of the normalized boron and sodium concentrations. This glass shows an acceleration of leach rate between about 100 and 280 days. This behavior is probably due to the fact that this glass has the largest amount of added Na_2O (20 wt%) which tends to decrease glass leach resistance. The WS-10 glass also exhibits slightly higher normalized boron concentrations than the other Weldon Spring glasses.

Overall, the performance of the Weldon Spring glasses compares very well with that of the high-level nuclear waste glasses, even after leaching for extended periods of time under the aggressive conditions of the PCT procedure.

3.1.5 Phase Stability

Since glass is intrinsically metastable with respect to a crystalline assemblage it is important to assess the potential impact of devitrification on both the production process and on the leach resistance. Crystal formation during production 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 crystalline phases that are more soluble than the glass. Several measurements were made to assess the extent of crystal formation in these glasses and the subsequent effect on the leach resistance.

Six representative compositions were heat-treated at 1100°C and 1000°C for 24 hours in order to determine the phase stability at the lower-temperature range of potential melting temperatures. The heat-treated samples were sectioned, polished, and carbon-coated for subsequent analysis by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS). Heat treatments were also performed at 900°C for 24 hrs to induce more extensive crystallization in these glasses in order to investigate the range of crystalline phases that form. The phases most frequently observed were augite; an apatite phase incorporating Ca, P, V, As, and F; CaF_2; $CaSO_4$; and uranium-enriched regions in an unidentified phase. Phases occurring less frequently included a molybdate phase, a pyroxene or other silicate phase incorporating Na, Mg, Al, Ca, and Fe, and a calcium silicate phase with small amounts of Fe, Al, and Mg.

The total volume fraction of crystals was estimated for each of the 1000°C and 1100°C heat treatments with the results shown in Table 3-11. The total crystallinity of the WS-14M2 glass (70:30 sludge:liner) was more than 30% after 24 hours of heat-treatment at 1100°C, suggesting that higher melting temperatures would be required for this composition. However, the other 5 glasses showed considerably less ($\leq$ 2%) total crystallinity under the same heat-treatment conditions. Glasses WS-2 and WS-12 were also heat treated at 1000°C since no crystals were found at 1100°C; minimal crystallization was observed ($\leq$ 1%) for these glasses, even at this lower temperature. Since the heat-treated WS-14M2 glass exhibited the greatest total crystallinity, this glass was selected to assess the effect of crystallization on the leach resistance. A sample of this glass was heat treated for 24 hrs at 900°C to induce almost complete crystallization. Table 3-12 shows the results of the 7 day PCT leach test for the heat-treated (900°C for 24 hrs) WS-14M2 glass as compared to the as-melted WS-14M2 glass. The data clearly indicate that there is no substantial change in the leachate concentration between the heat treated and as-melted glass. The sodium and potassium concentrations are increased by crystallization but this change is insignificant compared to the performance of the high-level waste glass standards. Figure 3-8 shows the behavior of the normalized leachate concentrations of sodium and lithium with time for the WS-14M2 glass before and after heat treatment as determined by PCT testing. The lithium and sodium concentrations remain below about 1.5 g/l for both glasses, even after extended test times. The data indicate that the leach resistance of these glasses remains quite comparable to that of the high-level waste glasses even after very extensive crystallization.

Table 3-11. Effect of Heat Treatment on Crystal Content of Weldon Spring Glasses

		Volume % Crystals After 24 hrs at Temperature of:	
GLASS	COMPOSITION	1100°C	1000°C
WS-14M2	70:30	>30%	
WS-4	(70:30):10Na_2O	~ 1%	
WS-13B	60:40	~ 2%	
WS-2	(50:50):20 Na_2O	0%	<1% after 1 hr
WS-11	(50:50):10 Na_2O + 10CaO	< 1%	
WS-12	(50:50):10 Na_2O + 10 B_2O_3	0%	~ 1%

Table 3-12. Effect of Heat Treatment on 7-Day PCT Leach Test Results for Weldon Spring WS-14M2 Glass

	Leachate Concentration, ppm	
Element	As Melted	24 hours at 900°C
Si	19.68	22.55
B	4.42	4.28
Na	3.5	14.65
Ca	32.41	35.72
K	2.67	4.57
Li	0.74	0.76
V	4.04	4.25
U	2.62	2.52
pH	9.98	9.72

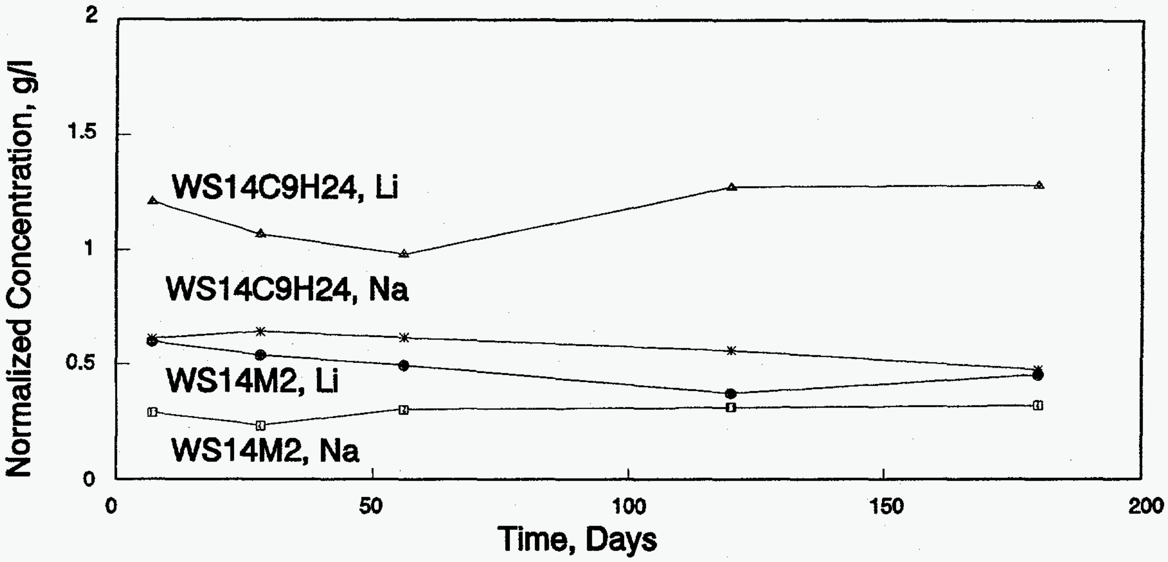


Figure 3-8 **Comparison of PCT leach results (Na and Li concentrations) for as-melted (WS14M2) and heat treated (WS14C9H24) Weldon Spring glasses.**

3.1.6 Continuous Melter Tests

Several runs were conducted in a Duramelter joule-heated vitrification system with a nominal glass output rate of 10 kg/day. Three test compositions were formulated on the basis of Weldon Spring glass characterization data, as shown in Table 3-13. The first two glasses, WS655 and WV50-56, were simplified versions of Weldon Spring formulations but without sulfates or fluorides. Crucible melts of these glasses were prepared in order to check that the electrical conductivity and viscosity were representative of the previous Weldon Spring melts and suitable for melting in the available vitrification system; these data are shown in Table 3-14. A third glass was formulated with both sulfates and fluorides, as shown in Table 3-13.

Table 3-13. Compositions of Weldon Spring Glass Used in Continuous Melter Test Runs (wt%)

Oxide	WV65	WV50S6	WSS-1
SiO_2	42.3	41.27	37.27
Al_2O_3	4.73	6.24	7.37
B_2O_3	10.09	10.64	9.05
Fe_2O_3	12.54	9.76	4.61
CaO	14.20	21.40	13.75
MgO	2.00	3.08	0
K_2O	3.79	2.88	0
Na_2O	10.34	4.74	8.96
$CaSO_4$	0	0	11.79
MgF_2	0	0	7.20

The slurry feeds for the Duramelter runs were prepared from the appropriate precursors, primarily carbonates, oxides and hydroxides. A colloidal ferric hydroxide sludge was used as the source of iron in order to increase the stability of the suspensions. The water content of the feeds varied between 64 and 71 wt%. Slurry feed rates of up to 140 ml/min. were sustainable and gave rise to below 75% cold-cap formation (i.e., 75% of the melt surface area covered by reacting feed). Under these conditions, the melter was producing about 2.7 kg of glass per hour or 64 kg/day, far in excess of the nominal 10 kg/day design basis. The throughput enhancements over a standard joule-heated melter are the result of proprietary design features incorporated into the Duramelter vitrification system. A useful basis for comparison of throughput rates is the ratio of the mass of glass produced per unit time, per unit surface area of glass melt. This is so since the melting of fresh feed into the glass pool is essentially a reaction at a surface and therefore throughput rate should scale approximately as the surface area. Standard joule-heated melters for processing high-level nuclear waste exhibit throughput ratios of around 500-1000 kg/m^2/day. With the present Weldon Spring feeds the Duramelter system achieved throughput ratios of almost 4000 kg/m^2/day. This enhancement is important since higher throughput ratios translate into a smaller melter system for given throughput which results in reduced capital costs.

Table 3-14. Conductivity and Viscosity of Cold Run Weldon Spring Glasses Used in Continuous Melter Test Runs

Glass	Temperature, °C	Conductivity (S/cm)	Viscosity (Poise)
WS65S	900	0.033	
	950	0.064	291
	1000	0.101	125
	1050	0.140	66.8
	1100	0.192	40.8
	1150	0.218	27.6
	1200	0.255	
WV50-S6	900	0.000	
	950	0.002	35000
	1000	0.006	2130
	1050	0.013	448
	1100	0.023	166
	1150	0.034	83.0
	1200	0.046	

For a small system such as the one used in this study radiative losses form a significant fraction of the energy requirements. Thus, the energy required per kilogram of glass dropped from about 5.5 kW hr/kg at a production rate of 8 kg/day to about 1.1 kWhr/kg at 64 kg/day. The latter number approaches quite closely the typical value found in large-scale (e.g. 500 ton/day) commercial glass melting of about 0.8 kWhr/kg for dry feeds.

3.1.7 Conceptual Process Options

A variety of process options were considered for optimum treatment of the sulfates in a full-scale process which necessitates characterization of both the glass phase and the sulfate phase. We have considered five general approaches to this issue:

(i) In principle the sulfates might be washed out of the sludge before vitrification. However, our experiments have shown that acid washing removes only about 10% of the total sulfates since most are in the form of calcium sulfate. Furthermore, the wash solution then contains significant amounts of the hazardous components.

(ii) Tailor the composition in such a way that both the glass phase and the sulfate phase are sufficiently leach resistant to form viable waste forms. This is difficult since the sulfate phase consists predominantly of very soluble alkali sulfates.

(iii) Removal of sulfates through off-gas. By operating the melter under reducing instead of oxidizing conditions sulfates can be reduced to sulfites which are then expelled as SO_2 into the off-gas system. Above about 1450°C the alkali sulfates are volatilized which would be another approach to sulfate removal via the off-gas system.

(iv) Treat the sulfate phase and recycle the contaminants back to the vitrification process to produce a vitreous waste form and a clean sulfate material.

(v) Use a melting process, such as the Duramelter system, that can accommodate low-conductivity melts which then permits the use of alkali-free feed formulations. The waste form produced is then a fine dispersion of a calcium sulfate phase in a glassy matrix; such materials were shown to have good leach resistance.

We conducted a number of sludge-washing experiments which confirmed our suspicions that (i) is not a viable approach since most of the sulfate is present as the relatively insoluble calcium sulfate. Leaching measurements on the various sulfate phases indicated that the solubility of those phases increases as more sodium is added to the vitrification feed, since sodium tends to accumulate in the sulfate phase as the highly soluble sodium sulfate. Alternatives (iv) and (v) appear to be the most promising process approaches at present. In one version of alternative (iv), the sulfate phase would be dissolved, the sulfates precipitated as calcium sulfate, and the solution containing residual contaminants would be recycled to the vitrification feed stream. A potential problem here might be coprecipitation of hazardous and radioactive components. In a second version, after dissolution the sulfate solution would be subjected to ion exchange to remove residual contaminants to produce a non-hazardous solution. If Duratek's Durasil® glass ion exchange media were used, the spent contaminated media could be recycled to the vitrification feed stream. The result of either of these approaches would be that the hazardous and radioactive contaminants would be concentrated essentially exclusively in the highly leach resistant glass waste form. Alternative (v) relies on the ability to process low-conductivity melts and the stable suspension that is produced (since sedimentation of a solid phase during processing can lead to clogging of the melter over protracted periods of operation); the leach resistance of such a waste form does not seem to be a problem.

Depending on the process option selected it seems likely that both the sulfates and fluorides will impose an upper processing temperature limit to prevent excessive accumulation in the off-gas system. The processing range selected for these studies was 1100-1500°C, but the lower end of this range is probably most appropriate for these materials.

3.2 Oak Ridge

3.2.1 Soil Preparation and Characterization

The soil required for testing in this program was supplied in two 55-gallon drums. Unfortunately, upon opening the drums, mercury vapors were identified as a significant health and safety issue. In the previous testing (Grant et al., 1991) on soil from the same site, the mercury vapors were not a significant problem. In the previous sample, the mercury was in the form of a mercury-uranium crystalline compound, which had a very low volatility. The presence of mercury vapors resulted in the need to minimize the exposure of personnel to the soil, and to contain the material, particularly when it was dry. This resulted in much longer testing times than originally anticipated. Also, as will be discussed, the relatively high volatility of the mercury resulted in the need to modify the remediation approach.

Grab samples were taken from the drums to generate some initial characterization data. Bulk density, moisture content, and particle size distribution data were determined for the material. The bulk density of the material is between 1.53 and 1.63 g/ml, and the moisture content is approximately 1.3%. The particle size and contaminant distribution is given in Table 3-15.

The data shows that 90 wt.% of the soil is greater than 300 microns, which contains less than 25% of the uranium and about 55% of the mercury. By segregating the minus 200 micron fraction, the uranium level is reduced from 580 ppm to 150 ppm, and the mercury is reduced from 1150 to less than 700 ppm. Segregation of the minus 300 micron size fraction is thus an effective means to reduce the contaminant level in a majority of the soil. However, both contaminant levels in the plus 300 micron size fraction are still above the targeted remediation levels: uranium (as U-238) < 90 ppm and mercury < 12 ppm. Further processing of the larger size fraction is thus still required. Note that the previous testing on this soil type had shown that segregation of the fines resulted in an acceptable uranium level, and thus only additional mobilization of the mercury was required. In this earlier study, the mercury was removed from the soil using sodium hypochlorite. The soil sample tested here required mobilizing both uranium and mercury. Note that while uranium extraction was not originally planned for this study, it was demonstrated in batch extraction tests.

The effect of attrition scrubbing on the soil size and contaminant distribution was also examined here. Attrition scrubbing is an effective means to remove contaminated fines from the surface of larger particles. These results given in Table 3-16 show that, while there was little effect on the uranium distribution, the fraction of the mercury contamination in the fines increased. The mercury contamination is thus present to a greater degree on the surface of the soil and is associated with the fine particulates, which adhere to the surface of larger particles. Attrition scrubbing improves the segregation by particle size of the mercury contamination.

In order to provide representative samples for bench scale testing and manageable samples for subsequent pilot scale testing, it was necessary to remove the soil from the drums and blend it into samples of usable size. The soil was removed from the drums and then sieved to remove the plus 0.25 inch material and the minus 250 micron material. Each size fraction was placed into separate 5-gallon buckets. The large soil fraction was removed because the size analysis had shown that this fraction was not significantly contaminated and because the pilot scale equipment to be used to wash this soil can not handle material greater than 0.25 inch in size. The results of the sieving performed on both of the drums is given in Table 3-17. The weight and contaminant distribution is essentially identical to that achieved with the small grab samples.

Table 3-15
Wet Sieve Analysis on Oak Ridge Sewer Sediment

Particle Size		Wt.	Cum. Wt.	U	Hg	Fraction of Total Contamination	
Mesh	Microns	Fraction	Fraction	ppm	ppm	U	Hg
> 10	>1920	0.47	0.47	50	260	0.04	0.11
20<<10	840<<1920	0.07	0.54	292	370	0.04	0.07
50<<20	297<<840	0.36	0.90	250	694	0.16	0.37
100<<50	149<<297	0.03	0.94	4724	755	0.27	0.07
200<<100	74<<149	0.02	0.96	7491	819	0.21	0.07
325<<200	44<<74	0.01	0.97	4781	899	0.10	0.07
<325	<44	0.04	1.00	3068	1142	0.18	0.25

Table 3-16
Soil and Contaminant Distribution after Attrition Scrubbing

Particle Size		Wt.	Cum. Wt.	U	Hg	Fraction of Total Contamination	
Mesh	Microns	Fraction	Fraction	ppm	ppm	U	Hg
>10	>1920	0.47	0.47	50	260	0.06	0.07
20<<10	840<<1920	0.07	0.54	279	643	0.03	0.03
50<<20	297<<840	0.37	0.91	264	1440	0.23	0.31
<50	149<<297	0.09	1.00	3009	10463	0.67	0.59

Table 3-17
Sieve Analysis of Entire Contents of Two 55-Gallon Drums

Particle Size		Wt.	Cum. Wt.	U	Hg	Fraction of Total Contamination	
Mesh	Microns	Fraction	Fraction	ppm	ppm	U	Hg
>2	>5200	0.24	0.24	50	50	0.02	0.01
60<<2	250<<5200	0.69	0.93	515	904	0.63	0.52
<60	<250	0.07	1.00	3000	8731	0.35	0.48

3.2.2 Bench Scale Tests

3.2.2.1 Extraction Tests

The initial bench scale tests were performed to verify the mercury extraction results which were generated on the previously tested soil sample from Oak Ridge (Grant et al., 1991). The previous testing had shown that sodium hypochlorite adjusted to pH 6 was an effective extractant. Unfortunately, the low pH results in the generation of chlorine gas, which posed a significant health and safety problem. Testing was thus conducted here to determine the effect of both sodium hypochlorite concentration and pH. The testing was conducted on the soil fraction less than 0.25 inch and greater than 250 microns in size. This is the size fraction that would be aggressively washed in the actual soil washing system. Note that the procedures followed have been successfully used to scale the soil washing system to a 20 ton/hour process.

The results of the mercury extraction tests are given in Table 3-18 and shown graphically in Figure 3-9. The results show that the mercury removal increases with increasing sodium hypochlorite concentration (in the range of 5 to 20 g/l) and with decreasing pH (in the range of pH 9 to 6). Using 10 to 20 g/l sodium hypochlorite at a pH of 6, 80% of the mercury can be removed from the soil. At 20 g/l, the pH can be maintained at pH 8 and the solution still removes 76% of the mercury. To minimize chlorine off-gassing problems, the mercury extraction was carried out at a sodium hypochlorite concentration of 20 g/l and pH 8. Note that even with 80% of the mercury removed, the residual mercury level is still much higher than the required level. However, previous testing has shown that, as expected, the remaining mercury is not mobile and the soil is non-hazardous as determined by the EPA's Toxicity Characteristic Leaching Procedure (TCLP).

Although not originally planned for this study, uranium extraction tests were also performed because the characterization data on this soil had shown that size segregation alone would not be sufficient to achieve the desired uranium level (90 ppm). The uranium extraction results, summarized in Table 3-19, show that a combination of sodium hypochlorite and sodium carbonate is required to mobilize the uranium. Neither agent alone solubilizes any significant

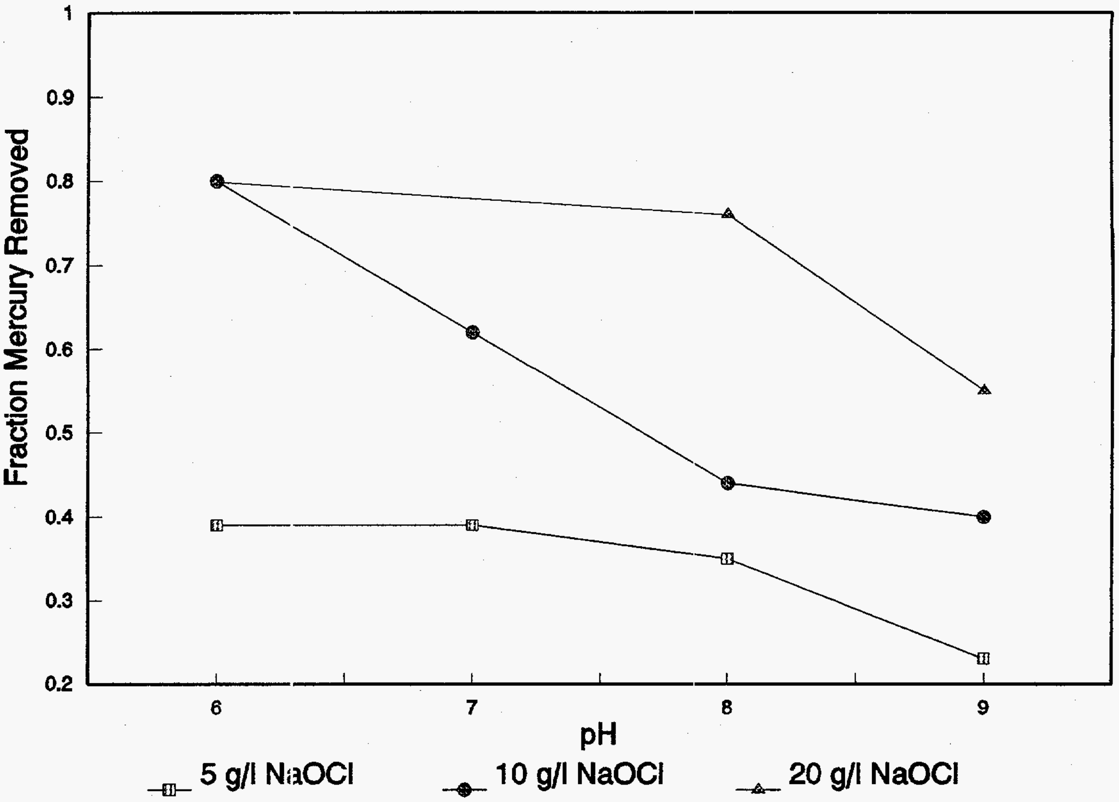


Figure 3-9 Mercury removal improves with increasing NaOCl and decreasing pH.

amount of uranium. The hypochlorite is required to oxidize the uranium to the soluble plus six state and the carbonate is required to complex the oxidized uranium into the soluble uranyl carbonate species. Note that the hypochlorite was used here because the previous testing (Grant et al., 1991) had shown that it was required for mercury extraction. For the oxidation of uranium, other reagents, such as hydrogen peroxide or dissolved oxygen that do not have the corrosion problems of chlorine, could also be used for oxidation of uranium.

Using 20 g/l sodium hypochlorite and 21 g/l sodium carbonate, a total of 47% of the uranium was removed. Based on the contaminant distribution data given in Table 3-15 and 3-16, it can be shown that by segregating the minus 300 micron material and by removing 47% of the uranium from the remaining soil, an average uranium level of less than 90 ppm in the plus 300 micron material will be achieved, thus meeting the remediation requirement.

Table 3-18
Mercury Extraction Results

NaOCl g/l	pH	%Hg Removed	Final Hg Level, ppm
5	6	39%	550
5	7	39%	550
5	8	35%	580
5	9	23%	690
10	6	80%	180
10	7	62%	340
10	8	44%	505
10	9	40%	540
20	6	80%	190
20	7	---	---
20	8	76%	220
20	9	55%	400

Table 3-19
Uranium Extraction Results

Extraction Chemistry	Uranium % Removed	Residual U Level, ppm
Contact #1: 20 g/l NaOCl	1.7	506
Contact #2: 21 g/l Na_2CO_3	45	286
21 g/l Na_2CO_3	3.7	496
10 g/l NaOCl + 10.5 g/l Na_2CO_3	29	365

3.2.2.2 Solution Processing

In the soil washing process, it is essential that the mobilized contaminants be removed from the extraction solution, so that the extraction solution can be reused, and the contaminants can be effectively concentrated. Precipitation tests were thus conducted to confirm the ability of ferrous sulfate to remove mercury and uranium from solution. The results of precipitation testing on a combined uranium and mercury extraction solution are summarized in Table 3-20. The data shows that ferrous sulfate is an effective precipitation/coprecipitation agent for the removal of uranium and mercury from solution. The residual solution level for both contaminants was less than 1 ppm.

Table 3-20
Extractant Solution Treatment
Ferrous Sulfate Precipitation

Contaminant	Initial Level, ppm	Final Level, ppm	% Removed
Mercury	141	<1 ppm	> 99%
Uranium	62	<1 ppm	> 98%

In addition to the need to be highly concentrated in contaminants, the precipitated solids produced must also be readily separable from the decontaminated extraction solution. The fine precipitated solids did not settle rapidly (>1 hour) and were not readily filterable. Flocculation tests were thus conducted to improve the separation obtainable. Using a polyacrylamide polymer, the solids settled rapidly (<1 minute) and were easily separated from the solution.

3.2.2.3 Thermal Desorption

While the soil can be effectively washed to produce a non-radioactive, and non-hazardous (as defined by the TCLP) material, the process does not produce a material with the desired mercury level (12 ppm). Due to the high mercury volatility of the soil sample tested here, an option for achieving lower mercury levels is thermal desorption. In addition to soil washing, Westinghouse has also successfully developed and demonstrated the use of thermal desorption as a remediation technique. A preliminary test was thus performed here to evaluate this approach.

A sample of the highly contaminated fines was tested in the laboratory thermal desorption apparatus shown schematically in Figure 3-10. This laboratory has been used to generate data for the successful scale-up of a 10 ton per hour thermal desorption system, and thus the data generated is valid for establishing the potential for successfully implementing the approach on a much larger scale.

The testing was conducted on the highly contaminated fines to provide data on a worse-case basis. That is, the fines have much higher levels of contamination, and the highly surface

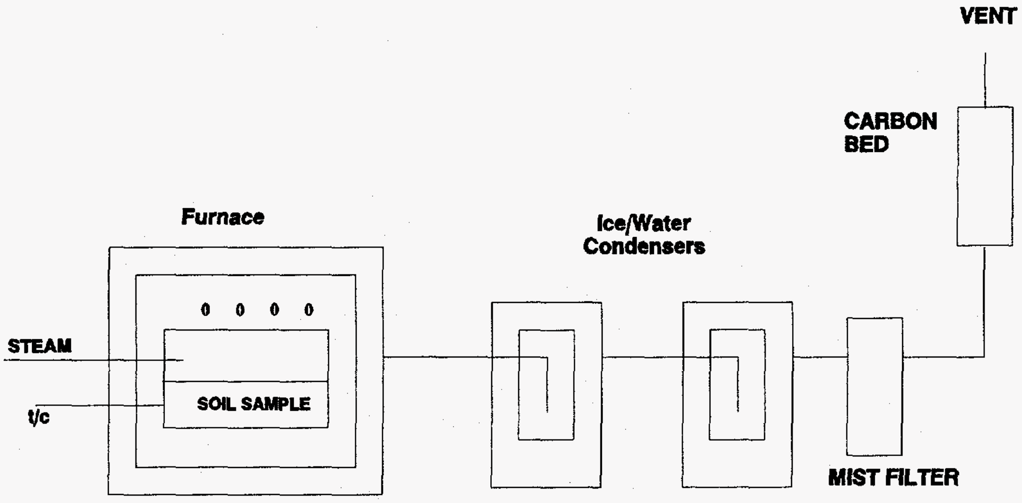


Figure 3-10 Flow diagram of bench scale thermal desorption system.

active fines will hold the contamination more tenaciously. The higher levels of contamination are important both from the standpoint of determining the remediation level of mercury achievable, and in determining what uranium contamination in the off-gas stream can be expected. The contamination of the off-gas with uranium, which will occur by particulate carryover, is not desired because it results in mixed waste rather than just a mercury waste, or more preferably, a mercury product. The high uranium levels and the fine particle size of the material being treated will again provide data on the most demanding conditions for the process.

The results of the thermal desorption testing performed are summarized in Table 3-21. The results show that greater than 99.7% of the mercury was removed from the soil, while no detectable uranium was removed. Visually, elemental mercury (i.e. a bead of mercury) was recovered in the off-gas condenser, with no uranium. A mercury product, rather than a waste, is thus recovered in this process.

Table 3-21
Thermal Desorption of Mercury from Sewer Sediment

Initial Soil Contaminant Levels		Final Soil Contaminant Levels		% Removal	
Hg, ppm	U, ppm	Hg, ppm	U, ppm	Hg	U
8750	5000	23	5000	>99.7%	0%

The required 12 ppm was not obtained with the contaminated fines treated. However, it can be projected that with the inclusion of the coarser soil fraction, which experience has shown should be more amenable to thermal treatment, the remediation level will be readily met. That is, given the ability to achieve 23 ppm in the fine fraction, to meet the 12 ppm requirement for the entire soil, the mercury level in the coarse fraction (700 ppm) must be reduced to 10 ppm. This is a 98.5% removal, which should be readily achieved. Thermal desorption can thus achieve the desired mercury level in the soil.

The effect of the thermal processing on the mobility of the uranium and mercury which remained in the soil was also examined. The results of extraction testing performed on the thermally treated soil are summarized in Table 3-22. The results show that a combination of sodium hypochlorite and sodium carbonate is still required to mobilize the uranium. The remaining mercury was not mobile in any of the extractants tested, and thus does not pose any environmental hazard. In addition, the ability to now mobilize only the uranium allows the uranium and mercury to be successfully segregated.

Table 3-22
Extraction of Thermally Desorbed Soils

Extraction Chemistry	U % Removal	Hg % Removal
20 g/l NaOCl	15%	0
20 g/l NaOCl + 21 g/l Na_2CO_3	23%	0
21 g/l Na_2CO_3	0.4%	0

3.2.3 Pilot-Scale Tests

3.2.3.1 Soil Washing

Pilot-scale soil wash testing was performed to generate the amount of concentrates required for subsequent vitrification studies. The system used is shown schematically in Figure 3-11. The key components of the system consist of an attrition scrubber and a mineral jig. The attrition scrubber serves to provide intimate contacting of the soil with the extractant solution, and to remove fines from the surface of soil particles by causing particle to particle interaction. The mineral jig is not used here in the conventional manner; that is, it is not used as a density separating device. But rather, it is operated in a countercurrent rinsing device to displace contaminated extractant from clean soil. By proper selection of operating conditions (i.e., jig bedding material, upflow rate, and stoke length), the large clean particles pass through the bed of the jig and the fine contaminated fraction and contaminated extractant are carried over the top. As the coarse material passes through the bed of the jig, further scrubbing of the large particles occurs.

In the process, the highly contaminated fine fraction (<250 microns) was first removed from the soil by screening. The coarse fraction was fed into the attrition scrubber along with the extraction solution. To maintain aggressive scrubbing conditions, the soil to extractant ratio is maintained as low as possible. The slurry is discharged from the scrubber into the mineral jig. The clean soil is discharged form the bottom of the jig, and the contaminated extractant and any additional contaminated fines are discharged in the jig overflow. The overflow is treated

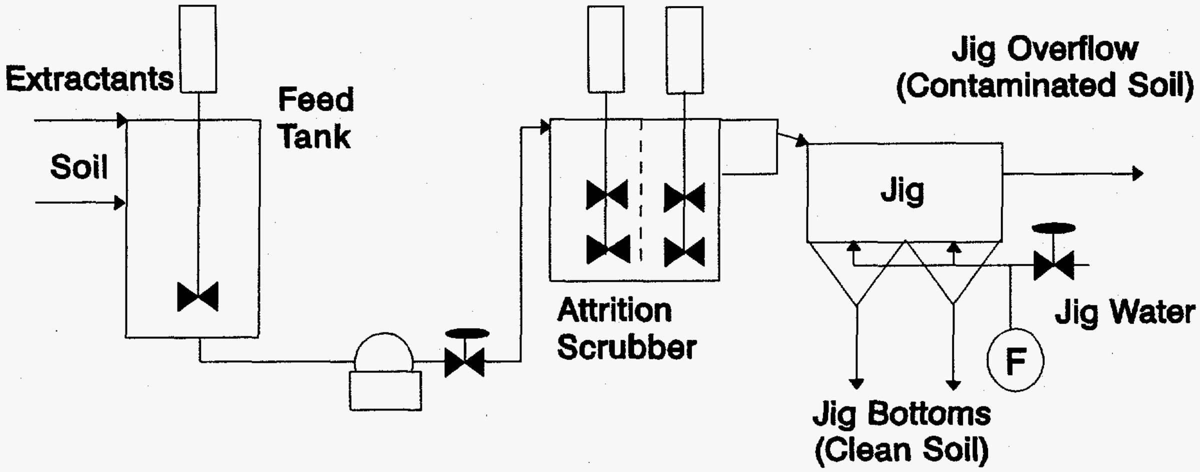


Figure 3-11. Schematic of soil washing process.

by precipitation and flocculation to concentrate the contaminants.

The conditions used in the pilot-scale testing are summarized in Table 3-23. The extractant used (20 g/l sodium hypochlorite, pH 8) targeted mercury removal, which the previous study (Grant et al., 199) had shown would be required. As noted above, the particular soil sample tested here also required uranium extraction, which was not performed in the pilot scale testing. The subsequent bench-scale testing conducted showed the uranium removal could have been accomplished using a carbonate extraction. Subsequent testing should use a combination of hypochlorite and carbonate to insure that the desired uranium levels have been achieved.

Table 3-23
Pilot-Scale Soil Washing Operating Conditions

Extraction Chemistry:	20 g/l Sodium hypochlorite, pH 8
Extractant to Soil Weight Ratio:	1.2
Contact Time:	2-3 minutes
Soil Processing Rate:	1700 lb/hr
Jig Upflow Rate:	3 GPM

The material and contaminant balances generated are summarized in Table 3-24. The soil mass balance shows that only 80% of the soil feed is recovered in the output streams (i.e., overflow and bottoms) from the mineral jig. This is due to some of the soil feed remaining in the attrition scrubber. While the attrition scrubber was filled with soil and extractant just prior to the start of the feed streams, a sample of the slurry in the attrition scrubber showed it mistakenly contained 20 wt.% solids rather than the desired 50 wt.% solids. Thus, during the initial part of the run (~ 2-3 minutes), the slurry being discharged to, and recovered from, the mineral jig contained much lower solid levels than the slurry being fed into the system. This accounts for the lower solids recovery in the system.

Table 3-24
Mass and Contaminant Balances on Soil Washing Pilot Test

Stream	Solid Balance, lb		Contaminant Levels, ppm		U Balance, g		Hg Balance, g	
	Input	Output	Hg	U	Input*	Output	Input**	Output
Soil Feed	200		904	515	36.3		63.7	
Jig Bottoms		147	208	400		26.7		13.9
Jig Overflow Solids		11	481	497		2.5		2.5
Jig Overflow Solutions		158	167	62	36.3	14.9		40.1
Totals:	200	158				44.1	63.7	56.6
% Recovered				79%	121%		89%	

* Based on 158 lb soil input

** Jig Overflow Solution: 539 lb collected

The contaminant balances on the process show a 90% recovery for the mercury. The low recovery is likely due in part to mercury adhering to the surface of the equipment. The mercury level reached in the soil (~ 200 ppm) was the same as that achieved in the batch extraction tests.

The uranium recovery was 120%. The uranium level in the extraction solution was much higher than expected using just a sodium hypochlorite extractant. That is, the batch extraction tests had shown that the sodium hypochlorite alone would mobilize only about 2%. The analysis of the jig overflow solution indicates that over 40% of the uranium was extracted. It is not clear why the removal was much greater in the pilot-scale test. The higher uranium recovery in the contaminant balance would indicate that perhaps the uranium extraction was actually lower than indicated. Sampling or analytical problems or the presence of contaminated fines in the solution, may have given the appearance of higher than the actual uranium solution level. The uranium level in the soil product (~ 400 ppm) was lower than that projected by the batch extraction tests (500 ppm). The inclusion of contaminated fines with the extraction solution, rather than with the soil, would account for this lower soil product level.

The process generates two waste streams for subsequent vitrification studies: the highly contaminated fines (~ 7 wt.%) and the precipitated solids generated from the clean-up of the extraction solution (~ 7 wt.%). The total waste stream is thus projected to be 14 wt.% of the initial soil weight.

3.2.3.2 Thermal Desorption

While the original intent of this program was to vitrify the concentrates from the soil washing process, it was projected that the high mercury content of the concentrates would make successful vitrification extremely difficult. As noted previously, thermal desorption offers the means to segregate the mercury contamination and generate no mixed waste. Utilizing the available laboratory thermal unit, four batch tests were conducted on the contaminated fine fraction to generate mercury-free, high-uranium contaminated soil for subsequent vitrification studies.

The thermal desorption conditions followed were based on the previously conducted test. In each test, 300 g of soil was heated until the temperature of the soil reached 950°F. The results, summarized in Table 3-25, again show that a mercury level of less than 30 ppm is achieved with thermal desorption. The slightly higher mercury level obtained in these tests is likely due to the greater amount of material tested here. That is, a thinner soil layer and/or longer residence time would have resulted in lower contaminant levels. The product soil generated here was used in subsequent vitrification studies.

Table 3-25
Thermal Desorption Test Results

Soil Temperature:	950°F
Total Initial Soil Weight:	1200 g
Total Final Soil Weight:	1114 g
Initial Mercury Level:	8750 ppm
Final Mercury Level:	28 ppm
Total Mercury Recovered in Off-Gas:	10.6 g

3.2.4 Results of Vitrification Study

Approximately 1 kg of the soil-washing contaminant-enriched fraction that had been treated by thermal desorption was shipped from Westinghouse to VSL for vitrification studies. The amount was smaller than had been planned but the need for thermal desorption had not been anticipated. A small sample of the material was dried for four hours at 1100°C and the weight loss of the soil was determined to be about 14%, (86% solids). The dried soil was then dissolved and analyzed by DCP; the results are shown in Table 3-26. The total organic carbon (TOC) content of a sample of the as-received material was also measured. The average of six measurements indicated that there was only about 1% TOC present in the soil.

Table 3-26
Chemical Analysis of the Washed Oak Ridge Soil after Thermal Desorption Followed by Drying at 1150°C

Oxide	Wt.%
Al_2O_3	10.35
B_2O_3	0.05
BaO	0.48
CaO	14.0
Cr_2O_3	0.04
Fe_2O_3	7.69
K_2O	2.36
Li_2O	0.13
MgO	4.14
MnO_2	0.30
Na_2O	0.29
NiO	0.17
P_2O_5	0.3
SiO_2	57.87
SrO	0.02
TiO_2	0.66
U_3O_8	1.1
ZrO_2	0.05

Three small (50 g) test melts (ANL1G-1, ANL1G-2, ANL1G-3) were made in order to obtain qualitative information on melting temperatures, melt viscosity, and glass crystallinity prior to determining the compositions for larger melts. The approximately 900 g of soil remaining was divided evenly between three larger glass melts to provide sufficient glass for detailed testing. The target compositions of all six of these glasses are shown in Table 3-27a; Table 3-27b shows the analyzed compositions of the three glasses that were produced in larger quantities. The formulations used for the three glasses subjected to detailed testing are summarized in Table 3-28. The conductivity and viscosity of the Oak Ridge glasses were measured at five temperatures to span the range of likely processing parameters. The results of these measurements are shown in Tables 3-29 and 3-30. While only a small number of melts could be made due to the small amount of material available these results clearly indicate that glasses with acceptable viscosity and conductivity can be formulated with high waste loadings. All of the glasses produced were good glassy materials with no indication of crystallization.

Table 3-31 presents the results of TCLP testing of these glasses. As expected, all of the glasses pass this test by a wide margin. Figure 3-12 shows the normalized leachate concentrations obtained after 7 days of PCT testing. As with the Weldon Spring glasses discussed in Section 3.2, all of these glasses exhibit leach resistance that compares very favorably with that of high-level nuclear waste glasses.

Together these data suggest that processable, high-waste loading glasses that exhibit excellent leach resistance can be formulated for the soil washing concentrates from the Oak Ridge material once the mercury has been removed by thermal desorption.

Table 3-27a
Target Compositions of Oak Ridge Glasses (wt %)

	ANL1G-1	ANL1G-2	ANL1G-3	ANL1G-4	ANL1G-5	ANL1G-6
Al_2O_3	9.31	8.28	9.02	8.28	7.63	9.02
B_2O_3	0.05	0.04	2.68	0.04	5.31	2.67
BaO	0.43	0.38	0.42	0.38	0.35	0.42
CaO	12.59	11.20	12.20	11.20	10.31	12.20
Cr_2O_3	0.03	0.03	0.03	0.03	0.03	0.03
Fe_2O_3	6.92	6.15	6.70	6.15	5.67	6.70
K_2O	2.12	1.89	2.06	1.89	1.74	2.06
Li_2O	0.12	0.10	0.11	0.10	0.10	0.11
MgO	3.72	3.31	3.60	3.31	3.05	3.60
MnO_2	0.27	0.24	0.27	0.24	0.22	0.27
Na_2O	10.31	20.25	10.48	20.25	21.27	10.48
NiO	0.15	0.13	0.14	0.13	0.12	0.14
P_2O_5	0.26	0.24	0.26	0.24	0.22	0.26
SiO_2	52.06	46.29	50.43	46.29	42.64	50.43
SrO	0.02	0.02	0.02	0.02	0.02	0.02
TiO_2	0.59	0.53	0.58	0.53	0.49	0.58
U_3O_8	0.99	0.88	0.96	0.88	0.81	0.96
ZrO_2	0.05	0.04	0.05	0.04	0.04	0.05
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00

Table 3-27b
Results from Chemical Analysis of Oak Ridge Glasses (wt %)

	ANL1G-4	ANL1G-5	ANL1G-6
Al_2O_3	9.13	8.04	8.98
B_2O_3	0.39	5.36	2.77
BaO	0.41	0.36	0.40
CaO	11.23	9.81	12.03
Cr_2O_3	0.25	0.20	0.24
Fe_2O_3	6.97	6.07	6.80
K_2O	2.07	1.85	2.08
Li_2O	0.12	0.10	0.11
MgO	3.63	3.06	3.54
MnO_2	0.26	0.23	0.27
Na_2O	19.06	19.74	10.07
NiO	0.16	0.12	0.19
P_2O_5	0.21	0.20	0.20
SiO_2	43.34	42.58	50.33
SrO	0.02	0.02	0.02
TiO_2	0.53	0.48	0.56
U_3O_8	0.96	0.86	0.96
ZrO_2	0.06	0.05	0.06
TOTAL	98.78	99.13	99.61

Table 3-28
Composition of Oak Ridge Glasses

Glass	Composition (wt %)
ANL1G-4	80% soil + 20% Na_2O
ANL1G-5	75% soil + 20% Na_2O + 5% B_2O_3
ANL1G-6	87.5% soil + 10% Na_2O + 2.5% B_2O_3

Table 3-29
Viscosity (Poise) of Glasses Produced from Soil Washed and Thermally Desorbed Oak Ridge Waste

Temperature, °C	ANL1G-4	ANL1G-5	ANL1G-6
950	989	223	3770
1000	470	115	1420
1050	240	65.7	626
1100	130	40.5	312
1150	74.6	26.7	171
1200	44.7	18.5	101
1250	27.9	13.4	63.8
1300	18.1	10	42.4
1350	12.1	7.73	29.5

Table 3-30
Electrical Conductivity (S/cm) of Glasses Produced from Soil Washed and Thermally Desorbed Oak Ridge Waste

Temperature, °C	ANL1G-4	ANL1G-5	ANL1G-6
950	0.135	0.225	0.000
1000	0.217	0.282	0.004
1050	0.289	0.346	0.021
1100	0.348	0.416	0.048
1150	0.399	0.493	0.080
1200	0.441	0.576	0.118

Table 3-31
Result of TCLP Tests for the Oak Ridge Glasses (ppm)

Element	ANL1G-4	ANL1G-5	ANL1G-6	EPA Limit
As	0.6	0.2	0.5	5.0
Ag	0.01	0.01	0.01	5.0
Pb	0.3	0.43	0	5.0
Ba	1.69	1.78	0.26	100.0
Cr	0.03	0.03	0.01	5.0
Cd	0.003	0	0	1.0
Hg	0	0	0	0.2
Se	0	0	0	1.0

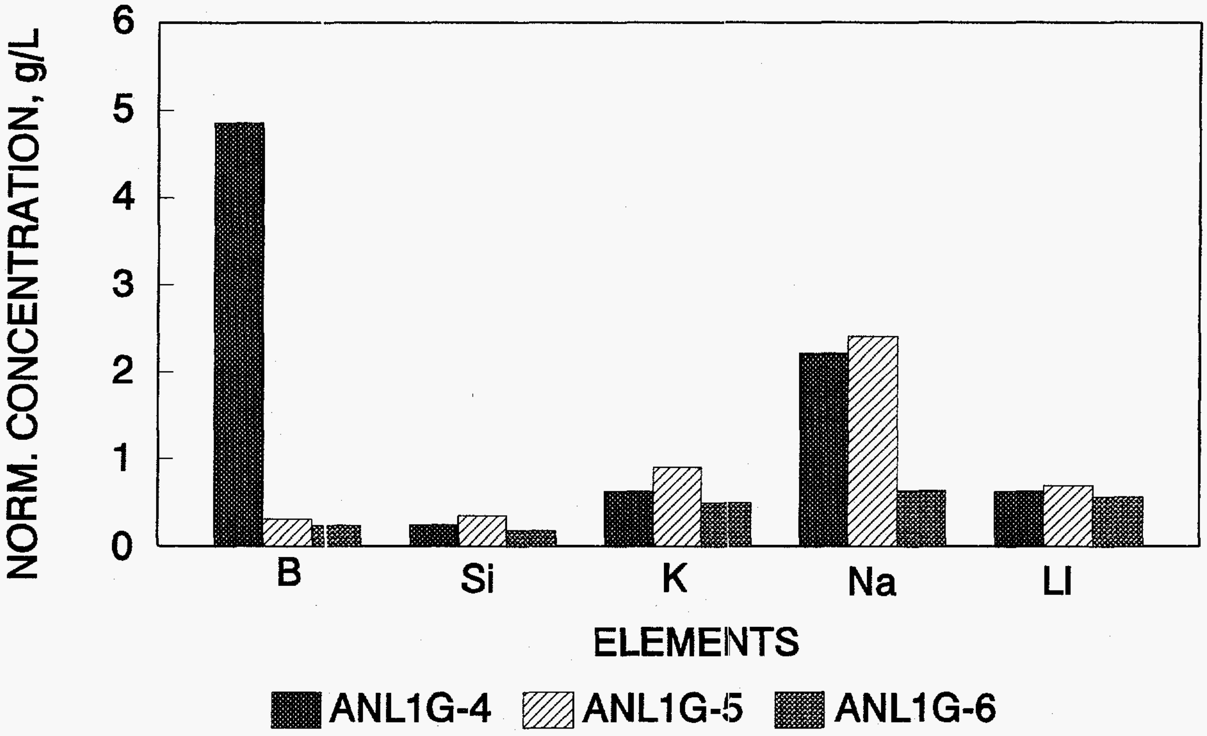


Figure 3-12. Results from 7-day PCT leach testing of Oak Ridge Glasses.

3.2.5 Conceptual Process Design

The process required to effectively decontaminate the uranium/mercury contaminated soil is shown in Figure 3-13. The process presented combines thermal desorption with soil washing, which results in the elimination of all mixed waste, the production of a relatively pure mercury stream, a concentrated uranium stream suitable for vitrification, and the recovery of 90% of the soil as clean.

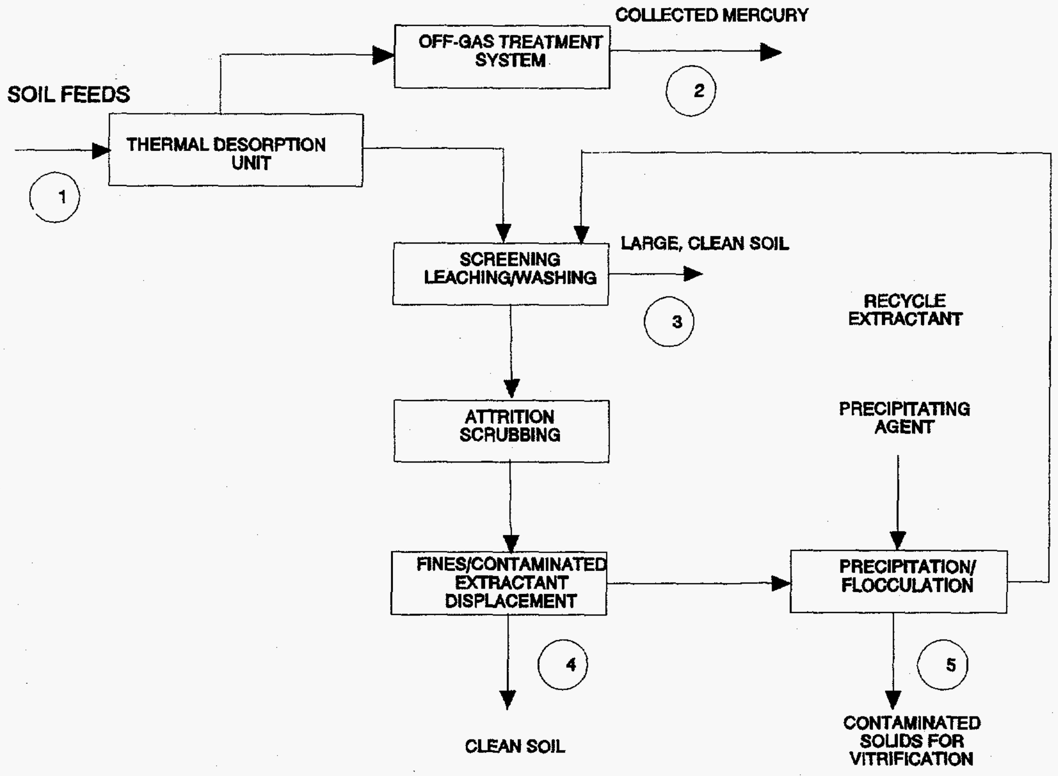


Figure 3-13. **Schematic of thermal desorption/soil washing/vitrification process for treatment of Oak Ridge mercury/uranium contaminated soil.**

The projected material balance on the process, which assumes a 10 ton/hour soil feed rate, is given in Table 3-32. In the process, all of the contaminated soil was fed into the thermal desorption system, which removes essentially all of the mercury. Based on the testing conducted here, it is projected that 99.7% of the mercury will be removed. The mercury is condensed and collected from the off-gas stream as elemental mercury. Assuming a mercury level in the feed of 1150 ppm, then approximately 23 lbs (10.5 kg) of mercury will be recovered per hour. To minimize remediation costs, potential uses for this stream should be explored.

Table 3-32
Material Balance on Thermal Desorption/Soil Washing Processing of Uranium/Mercury Contaminated Soil

Stream No.	Description	Rate lb/hr	Uranium ppm	Mercury ppm
1	Soil Feed	20,000	580	1150
2	Desorbed Mercury	23	0	1×10^6
3	Soil > 2000 microns	9,400	27	< 12
4	300 microns < Soil < 200 microns	8,600	136	< 12
5	Contaminated Fines and precipitates	2,800	3630	< 30

The thermally treated soil, which now contains less than 5 ppm mercury, is fed into the soil washing system to remove the uranium. Experience has shown that the larger size soil fraction (>2000 microns) can be readily cleaned (with extractant, if necessary), rinsed, and removed from the system. The smaller size soil fraction must be more aggressively scrubbed and contacted with extractant. The clean soil is then separated from the highly contaminated fines (<300 microns) and the contaminated extractant. The contaminated extractant is decontaminated by precipitation, and then reused. The precipitated contaminants are collected with the fine fraction by flocculation and settling.

Based on the tests conducted in this study approximately 47% of the uranium can be mobilized by chemical extraction in a single contact. With this degree of removal, the uranium level in the combined soil product streams (i.e., all soil greater than 300 microns in size) will contain less than 80 ppm, which is below the required level (~90 ppm). The soil produced will thus no longer be a radioactive or hazardous material. Note that due to the variability in the characteristics of the soil that has been experienced in the two studies conducted, additional testing on soil from several different containers is recommended to verify the ability to achieve the desired uranium removal.

The uranium waste stream in this process will be produced at a rate of 1.4 tons of solids/hour (i.e., 14 wt.% of the soil feed). This high uranium (>3500 ppm), low mercury (<30 ppm), relatively high volume stream is an ideal candidate for volume reduction by vitrification. Treatment of this stream by vitrification would require a melter system with a production capability of about 40 tons/day assuming an 80% waste loading; this is a mid-sized melter system. The combined treatment system of these specifications could process about 70,000 tons of waste annually assuming 80% operating time.

Figure 3-14 shows a flow diagram for this multiple technology system for treatment of the Oak Ridge materials with estimates of the treatment costs. An ion exchange process was substituted for ferrous sulfate precipitation in this conceptual process in order to permit feeding of all contaminant streams into the melter without introducing sulfates. A typical range of treatment costs is used for each process and, using the estimated flows along each stream, the contribution to the overall cost is estimated. Thus, a rough estimate yields very reasonable treatment costs of about $260-420/ton of waste processed with this integrated system.

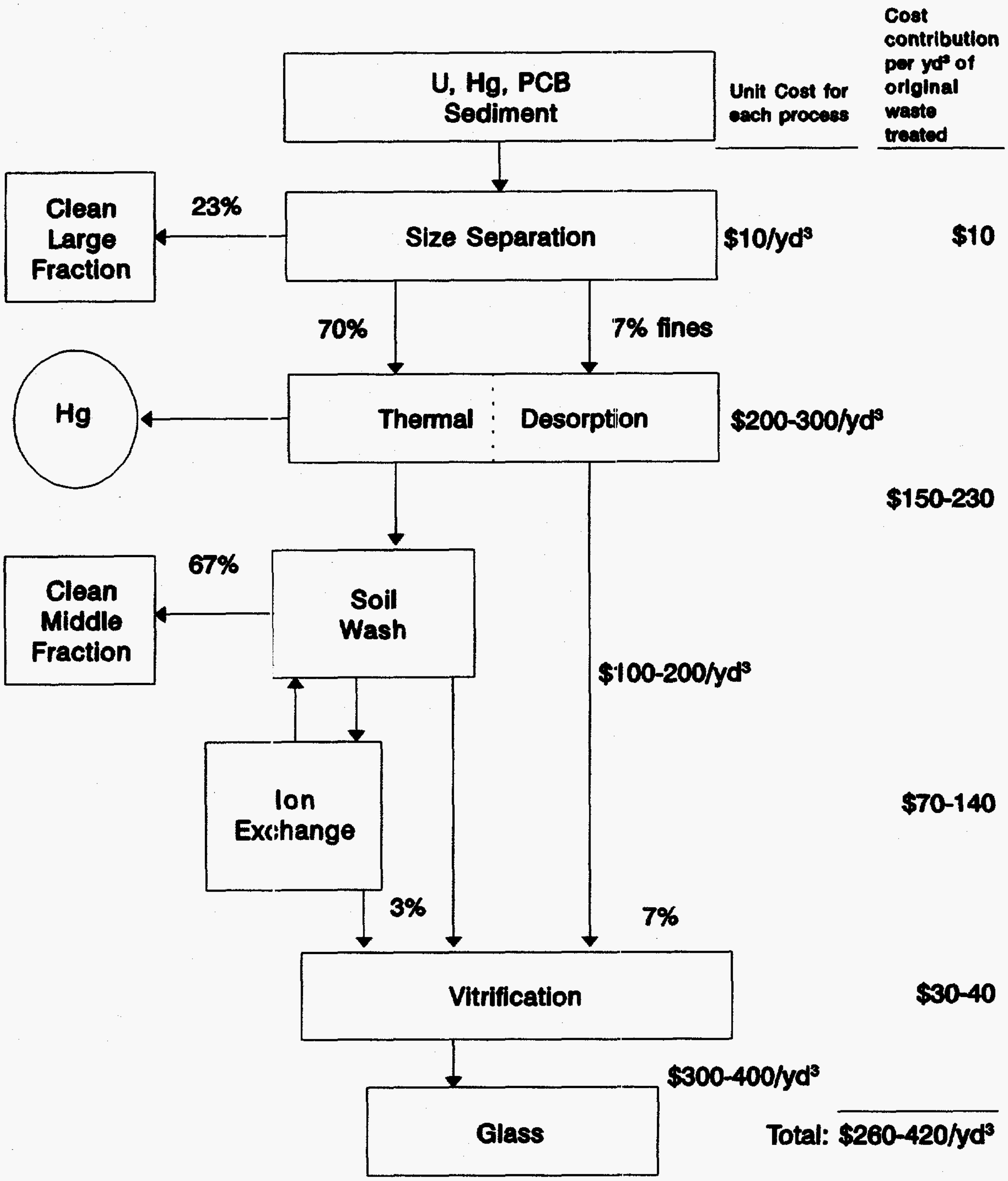


Figure 3-14. Conceptual process for Y-12 storm sewer sediment treatment.

4.0 TECHNOLOGY STATUS

4.1 Technology Development Evaluation

From a vitrification perspective, waste streams can be broadly classified on a spectrum of *silica-rich* to *flux-rich*; these extremes have opposite effects on melt temperature and viscosity. In many site remediation situations, the total waste mix is dominated by the silica-rich components due mainly to the very large volumes of contaminated soils that are frequently present.

Several options are then available. One is to increase the processing temperature, as is the case with many plasma torch systems. The drawback here is increased off-gas problems due to volatilization of hazardous (e.g. As, Se, Cd, etc) or radioactive species (e.g. Cs, Pu, Tc, etc) with the result that these species are not completely retained in the final waste form. A second option is to reduce the required processing temperature by introducing fluxing additives (e.g. soda ash). The disadvantages here are that the additives (a) must be purchased and (b) diminish the overall volume reduction factors that can be achieved.

The combined soil wash - vitrification system that has been under development under this program takes an alternative approach. Soil washing is used on the high-silica fraction of the waste stream which includes contaminated soils and sediments. In this way the contaminants can be concentrated in a minority fraction leaving the major fraction decontaminated. For the Oak Ridge Y-12 sediments used in this study volume reductions of up to 90% have been demonstrated at this stage. Larger volume reductions may be possible with some contaminated soils. An interesting development of this study was recognition of the need for and demonstration of the application of the introduction of a third technology - thermal desorption - to remove the mercury from the soil washing contaminant-enriched fraction to produce a waste stream suitable for stabilization by vitrification. The further important innovation is to recognize that raffinate sludges, such as those from the Weldon Spring site, are generally low in silica and high in calcium, magnesium, and fluorides and therefore offer the possibility of playing the role of fluxes if appropriate blending schemes and glass composition formulations can be developed. This combined-technology approach therefore offers the potential of large volume reduction factors, reduced need for chemical additives, and all of the advantages of an extremely leach resistant glass waste form.

Samples of soils and raffinate sludges from the Weldon Spring site have been extensively characterized in this study. An important finding was that previous analyses of the raffinate sludges grossly underestimated anion concentrations (especially sulfates and fluorides), a result that impacts both of the present baseline technologies (vitrification and cementation) at Weldon Spring. The characterization data have been used to formulate a range of soil-sludge blends that have been vitrified with and without additives. The resulting glasses show excellent leach resistance: all pass the EPA TCLP test and most show performance comparable with high-level nuclear waste glasses using the SRL PCT leach procedure. Melt viscosities and electrical conductivities have been determined over a range of temperatures since these are critical processing parameters. Raffinate sludge loadings of up to 70% with 30% site soil (i.e. zero additives) produce melts with acceptable viscosities for processing at temperatures that are low enough (about 1150°C) to keep off-gas problems to a minimum. Due to the low alkali contents of these melts their electrical conductivities are lower than would be needed for direct application of existing joule-heated ceramic melter technology (JHCM) such as has been developed for the high-level nuclear waste program. However, Duratek's advanced JHCM (Duramelter) is able to process these formulations with little or no additives.

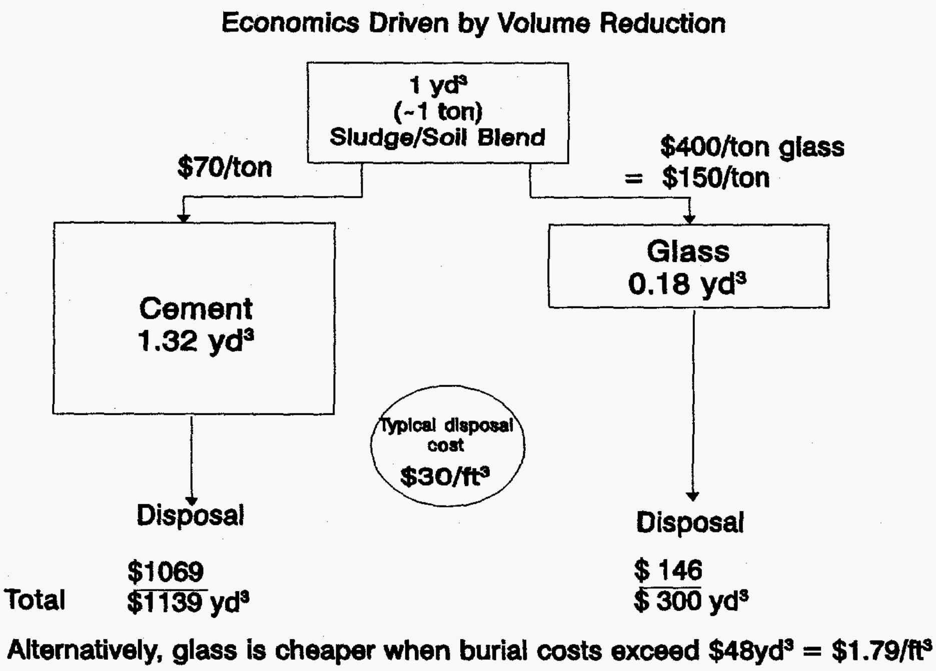
Technologies that produce "enhanced" final waste forms, i.e. those with extremely low leachabilities, are often perceived as expensive with respect to alternatives that produce satisfactory, but often much more leachable waste forms. However, when the volume-based cost of disposal of the final waste form is taken into consideration together with the cost of actual treatment, technologies that produce enhanced final waste forms can actually become economically preferable. As a specific example, vitrification would produce an enhanced waste form whereas solidification by cementation would not. Furthermore, while the unit cost of vitrification is typically a factor of 3-6 times that of cementation, the former process produces a waste form of between about one-fourth to one-seventh the volume of the latter. Thus, when life-cycle costs are considered - that is, the cost of ultimate disposal, as well as the cost of treatment itself - disposal costs can dominate the selection of the most cost-effective treatment technology. The argument is shown schematically in Figure 4-1. For quite conservative unit costs ($400/ton and $70/ton, respectively) and volume reductions (or increases) for vitrification and cementation, a break-even point is reached at disposal costs of about $1.80/ft^3 for the 70% sludge formulation described above; for disposal costs lower than this cementation is cheaper, whereas for disposal costs above this, vitrification is cheaper. A reduction of the unit cost of vitrification to $250/ton reduces this figure to $0.03/ft^3. Note that the volume increase for cementation (quoted by Weldon Spring site personnel) is uncharacteristically small; 50%, or even 100% volume increases on cementation are more typical. This simple, but very fundamental argument does not take into account the additional benefits associated with enhanced waste forms that were discussed above.

The role of the soil washing process is then to reduce a site-wide excess of siliceous material to a quantity that provides a suitable balance with the available fluxing materials (such as raffinate sludges). Soil washing volume reductions of around 80% would be optimal at both the Weldon Spring and Fernald sites; this study suggests that such figures should be easily achievable.

4.2 Technology Integration Evaluation

This study has demonstrated the potential value of integrating multiple technologies (soil washing, thermal desorption, and vitrification) and blending multiple waste streams. The general approach is based on a highly leach resistant and volume-reduced final waste form using vitrification technology. A variety of multi-technology system configurations, such as the one outlined in Figure 3-14, can be developed from this basic philosophy in order to meet site-

Figure 4-1 Comparison of cost of cementation and vitrification based on Weldon Spring formulations. Economics are driven by volume reduction.



specific remediation needs. Simple, but fundamental, economic arguments have been presented to substantiate our contention that such an approach can be cost effective in comparison to what are perceived to be "cheaper" alternatives while in addition yielding a superior waste form in terms of leach resistance and volume reduction.

These innovations have been incorporated into the "Minimum Additive Waste Stabilization" (MAWS) system for laboratory development and on-site demonstration at Fernald. The objective of this program is to demonstrate a system which, through the treatment and blending of multiple waste streams in a multi-technology system, results in a minimum additive stabilization process. The integrated treatment system will fully exploit the chemical nature of individual waste streams. By blending them in the optimum proportions, overall volume reduction of the final waste form can be maximized, and the requirements for additives that would otherwise be necessary for the vitrification process can be minimized. The program relies on the integration of soil washing, ion exchange, and vitrification technologies, all of which individually impart substantial volume reductions. These volume reductions are further enhanced by the synergistic use of their waste products in combination with other waste streams. The end result is an integrated process, centered on stabilization by vitrification, which maximizes volume reduction and minimizes the overall cost of treatment and disposal of multiple waste streams.

The proposed integrated system is especially innovative in that waste streams are viewed as *resources* for the process to be fully exploited, and a "portfolio" approach is adopted to maximize the economic benefits of blending the optimum proportions of multiple waste streams and alternative technologies. The MAWS project began in June 1992 and on-site demonstration at Fernald is expected to commence in mid-1993.

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