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**OPERABLE UNIT 4 TREATABILITY STUDY  
REPORT FOR THE VITRIFICATION OF  
RESIDUES FROM SILOS 1, 2, AND 3  
MAY 1993**

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REPORT**

**OPERABLE UNIT 4 TREATABILITY STUDY REPORT**  
**FOR THE VITRIFICATION OF RESIDUES**  
**FROM SILOS 1, 2, AND 3**

**Fernald Environmental Management Project**  
**Fernald, Ohio**



**May 1993**

Fernald Office  
**U.S. DEPARTMENT OF ENERGY**

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## LIST OF ACRONYMS

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BDAT	Best Demonstrated Available Technology
CEP	Controls for Environmental Pollution
°C	Degrees Celsius
DOE	United States Department of Energy
DOE-FN	United States Department of Energy-Fernald Office
EA	Environmental Assessment
EP	Extraction Procedure
EPA	United States Environmental Protection Agency
FEMP	Fernald Environmental Management Project
FFCA	Federal Facilities Compliance Agreement
FMPC	Feed Materials Production Center
FS	Feasibility Study
g	grams
g/m <sup>2</sup> /day	grams/squaremeter/day
g/cm <sup>3</sup>	grams/cubic centimeter
IC	ion chromatography
ICP	inductively coupled plasma-atomic emission spectroscopy
in.	inches
kg	kilograms
L/min	liters per minute
m <sup>2</sup>	square meter
m <sup>3</sup>	cubic meters
mg/L	milligram/liter
mL	milliliters
mm	millimeters
mR/hr	milliREM/hour
nCi/g	nanoCuries/gram
(ohm•cm) <sup>-1</sup>	inverse ohms centimeter
OU	Operable Unit
Pa•s	pascal seconds
pCi/hr	picoCuries/hour
pCi/L	picoCuries/liter
pCi/g/hr	picoCuries/gram/hour
pCi/m <sup>2</sup> /s	picoCuries/meter <sup>2</sup> /second
PCT	Product Consistency Test
PNL	Pacific Northwest Laboratories
ppm	parts per million
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Program Plan
RI/FS	Remedial Investigation/Feasibility Study
SAP	Sampling and Analysis Plan
TCLP	Toxicity Characteristic Leaching Procedure

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TPD            tons per day  
VOA            Volatile Organic Analytes  
WMCO          Westinghouse Materials Company of Ohio

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## EXECUTIVE SUMMARY

Vitrification tests were carried out in support of the Remedial Investigation/Feasibility Study (RI/FS) process currently underway at the Fernald Environmental Management Project (FEMP). The tests were carried out as specified by the Operable Unit 4 (OU4) Treatability Study Work Plan for the Vitrification of Residues from Silos 1, 2, and 3. The purpose of these tests was to allow the performance of vitrification to be compared to other remediation technologies. The criteria upon which this comparison was to be based were the leachability of the waste form, the waste volume reduction achieved, and the reduction in radon emanation from the waste.

The treatability laboratory received samples of K-65 material from Zones A, B, and C of Silos 1 and 2, as well as samples of a composite material from all zones of Silo 3. Characterization of the physical and chemical properties of the Silo 3 material and the K-65 material from each zone was carried out to provide data for use in developing glass formulations and for use in evaluating the performance of vitrification. A sample of BentoGrout, present in Silos 1 and 2 as a cap over the material to reduce radon emanation, was also received for use in the treatability testing.

The material from each zone of Silos 1 and 2 was combined into a single mixture for use in the vitrification tests. Four different combinations of wastes were investigated. Sequence A considered the K-65 material alone, Sequence B investigated a 50:50 mixture by dry weight of the K-65 material and BentoGrout, Sequence C consisted of the Silo 3 material alone, and Sequence D considered a 70:30 mixture by dry weight of the K-65 and Silo 3 material respectively. The four sequences represent potential waste compositions expected from various retrieval options.

Screening melts of about 100 grams (100 g) each were carried out to investigate different glass formulations (waste plus additives) for each sequence. Two of the screening melts performed for each sequence were tested by the Toxicity Characteristic Leaching Procedure (TCLP) to verify the durability of the formulations.

Eight bench-scale melts of approximately 1000 g each were then performed using the glass formulations chosen for each of the sequences. Duplicate melts of each sequence were performed, and the radon released during vitrification was measured during the first melt from each sequence. Samples of the glass from each of the melts were tested for durability using the TCLP and the Product Consistency Test (PCT). The conductivity and viscosity of the glass from each sequence were measured as a function of temperature. Other measurements on the vitrified waste were also performed (glass density, radon emanation) for use in evaluating the performance of vitrification. Results obtained from these tests are summarized below.

- The composition of the Silo 1 material was essentially uniform throughout all three zones, while variability in the composition of the different zones of Silo 2 was observed for several components (lead, iron, barium). Variability in composition between Silos 1 and 2 was also observed, with the Silo 2 material lower in lead and barium and higher in iron and calcium. Nevertheless, the

material from all zones was sufficiently similar that it could be combined into a single mixture for use in the treatability tests.

- The radon emanation rate from the vitrified K-65 material ranged from 0.01 to 0.06 pCi/m<sup>2</sup>/s, more than two orders of magnitude less than the United States Environmental Protection Agency (EPA) limit of 20 pCi/m<sup>2</sup>/s for radon emanation from uranium mill tailings. The measured radon emanation rate from the glass is approximately equal to the emanation rate from natural building materials such as brick and concrete, even though the radium content of the waste glass is 10<sup>3</sup> to 10<sup>6</sup> times greater than that of natural building materials. A reduction in the radon emanation of about 500,000 times was obtained in the bench-scale vitrification tests.
- Essentially all of the radon initially present in the sample is released during vitrification, providing an upper bound to the expected radon concentration in the off-gas from the vitrification system.
- The final glass product (density from 2.7 to 2.9 g/cm<sup>3</sup>) has a volume of about 32 percent to 50 percent of the initial waste volume, representing a volume reduction of 50 percent to 68 percent.
- The PCT results show the durability of the glasses from all four sequences to be comparable to the durability of glasses developed for high-level waste. The normalized leach rates for the elements considered (K, Na, Si, Li, B, U, Th, Ra-226) ranged from 0.0002 to 0.09 g/m<sup>2</sup>/d. Leaching of radium-226 was one to two orders of magnitude less than the leaching of the major constituents of the glass.
- The vitrified residue from all sequences tested nonhazardous as measured by the TCLP. Previous testing found the untreated K-65 and Silo 3 materials to test hazardous for several metals (lead for K-65; arsenic, cadmium, chromium, and selenium for Silo 3). Lead concentrations in the leachate from the glass were reduced several hundred times relative to the untreated K-65 material, while for the Silo 3 material, arsenic was reduced about 100 times, and cadmium, chromium, and selenium were reduced to less than or near less than detection limits.
- The fractional release of radionuclides from the glass was similar to that of the major constituents of the glass, indicating that selective leaching of radionuclides did not occur.

- Test results show a wide variation in the fractional release of elements from the untreated waste, indicating that different elements are leached from the untreated waste at widely varying rates. Such behavior is thought to result from solubility limitations of some elements in the leachate. The data show that the leachate concentrations of radium-226 from the untreated waste appear to be limited because of the relatively high sulfate concentration in the leachate and the low solubility of radium sulfate, thereby explaining the relatively modest reduction in leaching of the radium achieved by vitrification.
- Further development of the glass formulations during the remedy design phase is necessary. The remedy screening/selection treatability tests described herein demonstrated that the OU4 wastes can be vitrified and that the vitrified product immobilizes the hazardous constituents in the waste. However, only a minimal amount of development of the glass formulations was included in the treatability tests. Further development of the formulations should address issues which arose during the treatability tests (salt layer, reduced metal), processing concerns (viscosity), and potential variability in the waste feed.
- The viscosity and conductivity are within typical processing ranges for all glasses except the Sequence B glass. Further modification of the glass formulation will be required to assure that the Sequence B glass can be processed at a reasonable temperature ( $< 1500^{\circ}\text{C}$ ).
- The formation of a thin salt layer or a small nodule of reduced metal was observed in some of the bench-scale melts, even though the formulations used did not show this behavior in the screening melts. Although this result is not desirable from a processing standpoint, the properties of the glasses which showed this behavior are not expected to differ significantly from the properties of glasses which did not. Therefore, these glasses were used in the treatability tests for determining durability and other properties of the vitrified waste form. Further development of the glass in the remedy design phase must address the issue of avoiding the formation of a salt layer or a reduced metal phase. Results from the 100 g melts indicate that these problems should be able to be resolved through adjustments to the formulations.

## 1.0 INTRODUCTION

The purpose of this report is to document the results of the treatability study conducted in accordance with the "Operable Unit 4 Treatability Study Work Plan for the Vitrification of Residues from Silos 1, 2, and 3" approved by the EPA in April 1992. This report was generated following the guidelines established by the EPA in the "Guide for Conducting Treatability Studies under CERCLA" dated October 1992.

On July 18, 1986, a Federal Facilities Compliance Agreement (FFCA) was jointly signed by the EPA and the United States Department of Energy (DOE) to ensure that environmental impacts associated with past and present activities at the FEMP are thoroughly investigated so that appropriate remedial actions can be assessed and implemented. A RI/FS has been initiated to develop these remedial actions. The FEMP has been segregated into five operable units. Operable Unit 4 consists of four waste storage silos: Silos 1 and 2 (K-65 Silos), Silo 3 (metal oxide silo), the unused Silo 4, and their ancillary structures and the surrounding soils. Operable Unit 4 is located at the western periphery of the site, southwest of the waste pit area.

The purpose of conducting treatability studies is to provide additional information for evaluating remedial process options. The remedial process options being considered for Operable Unit 4 include: cement stabilization; chemical separation; and stabilization by vitrification. The comparisons of the remedial process options will be performed during the detailed analysis of alternatives stage of the Feasibility Study (FS) for Operable Unit 4. The FS for Operable Unit 4 is considering remedial actions for the silo structures, for materials stored in the silos and for contaminants in the surrounding soils, perched water and other structures within the boundary.

### 1.1 SITE DESCRIPTION

#### 1.1.1 Site Name and Location

The FEMP, formerly the Feed Materials Production Center (FMPC), is a contractor-managed federal facility once used for the production of purified uranium metal for the DOE. The FEMP is located on 1050 acres (425 hectares) in a rural area approximately 18 miles (32 kilometers) northwest of downtown Cincinnati, Ohio, and lies on the boundary between Hamilton and Butler counties. Production operations at the FEMP were limited to a fenced in, 136 acre (55-hectare) tract of land, located near the center of the site.

The waste storage silos were constructed to provide storage for the residues resulting from the processing of pitchblende ores and uranium concentrates to extract their uranium content. The silos are large concrete structures which were built in 1951 and 1952. Each of the four domed silos is 80 feet (24.4 meters) in diameter, 36 feet (11 meters) high to the center of the silo dome, and 26.75 feet (8.2 meters) tall to the top of the vertical side walls. The side walls are 8 inch (20 cm) thick concrete wrapped with steel post-tensioning wires. The silo sides are covered with a 0.75 inch (1.9 cm) thick layer of gunite. The dome roofs are made of reinforced concrete and taper from 8 inches (20 cm) thick at the silo walls to 4 inches (10 cm) thick at the dome's center.

### 1.1.2 History of Operations

Silos 1 and 2 were used for the storage of radium-bearing residues which are by-products of uranium ore processing. Silos 1 and 2 received approximately 8000 cubic yards (6117 cubic meters) of residues from 1952 to 1958. Raffinates (residues resulting from uranium solvent extraction) were pumped into the silos as a slurry where the solids would settle. The free liquid was decanted through a series of valves and piping placed at various levels along the height of the silo wall. This procedure, pumping of slurry, followed by the settling and decanting, continued until the waste material was approximately 4 feet (1.2 meters) below the top of the vertical wall. Historic analyses of the K-65 Silo residues indicate that approximately 24,500 lbs (11,200 kg) of uranium (0.71 percent U-235) are present in Silos 1 and 2. Analytical results of residue samples, taken in July 1988, indicated uranium concentrations was 1400 parts per million (ppm) in Silo 1 and 1800 ppm in Silo 2. In addition, the estimated concentration of radium was between 0.13 to 0.21 ppm in the K-65 residues.

Radon and the elements resulting from its decay (referred to as daughter products, or progeny) are the nuclides of concern from a health and environmental perspective. Radon is known to be emanating from the silos via cracks and at structural joints. Radon and its daughter products are relatively mobile and capable of migrating through air and water. Through the RI/FS characterization efforts, it was found that the berms and subsoils contain elevated levels of lead-210 (Pb-210) and polonium-210 (Po-210).

Silos 3 and 4 were constructed in 1952 in a manner similar to Silos 1 and 2; however, the silos were designed to receive dry materials only. Raffinate slurries from refinery operations were dewatered in an evaporator and spray-calcined to produce a dry waste for placement in Silo 3. The material was blown in under pressure to fill Silo 3. Silo 4 was never used and, except for rainwater infiltration, remains empty today.

Silo 3 contains approximately 5200 cubic yards (3900 cubic meters) of calcined residues consisting of silica, uranium 39,500 lbs (18,000 kg), and a very small amount of radium, thorium, and other metal oxides. Silo 3 is not a significant radon source because of the physical and chemical characteristics of its contents. Nevertheless, Silo 3 will be considered a potential hazard because its contents are radioactive and in its dry powdery state susceptible to airborne dispersal if exposed to wind.

### 1.1.3 Prior Removal and Remediation Activities

As part of the Silos 1 and 2 Removal Action, Removal Action Number 4 per the Consent Agreement, a layer of BentoGrout was placed over the K-65 residues in Silos 1 and 2 to attenuate the radon releases to the environment and to reduce the risk of airborne contaminants in the case of a tornado. It is presupposed that the added BentoGrout will be remediated in the same manner as the K-65 material. Data was collected during the bench-scale vitrification Sequence B testing, as defined in the "Operable Unit 4 Treatability Study Work Plan for the

Vitrification of Residues from Silos 1, 2, and 3", to provide information to evaluate the vitrification of the BentoGrout with the K-65 material.

## 1.2 WASTE STREAM DESCRIPTION

### 1.2.1 Silo Residue Characteristics

Several sampling attempts have been conducted that provided data on the waste material contained in Silos 1 and 2 (K-65 material) and Silo 3 (metal oxide). The results of several of these studies and further information on the characterization of the waste within the OU4 boundary can be found in the "Remedial Investigation Report for Operable Unit 4". Also, to verify the composition of the wastes to be vitrified as part of the treatability study, laboratory screening tests included performing chemical and radiochemical analyses on the material provided for the bench-scale vitrification tests. The results of these analyses are listed in Section 4.1 of this report.

### 1.2.2 Constituents of Concern for Operable Unit 4

Chemicals and radionuclides of concern were identified by comparing available characterization data with background data, and these chemicals and radionuclides of concern are illustrated in Table 1.1.

## 1.3 DESCRIPTION OF REMEDIAL TECHNOLOGY

Vitrification is a versatile process that transforms waste solutions, slurries, moist powders, and/or dry solids into a chemically durable glass form. The feed used in the process can be either combustible or noncombustible. Organics are decomposed and oxidized in the melter plenum while the inorganic residue melts into a molten glass pool. The hazardous inorganic constituents actually become part of the chemical structure of the glass, not merely encapsulated in the waste form. As a result, the glass waste form will pass the TCLP as nonhazardous.

The technology was first adapted by Pacific Northwest Laboratories (PNL) for the DOE to transform highly radioactive wastes into a chemically durable glass solid. Reliable equipment and techniques were developed to permit processing of these hazardous wastes essentially without maintenance because the high radiation fields precluded human access to the waste and equipment. Thousands of hours of operating experience in several countries using simulated and radioactive feed have demonstrated the reliability of the ceramic melter for waste processing (Chapman and McElroy, 1989). Application of this technology to a variety of other waste streams is being actively pursued.

Table 1.1. Chemicals and Radionuclides of Concern for OU4

Silo 1 and 2		Silo 3	
Radionuclides	Chemicals	Radionuclides	Chemicals
Actinium-227 (Ac-227)	2-Butanone	Actinium-227 (Ac-227)	2-Nitrophenol
Protactinium-231 (Pa-231)	2-Hexanone	Protactinium-231 (Pa-231)	4-Nitrophenol
Lead-210 (Pb-210)	4,4' DDE	Lead-210 (Pb-210)	Arsenic
Polonium-210 (Po-210)	4,4' DDT	Radium-224 (Ra-224)	Barium
Radium-226 (Ra-226)	4-Methyl-2-pentanone	Radium-226 (Ra-226)	Beryllium
Thorium-228 (Th-228)	Acetone	Radium-228 (Ra-228)	Cadmium
Thorium-230 (Th-230)	Aldrin	Thorium-228 (Th-228)	Chromium
Thorium-232 (Th-232)	Antimony	Thorium-230 (Th-230)	Cobalt
Uranium-234 (U-234)	Aroclor-1248	Thorium-232 (Th-232)	Copper
Uranium-235/236 (U-235/236)	Aroclor-1254	Uranium-234 (U-234)	Lead
Uranium-238 (U-238)	Aroclor-1260	Uranium-235/236 (U-235/236)	Manganese
	Arsenic	Uranium-238 (U-238)	Mercury
	Barium		Nickel
	Benzoic Acid		Selenium
	Beryllium		Silver
	Bis(2 ethylhexyl) phthalate		Thallium
	Boron		Vanadium
	Butanoic Acid, methylester		Zinc
	Cadmium		
	Carbon Tetrachloride		
	Chlorform		
	Chromium		
	Cobalt		
	Copper		
	Cyanide		
	Di-n-butyl phthalate		
	Di-n-octyl phthalate		
	Dieldrin		
	Diethyl phthalate		
	Dimethyl phthalate		
	Endosulfan II		
	Endosulfan I		
	Endrin		
	Fluoranthene		
	Heptachlorepoxyde		
	Lead		
	Mercury		
	Methylene chloride		
	Molybdenum		
	Nickel		
	N-nitroso-di-n-propylamine		
	Phenol		
	Pyrene		
	Selenium		
	Silver		
	Tetrachloroethene		
	Thallium		
	Toluene		
	Total Xylenes		
	Tributylphosphate		
	Vanadium		
	Zinc		

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### 1.3.1 Treatment Process and Scale

The heart of the vitrification system is the melter, a refractory-lined cavity with submerged electrodes. After preheating the cavity and the initial charge, the melt becomes electrically conductive. With an alternating current placed between pairs of electrodes, the molten glass is self-heated. The waste material is mixed with chemical additives as required to achieve suitable product durability or processability. The waste is fed onto the surface of the melt, and molten glass is continuously removed from the melt cavity. The molten glass can be cast into monolithic shapes, formed into smaller shapes, or quenched to a frit. Off-gases containing particulates and other pollutants are removed and treated using conventional air pollution control equipment. Recycle of this stream minimizes secondary wastes.

The scale of operations for the ceramic melter can range from one to hundreds of tons per day (TPD). Pilot-scale systems at the treatability laboratory can process from hundreds of pounds to several TPD. These systems have demonstrated processing of slurry and dry feed solid inorganic wastes. Although larger systems have yet to be demonstrated for hazardous waste processing, experience within the commercial glass industry demonstrates that it is feasible to process on a scale of hundreds of TPD. The throughput of a given melter will depend on both the feed used and the method of feeding. The conceptual design for the OU4 treatment system included a 15 TPD melter with a slurry feed. This same melter with dry feeding could process as much as 60 TPD.

### 1.3.2 Operating Features

The ceramic melter has several features that benefit waste processing. First is the capability to handle a large variety of waste forms. Wastes can be solid, slurry, or liquid. They can be combustible, noncombustible, or a mixture of both. The melter design will remain the same with modification required only in the feed, and possibly the off-gas system.

Second, the melter is useful for treating mixtures of inorganic and organic wastes. The organic contaminants are thermally destroyed at the high processing temperatures (up to 1500°C) while the inorganic contaminants are incorporated into the molten glass. As previously stated, the inorganic contaminants become a part of the chemical structure of the glass; thus, the entire glass structure must be destroyed for the hazardous constituents to be removed from the vitrified waste.

Third, the ceramic melter has a large volume with a corresponding long residence time for the waste glass. This is significant in terms of the consistency of the glass product and the ability to handle variations in the waste stream. Since the residence time of the glass in the melter can range from several hours to several days, variations in the feed stream composition are averaged over a period of days, and the resulting glass product remains very homogeneous with much smaller chemical variation than is present in the feed.

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Fourth, secondary streams can be minimized by recycling the streams to the melter. Particulate carryover from the melter can be removed from the off-gas stream and returned to the melter for processing.

Finally, the vitrification process typically will produce a waste form which is only a fraction of the volume of the initial waste. This volume reduction ranges from 50 percent to 70 percent for soils and inorganic wastes to 99 percent or greater for combustible solids. The reduced volume and the nonleaching characteristic of glass are benefits of the vitrification treatment process.

#### 1.4 PREVIOUS VITRIFICATION LABORATORY TESTING BY PNL IN 1991

In February 1991, the Westinghouse Materials Company of Ohio (WMCO) published the results of FEMP K-65 residue vitrification tests in the Treatability Study report, "Characteristics of Fernald's K-65 Residue Before, During, and After Vitrification." The following is a summary from the report, detailing the background for conducting the vitrification tests, as well as several key findings and results of the tests:

... "Vitrification of radioactive and hazardous wastes have been under thorough investigation since the mid-1950s. During the high-level waste development program, the U.S. Department of Energy accumulated over 40 years of operating experience with the vitrification process (Chapman and McElroy, 1989). Vitrification has endured international scrutiny and is the preferred international treatment method for the most radioactive and hazardous high-level radioactive wastes (DOE/RL-90-27). Other compelling factors support the use of vitrification for treating many types of hazardous and radioactive wastes:

- The EPA has promulgated vitrification as the treatment standard {i.e., best demonstrated available technology (BDAT)} for high-level radioactive mixed waste (Federal Register, June 1, 1991), and a BDAT for arsenic-containing hazardous wastes (Federal Register, ca. May, 1990).
- The glass, formed with, at most, minor chemical additions to the waste, generally tests by the Toxicity Characteristic Leaching Procedure (TCLP) or by the Extraction Procedure (EP) toxicity criteria as nonhazardous.
- Volume reduction for solids is typically greater than 60%.

In a vitrified matrix, the diffusion of gases with atomic radii equal to or greater than krypton (1.03 angstrom) and xenon (1.24 angstrom), such as radon (1.34 angstrom), is nil. Thus, once vitrified, release of radon from the residue will be limited to the modest amount of externally exposed surface area. It has been found that volcanic glass has the highest radon retention ability of the 59 rock samples studied. Based upon these favorable processing and product characteristics, vitrification of the K-65 residue is an environmentally progressive and technically sound option for treating this material.

For the work reported in February 1991, PNL received approximately 15 lbs (7 kilograms) of the K-65 residue from Silo 1 for vitrification tests. The objectives of the tests were to determine the quantity and composition of off-gas evolved during vitrification, the radon emanation rate from both the original K-65 residue and the vitrified product, and the leachability of the vitrified material.

- Vitrified K-65 residue (Specific Gravity = 3.1) has a volume that is 35% of dried, tamped K-65 residue (Specific Gravity = 1.06), a 65% volume reduction.
- The radon emanation flux from the K-65 residue was reduced by more than 33,000 times when vitrified. The flux from the original material was measured to be 1.5 million pCi/hr or 52,400 pCi/m<sup>2</sup>-S, while glass was 48 pCi/hr or 1.56 pCi/m<sup>2</sup>-S (an order of magnitude below the EPA limit of 20 pCi/m<sup>2</sup>-S). We predict that during full-scale processing, the flux may be further reduced by a total factor of up to 90,000 to 2,400,000 because the test crucible had both unmelted material and a coat of glass on the crucible walls. Therefore, the actual surface area exceeded the assumed surface area by a factor of more than 3.
- The off-gas data indicate that for the chemicals present, 99.5 percent to 99.95 percent is retained in the glass. This is typical of results obtained during thousands of hours of melter testing with simulated high-level radioactive waste slurries.
- As measured by the TCLP, the vitrified K-65 residue tests as nonhazardous. The two TCLP heavy metals present in the glass were barium at 4.4 wt% and lead at 9.9 wt%. The leachate concentrations were 0.98 ppm and 0.3 ppm for barium and lead, respectively, which is well below the limits of 100 and 5 ppm for barium and lead. Results from EP toxicity tests for this K-65 residue show a leachate concentration of 0.76 and 630 ppm for barium and lead, respectively. Thus, the vitrified product improved the leach resistance for lead by a factor of over 2000.
- The vitrified product is so durable that it could not be dissolved in a hot mixture of concentrated nitric and hydrofluoric acid by Controls for Environmental Pollution (CEP), Inc., during their analyses of the glass."

Also, the TCLP leachate results from the previous laboratory test for the vitrified K-65 waste are presented in Figure 1.1. The results are well below the established TCLP limits.

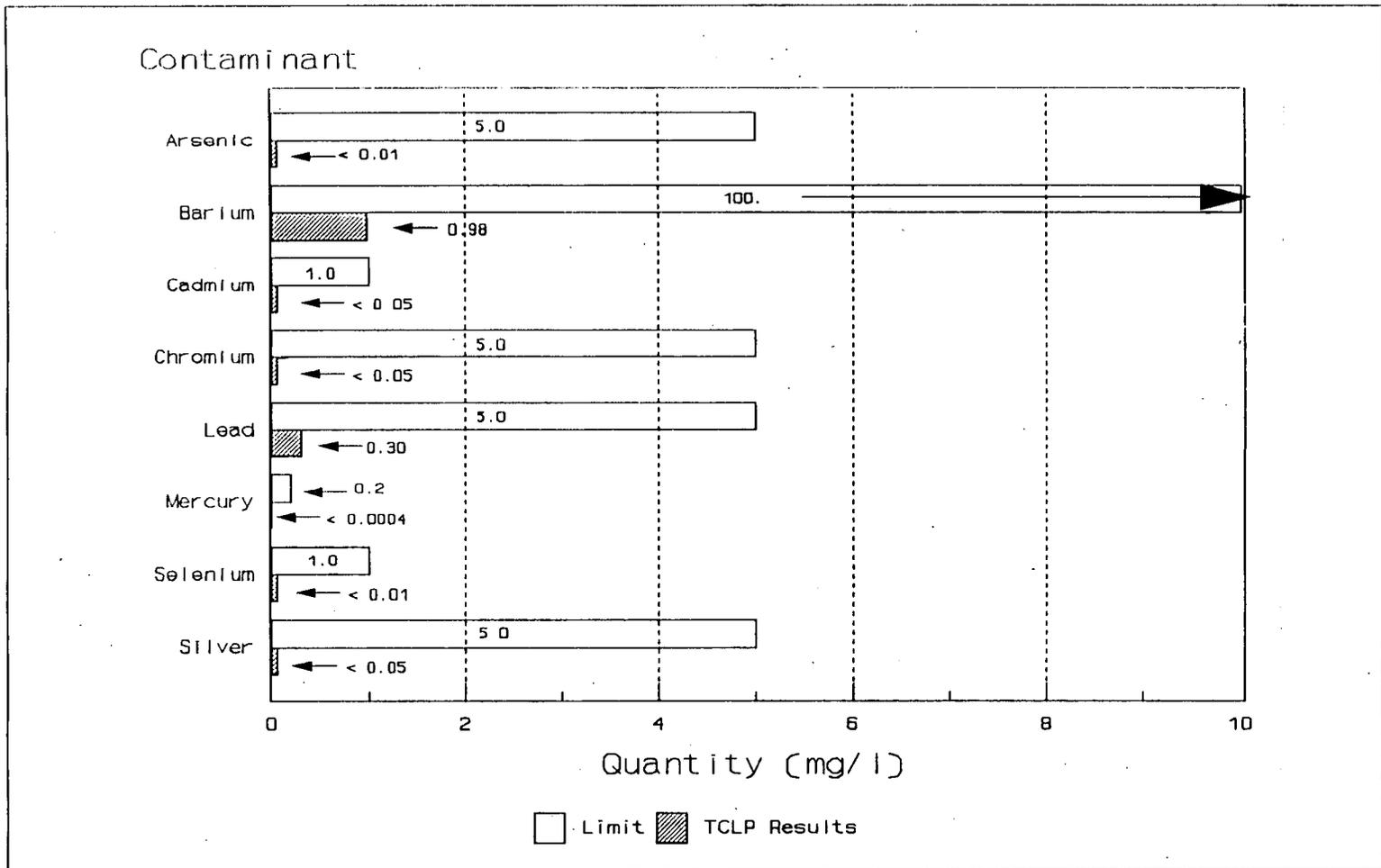


Figure 1.1. 1991 Previous Laboratory Vitrification Tests  
TCLP Leachate Results for Vitriified K-65 Material:  
Concentration of Metals in Leachate

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## 2.0 CONCLUSIONS AND RECOMMENDATIONS

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### 2.1 CONCLUSIONS

The objective of the vitrification treatability tests as described in the Treatability Study Work Plan was to provide data to allow comparison of vitrification to other remediation technologies based upon the criteria of leachability of the final product, reduction in volume achieved through processing, and reduction in radon emanation from the waste material. These data were obtained in the treatability test. Glasses were successfully made from the K-65 and Silo 3 material, both alone and in combination. The vitrified products were tested, and they demonstrated excellent performance based upon the above criteria, despite the minimal glass development which was included in the treatability study. Results of the current testing indicate that further development of the glass formulations during remedy design should be able to address the issues which arose from the current study.

Leach testing of the vitrified K-65 and Silo 3 residues demonstrated the effectiveness of vitrification as a treatment for the OU4 wastes. Results from the PCT showed the durability of the glasses made from the OU4 material to be comparable to the durability of glasses developed for high-level waste (Jantzen et al., 1992; Piepel et al., 1989). The normalized leach rate of radium-226 was one to two orders of magnitude less than the leach rate of major glass components. TCLP results showed that the hazardous constituents of the waste are retained in the vitrified product. All of the glasses tested nonhazardous by the TCLP for metals, whereas the untreated waste had previously tested hazardous for lead from the K-65 material and for arsenic, cadmium, chromium, and selenium from the Silo 3 material.

A comparison of the TCLP leachate concentrations of various radionuclides showed a wide variation in the degree of improvement in leach resistance achieved through vitrification. Values ranged from a several thousand-fold reduction for actinium-227 to a reduction of 10 to 20 times for radium-226 to no change for thorium-230. It was shown for the case of radium that the relatively modest reduction in leaching achieved through vitrification does not result from failure of the glass to contain the radionuclides, but rather, arises as a result of the limited solubility of radium in the leachate from the raw material. The limited solubility of radium in leachate appears to be a result of the high sulfate content of the waste and the low solubility of radium sulfate. The fractional release of radionuclides from the vitrified OU4 residues by the TCLP is about the same as the fractional release of the major glass constituents, demonstrating that radionuclides are not selectively leached from the glasses.

Measurements of the density of the vitrified product and of the initial waste allowed the calculation of the volume reduction achievable through vitrification of the OU4 wastes. For the waste mixtures examined in these tests, volume reductions of 50 percent to 68 percent were achieved. Vitrification was shown to reduce the volume of the waste to less than half of its initial volume.

Radon emanation from the K-65 material is a significant concern. The radon emanation from the untreated K-65 material and from the vitrified products was measured. The measured emanation rates from the glass ranged from 0.009 to 0.059 pCi/m<sup>2</sup>/s, levels two to three orders of magnitude lower than the EPA limit of 20 pCi/m<sup>2</sup>/s for radon emanation from uranium mill tailings. The radon emanation from the glass is actually of the same order of magnitude as emanation rates from natural building materials such as brick or concrete, despite radium concentrations in the glass which are 10<sup>3</sup> to 10<sup>6</sup> times higher. A simple comparison illustrates the degree of reduction in radon emanation achieved through vitrification. The emanation rate from the crucible of material in the open system test of Sequence A was measured to be about 30,000 pCi/m<sup>2</sup>/s, while the measured emanation rate from the vitrified residue from this same test was 0.059 pCi/m<sup>2</sup>/s, a reduction of more than 500,000 times.

In addition to the general objectives of the test, several specific objectives were listed in the Work Plan. These included the physical and chemical characterization of the K-65 and Silo 3 material and measurement of process parameters such as radon release during vitrification and off-gas and condensate composition. The physical and chemical characterization of the waste was used in developing the glass formulations, while the measurement of the radon release during vitrification showed that essentially all the radon in the waste would be liberated during vitrification. The composition of both the off-gas and the off-gas condensate resulting from the vitrification process was determined; however, the off-gas and condensate composition from a batch crucible-melt may not be representative of what would be observed in a continuous system. Further characterization of the off-gas and condensate should be considered during pilot-scale testing as part of the remedy design phase.

Vitrification has been shown to be very effective as a treatment means for the OU4 wastes. The hazardous and radioactive constituents of the waste are retained within the structure of the glass. Radon emanation from the vitrified waste is reduced hundreds of thousands of times relative to the untreated waste. Significant reductions in volume are achieved (i.e., the volume of waste after treatment is up to 68 percent less than the volume before treatment). These benefits have been demonstrated for the vitrified waste form in these treatability tests.

## 2.2 RECOMMENDATIONS

These tests have shown that glass is an effective waste form for the OU4 wastes. Vitrification itself is a well-developed technology; however, validation testing is required when applying this technology to new waste streams. Following are specific recommendations for future work as part of the remedy design phase:

- Development of waste form criteria is needed to evaluate the waste product and guide further glass development.
- Appropriate glass formulations should be developed and acceptable limits of compositional variability of the waste determined.

- Small-scale tests of systems for removal of radon from the off-gas stream are needed to provide data for designing a radon control system for processing operations.
- Pilot-scale testing in a continuous melter should be carried out to validate the glass formulations developed in crucible melts and to provide data necessary for sizing and design of the full-scale system.

Specific performance criteria for the glass waste form are needed to provide a basis by which to judge different glass formulations. Although some criteria were provided by existing regulations (i.e., leachate concentrations of TCLP metals), others were not defined during the treatability phase (i.e., radionuclide concentrations in the leachate). Performance criteria should also specify a maximum leach rate as measured by a leach test appropriate for measuring glass durability.

Further development of the glass formulations will reduce the risk of unexpected occurrences during the pilot-scale testing. The formulations developed in the treatability study are the product of only a minimum amount of glass development, as specified by the Work Plan. Further development should be based upon specific performance criteria as described above, and should also include processing considerations such as glass viscosity and maximum melt temperature. Additionally, the development of the glass formulations must address issues which arose during the treatability testing by preventing the separation of a salt layer or the formation of a reduced metal phase. Acceptable variations in the melter feed composition should also be defined based upon the estimated variability in the waste stream, providing an operating envelope for processing of the waste.

Control of the radon in the off-gas from the melter, as well as retrieval operations, is likely to be a significant concern. Small-scale tests should be designed to test different concepts for removing radon from the off-gas stream and to obtain sufficient data to allow for the design of a system to be used during pilot-scale testing.

Finally, pilot-scale tests will validate the previous work and will provide process data such as specific feed rates, off-gas flows, and condensate and off-gas compositions under actual operating conditions. Validation of the glass formulations under actual processing conditions is important to ensure that at the conditions encountered in the continuous melter, the melt behaves similarly to the bench-scale melts. Processing questions such as slurry versus dry feed and control of off-gas contaminants (including radon) can be investigated and appropriate solutions developed. With the information and the experience derived from the pilot-scale system, a full-scale vitrification treatment system can be designed and operated for the OU4 wastes.

The above recommendations form the basis of remedy design and are part of the logical progression of steps for the application of vitrification technology to the OU4 wastes. Although vitrification of the OU4 residue may be achievable without following all of the steps described

above, following these recommendations will minimize risk and maximize the chances of success. 4796

### 3.0 TREATABILITY STUDY APPROACH

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The purpose of this study as outlined in the Work Plan was to obtain quantitative data for assessing the performance of the vitrification process in support of the RI/FS. The batch crucible melts called for in this study were useful for obtaining performance data for the vitrified product but limited in their ability to provide process data necessary to design a full-scale plant. Therefore, these tests were mainly a demonstration of the applicability of vitrification to the treatment of OU4 waste.

#### 3.1 TEST OBJECTIVES AND RATIONALE

As identified in the Work Plan, the objective of these tests was to compare the performance of vitrification to that of other remediation technologies. The criteria upon which this comparison was to be based were the leachability of the waste form, the volume reduction achieved through vitrification of the waste, and the reduction in radon emanation from the waste. Specific objectives for the tests as identified in the Work Plan are discussed below.

##### 3.1.1 Determine Chemical and Physical Properties of the Wastes

The chemical and physical properties of the K-65 and Silo 3 material were to be measured. This included the cation, anion, and radioisotopic composition; the bulk density; the specific gravity; the radon emanation rate; and the moisture content. Information from the chemical analysis was used in developing appropriate glass formulations for the waste material. Results from the different zones in the silos also provided an estimate of the compositional variability of the wastes. The physical properties of the wastes were used to determine the reduction in volume and radon emanation achieved in the vitrified product.

##### 3.1.2 Develop Glass Formulations for Various Waste Combinations

Significant differences exist in the composition of the K-65 wastes and the Silo 3 wastes. There is also a significant quantity of BentoGrout material in the K-65 silos. Glass formulations (amounts of waste and additives) were developed for four potential waste compositions to demonstrate the ability of vitrification to treat the whole range of potential combinations of wastes from the silos. These compositions were the K-65 and Silo 3 materials alone, a blend of K-65 and Silo 3 material, and a blend of K-65 material and BentoGrout.

##### 3.1.3 Vitrify the Waste at the Kilogram Scale and Analyze the Product

For each of the waste combinations, melts of the scale of 1 kg were performed. The resulting glass was analyzed for leach resistance using the TCLP and PCT. The TCLP was used to measure the ability of the glass to retain hazardous constituents, while the PCT was used to compare the leach rates of the glasses to the existing database of glasses developed in the high-level waste program. The viscosity and conductivity of the glasses were measured as a function of temperature to provide data on the processability of the different glass formulations.

The radon emanation from the vitrified K-65 wastes was measured. The data obtained was compared to the radon emanation from the untreated residue to determine the reduction in radon emanation achieved through vitrification. The emanation rate was also compared with existing regulatory limits.

The specific gravity of the vitrified product was measured to determine the volume reduction achieved through the vitrification process. This calculation also used the data on waste density obtained during the characterization of physical properties of the waste.

#### 3.1.4 Measure the Radon Released During Vitrification

The amount of radon released during the treatment process is of significance in the design of systems to capture the radon and prevent its release to the environment. To design such a system, it is necessary to know the quantity of radon which is released during various steps in the treatment process. Therefore, the amount of radon released during vitrification was measured.

#### 3.1.5 Determine the Composition of the Off-Gas and Condensate

The composition of the off-gas and condensate from the vitrification process is important for determining treatment needs and potential secondary waste streams. The chemical composition of the off-gas and the condensate collected on cooling the off-gas was determined. All the off-gas generated was collected in a closed system and analyzed. The condensate collected on cooling the off-gases was analyzed for various chemical and radiochemical parameters.

### 3.2 EXPERIMENTAL DESIGN AND PROCEDURES

The OU4 vitrification treatability study was divided into two parts. The first part was screening tests, which consisted of determining the physical and chemical properties of the K-65 and Silo 3 materials. The second part consisted of vitrification tests in which various combinations of wastes and additives were melted together into a glass product for analysis. These two parts are described in more detail below.

#### 3.2.1 Laboratory Screening Tests

The laboratory screening tests were performed on the K-65 material from Silos 1 and 2 and the Silo 3 material. The main purpose of these tests was to provide information to assist in developing appropriate glass formulations for the bench-scale tests. Additionally, data from the screening tests was used in calculating the volume reduction and reduction in radon emanation. Details of the data to be obtained are discussed later in the section on sampling and analysis.

The K-65 material to be tested consisted of samples from three different zones ("A," "B," and "C") of both Silos 1 and 2. Screening tests were performed on material from each of the zones of each silo as well as a composite sample from each silo. The composite sample consisted of

equal dry weight mixtures of material from each zone. The screening tests allowed a comparison of the chemical and physical properties among the zones. Procedures used in determining the physical properties are included in Appendix A. Chemical analyses were performed by the treatability laboratory or by a subcontracted laboratory. The data from the chemical analysis identified variability within the silos. The appropriateness of mixing a composite sample of the K-65 material for use in the vitrification tests was determined based on the observed variability in the analyses and its potential effect on glass formation.

Based upon previous analyses, the composition of the Silo 3 material was expected to differ significantly from the composition of the K-65 material. Therefore, the analysis of the Silo 3 material was used in determining the applicability of vitrification to this waste material. This was achieved by comparing the waste composition to known glass compositions and by applying basic principles of glass chemistry. Potential glass formulations were thus identified.

The major use for the data from the screening tests was for the development of appropriate glass formulations. Using basic principles of glass chemistry, known glass compositions, results from the chemical analyses of the waste material, and experience from previous testing, glass formulations were developed for each of the combinations of wastes described in the vitrification testing section below. These formulations were an initial estimate of appropriate glass formulations and served as a starting point for the vitrification tests.

### 3.2.2 Bench-Scale Testing

The bench-scale tests for the remedy selection phase were designed to provide both qualitative and quantitative data so an evaluation of the vitrification treatment option could be performed. The objectives of the vitrification tests were to determine the leachability of the vitrified wastes, the radon emanation rate from the vitrified K-65 material, and the composition of the off-gas generated during vitrification. These objectives were assessed for four different combinations of waste materials as described below.

The Work Plan identified four different combinations of wastes for investigation and titled the four combinations Sequences A through D. Sequence A tests consisted of K-65 material alone, while Sequence B tests consisted of a mixture of 50 weight percent (dry basis) of both K-65 material and BentoGrout. Sequence C tests consisted of the Silo 3 material alone, while the Sequence D tests consisted of a mixture of 70 weight percent K-65 and 30 weight percent Silo 3 material on a dry basis.

Two melts of approximately 1000 g each were performed for each of the sequences. The first melt was performed in an open system with a continuous flow of air through the system to continuously monitor the radon concentration in the off-gas stream. This provided data not only on the total amount of radon released, but also on the release as a function of temperature for the vitrification process. The second melt was a duplicate of the first, except it was carried out in a closed system. The off-gas generated during this melt was collected for analysis. During both of the melts, condensate from the off-gas was collected for analysis.

On completion of the first melt in a sequence, a sample of the glass was analyzed for durability by the TCLP for metals. When it was verified that the glass passed the TCLP, the second melt was performed. After this second melt had also passed the modified TCLP, the remainder of both glasses was prepared for various analyses. These included the TCLP and PCT (performed by an independent laboratory), radon emanation from the vitrified waste, conductivity and viscosity of the glass as a function of temperature, and glass density.

Prior to the Sequence A through D tests, several small melts of approximately 100 g each were carried out. These melts were collectively referred to as the Sequence Zero tests, or the 100 g melts. The purpose of these melts was to perform a preliminary screening of possible glass formulations for Sequences A through D. Up to three 100 g melts were to be performed for each sequence and the resulting glasses analyzed for durability by the TCLP. Based upon the leachability data and the judgment of the experimenters, the most appropriate formulations for use in the Sequence A through D tests were chosen. Selection of the glass formulations was first based upon the results of the TCLP for metals. A glass was required to pass the TCLP for metals, meaning the leachate concentrations of the TCLP metals were less than regulatory limits. Selection was then based on more qualitative criteria as determined from visual observation of the glass and other factors which could impact the applicability of a given glass formulation. Visual observations included the homogeneity of the glass and the absence of secondary phases such as a salt layer or a reduced metal phase. Other considerations included foaming of the glass (since foaming of the glass could damage the furnace and result in insufficient material for analysis) and factors such as the waste loading in the glass. In addition to identifying appropriate formulations, the Sequence Zero tests were used to verify, and modify if required, the methodology for measuring the radon concentration in the off-gas. Table 3.1 summarizes the vitrification tests.

### 3.2.3 Procedures and Test Plan

Procedures specific to the OU4 Vitrification Treatability Study are included in Appendix A. A copy of the test plan developed by the treatability laboratory for carrying out the Work Plan is included in Appendix B. The test plan included a detailed checklist which was followed in carrying out the vitrification tests. This checklist was followed except for the final section describing the measurement of radon emanation from the vitrified waste. Changes required to obtain the desired data are discussed in more detail in Section 3.6 of this report.

### 3.3 EQUIPMENT AND MATERIALS

The experimental system used in the treatability study was custom designed and fabricated to meet the data collection needs specified in the Work Plan. Following is a description of the system, equipment, and materials used in the treatability study tests.

Table 3.1. Summary of Vitrification Tests for OU4 Treatability Testing

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Sequence	Test	Material	Approximate Amount of Dry Material	Description
Zero		K-65 Silo 3 BentoGrout	As required	Small melts of approximately 100 g to 150 g each to develop glass formulations for the Sequence A through D tests and to test the system and operating procedures.
A	Open	K-65	1 kg	K-65 material and glass-forming reagents as determined in the Sequence Zero tests. Radon concentration monitored in the off-gas stream.
A	Closed	K-65	1 kg	Duplicate of open system test. Off-gas collected for analysis.
B	Open	K-65 BentoGrout	0.5 kg 0.5 kg	K-65 material, BentoGrout, and glass-forming reagents as determined in the Sequence Zero tests. Radon concentration monitored in the off-gas stream.
B	Closed	K-65 BentoGrout	0.5 kg 0.5 kg	Duplicate of open system test. Off-gas collected for analysis.
C	Open	Silo 3	1 kg	Silo 3 material and glass-forming reagents as determined in the Sequence Zero tests.
C	Closed	Silo 3	1 kg	Duplicate of open system test. Off-gas collected for analysis.
D	Open	K-65 Silo 3	0.7 kg 0.3 kg	K-65/Silo 3 material and glass-forming reagents as determined in the Sequence Zero tests. Radon concentration monitored in the off-gas stream.
D	Closed	K-65 Silo 3	0.7 kg 0.3 kg	Duplicated of open system test. Off-gas collected for analysis.

### 3.3.1 System Design

Figure 3.1 shows a diagram of the treatability study tests. This figure shows the control system, the furnace, and the off-gas and monitoring system. Figure 3.2 shows a detailed view of the furnace design. The furnace was constructed of multiple layers of refractory insulating board assembled within a stainless steel sheet metal box. The maximum size of the furnace was limited by the size of the hood, and the interior dimensions were limited by the amount of insulation required to keep the exterior of the furnace sufficiently cool. The front plate was attached to the furnace box by clamps, providing a tight seal. Penetrations through the metal shell were provided for control and monitoring thermocouples, air inlet into the furnace, off-gas outflow, and electrical power feedthrough. The furnace was heated by four silicon carbide resistance heaters and was designed for operation at temperatures up to 1500°C. A control cabinet on the bench in front of the hood contained the ramp-and-soak furnace controller, overtemperature controller, chart recorder, and other monitoring equipment.

Air entered the furnace through a tubing line which was open to the atmosphere. A valve in this line allowed the inlet line to be sealed to the atmosphere. The off-gas from the furnace exited through a shell and tube heat exchanger attached directly to the side of the furnace which cooled the off-gas as it exited. Liquid which condensed in the heat exchanger drained into a collection bottle. From the heat exchanger, a number of different flow patterns were possible depending on the position of the valves. The various flow patterns either allowed the off-gas to be collected or routed the flow through the off-gas pump to radon monitors on the bench in front of the hood. After monitoring, the off-gas was returned to the hood and vented.

The bench-scale testing system provided capabilities not present in the previous system. Most significantly, the furnace was capable of higher temperatures, which allowed consideration of a wider range of glass formulations and higher waste loadings. The higher temperature may also be necessary to promote the decomposition of sulfates in the wastes and avoid the formation of a salt layer on the glass surface. The maximum temperature of the previous system was about 1200°C, while the new system was capable of performing melts at temperatures up to 1500°C. The off-gas system was designed to have the flexibility to perform the sampling and monitoring required by the Work Plan.

### 3.3.2 Measuring and Test Equipment

Measurement of radon emanation from the untreated wastes was performed using an Eberline RGM-3 continuous radon monitor. All other radon measurements were made using a Pylon Model AB-5 with either a 300A or 110A Lucas Cell. Calibrations were performed by the respective manufacturers. All thermocouples, recorders, controllers, and flowmeters were calibrated by the on-site calibration services.

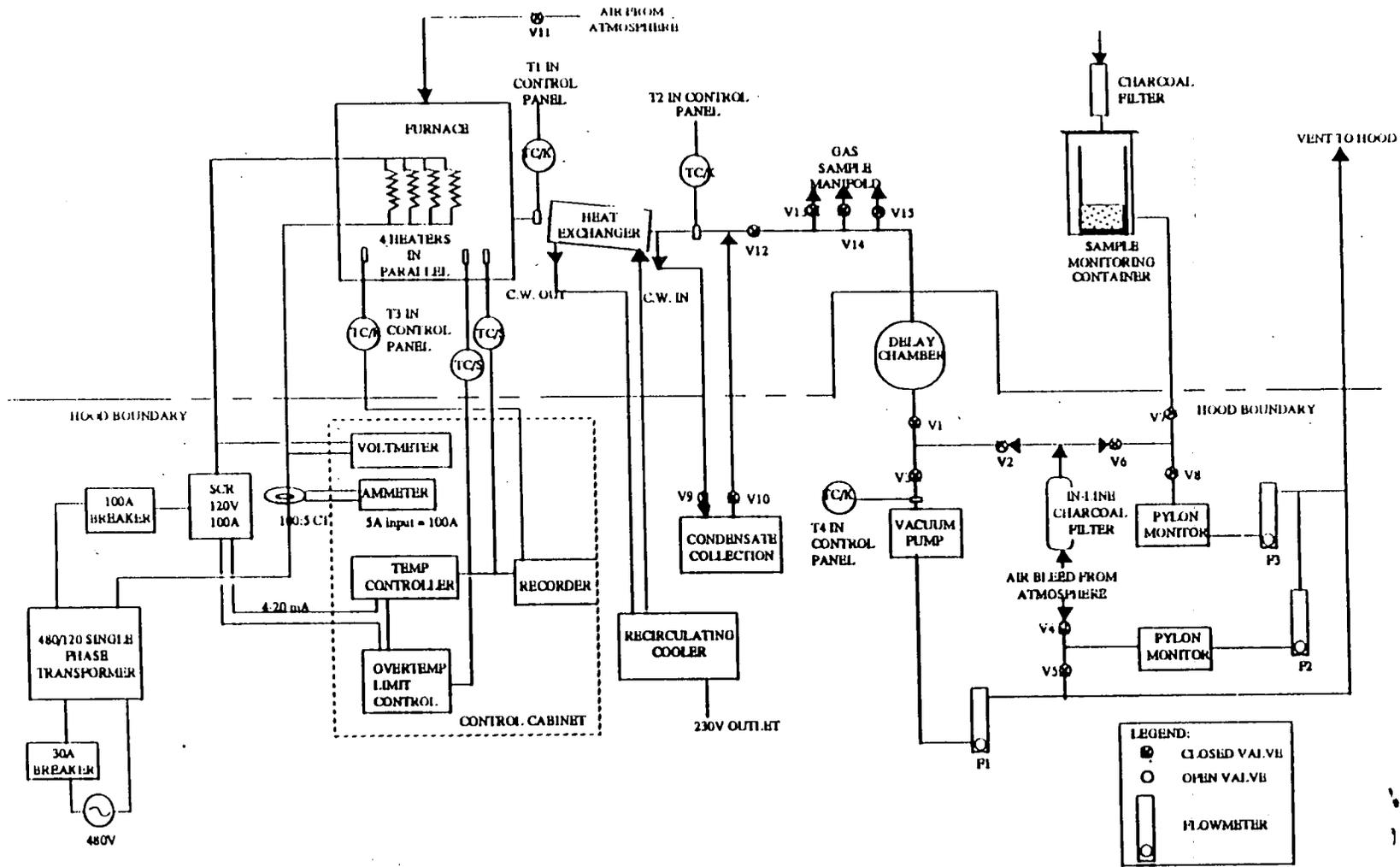
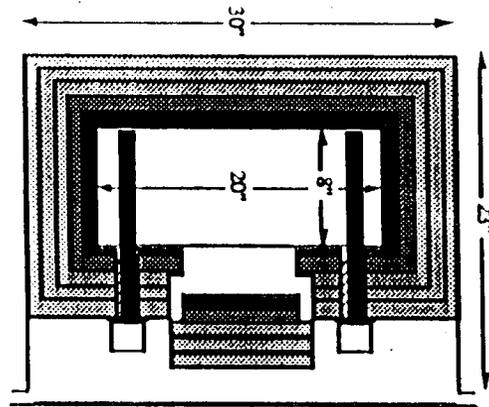


Figure 3.1. Vitrification Treatability Test System

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penetrations:

- A) air inlet
- B) thermocouple
- C) electrical feedthrough
- D) off-gas outlet

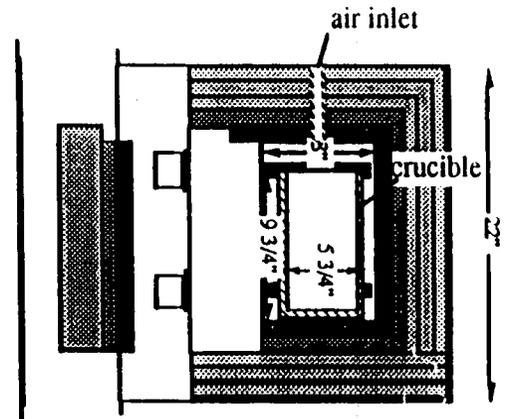
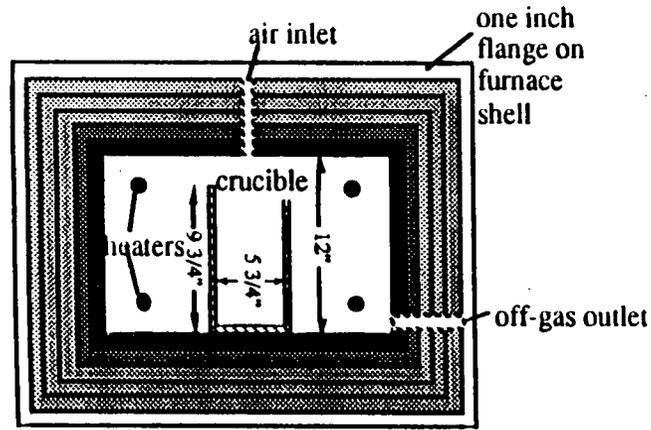
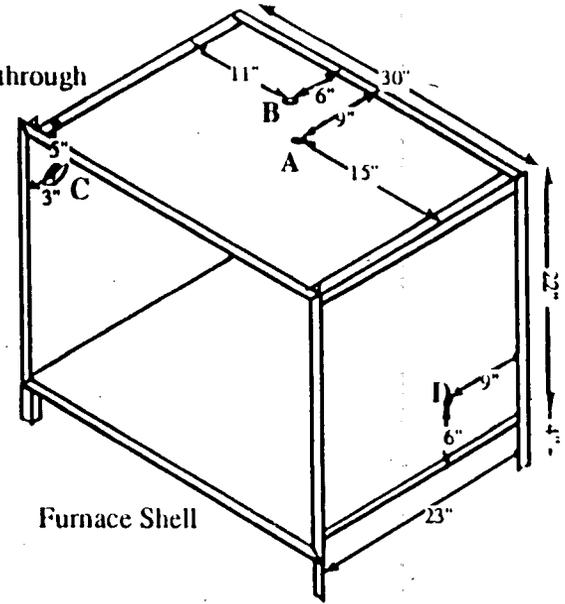


Figure 3.2. Furnace Design for Vitrification Treatability Testing

### 3.3.3 Materials

Waste materials from each of the zones of Silos 1 and 2 were combined and thoroughly mixed after the screening tests to provide a single K-65 waste mix for the vitrification testing. The Silo 3 samples were also thoroughly blended into a single mix. BentoGrout is a product of the American Colloid Company and was used as received. Table 3.2 gives the composition of the BentoGrout reported by the supplier. Glass formulation additives ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{Na}_2\text{CO}_3$ ) were of technical grade. Calgon-activated carbon type 30x140 was used as a reducing agent. Crucibles used in both the 100 g and 1000 g melts were either a porous, high alumina refractory crucible for use up to 1826°C (Ipsen Ceramics, ICOR-1000) or a high silica crucible for use up to 1515°C Denver Fire Clay, Fused Silica (DFC).

Table 3.2. Chemical Composition of the BentoGrout

<u>Component</u>	<u>Weight %</u>
$\text{SiO}_2$	56.20
$\text{Al}_2\text{O}_3$	13.60
CaO	1.53
MgO	5.40
$\text{Na}_2\text{O}$	2.92
$\text{K}_2\text{O}$	0.66
$\text{Fe}_2\text{O}_3$	3.07
$\text{TiO}_2$	0.22
$\text{Mn}_2\text{O}_4$	0.05
$\text{P}_2\text{O}_5$	1.22
Loss on Ignition	14.08
Other	1.05

### 3.4 SAMPLING AND ANALYSIS

The sampling methods for both the waste material and the treatment process are described in this section. The analyses required by the Work Plan as well as the methods to obtain the specified data are described below.

#### 3.4.1 Waste Stream

The sampling and analysis plan for the acquisition of residue samples is contained in the document entitled "Implementation Plan for the K-65 and Metal Oxide Sampling Project at the Feed Materials Production Center, Fernald, Ohio," Addendum-Sampling and Analysis Plan (SAP), October 10, 1990. The waste material used in these tests was shipped to the treatability laboratory in numerous small containers. The K-65 material from each zone was divided into 8 or 16 containers. The Silo 3 material was divided into 34 containers. Screening tests were performed on material from three cans selected at random from each zone. Additionally,

composite samples for Silos 1 and 2 made by combining equal dry weights of material from each zone were analyzed for chemical inorganic composition.

Table 3.3 lists the elements and compounds included in the inorganic analyses. Metals were determined by inductively coupled plasma-atomic emission spectroscopy (ICP) on dilutions of both sodium peroxide and potassium hydroxide fusions of the waste material. Sulfate was calculated assuming the total sulfur from the ICP analyses was present only as sulfate. The difference between the total carbon and the total organic carbon in the total carbon analyses was assumed to be inorganic carbon in the form of carbonate. Nitrate, chloride, and fluoride were determined by ion chromatography (IC) of a deionized water leach of the waste material. Table 3.4 lists the radionuclides screened for in these tests. The radioisotopic screening was performed by gamma energy analysis.

Table 3.3. Inorganic Analyte List for OU4 Waste Material

Aluminum	Iron	Silicon
Barium	Lanthanum	Sodium
Beryllium	Lead	Strontium
Calcium	Magnesium	Sulfate
Carbonate	Manganese	Thorium
Cerium	Molybdenum	Tin
Chloride	Neodymium	Titanium
Chromium	Nickel	Uranium
Cobalt	Nitrate	Vanadium
Copper	Phosphorus	Zinc
Fluoride	Potassium	Zirconium
	Selenium	

Table 3.4. Radionuclide Analyte List for OU4 Waste Material

Actinium-227	Protactinium-231	Thorium-228
Bismuth-214	Radium-223	Thorium-230
Lead-210	Radium-224	Thorium-232
Lead-211	Radium-226	Uranium-234
Lead-214	Radium-228	Uranium-235/236
Polonium-210	Radon-219	Uranium-238

### 3.4.2 Treatment Process

Sampling and analysis during the vitrification process consisted of monitoring the radon concentration in the off-gas, collecting the off-gas for chemical analysis, collecting the condensate from the off-gas, and collecting glass samples from the vitrified product.

#### 3.4.2.1 Radon Monitoring During Vitrification

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During the open system vitrification tests, the concentration of radon in the off-gas was monitored throughout the test. The initial concept for monitoring was to draw a continuous flow of air through the furnace using a vacuum pump. A slip-stream from the off-gas would be drawn through a continuous radon monitor. However, trial runs of the monitoring system during the Sequence Zero tests indicated that the monitoring procedure as initially designed would not perform adequately due to the large and rapid change in radon concentration in the off-gas. The radon measurement is based upon the concentrations of both radon and its daughters and 3.5 hours are required for the daughters to reach equilibrium levels. With a continuously changing radon source, the concentration of daughters never reaches equilibrium in the monitoring cell.

A second problem encountered was the buildup of daughter products in the monitoring cell. The qualitative measurements showed a peak in radon concentration and a rapid initial drop after the peak. A short time after this drop, the monitored concentration took on the shape of a decay curve. It became apparent that even if the radon concentration dropped to zero from the peak value, the daughters present at the peak concentration would remain in the cell for several hours. Therefore, quantitative measurements could not be obtained under the conditions of this test using a continuous measurement.

Since most monitors and monitoring procedures are designed for environmental radon levels and fairly steady concentrations, it became necessary to develop a specialized procedure for this particular situation. The requirements were to be able to measure rapid changes in radon concentration (up to two orders of magnitude in a few hours) and to limit excessive buildup of radon daughters in the monitoring cell. The procedure developed to meet these constraints was a grab-sampling method with a modified counting procedure. The measured gas was kept in the cell for only 4 minutes before being flushed out to limit daughter buildup. Grab sampling allowed data points to be taken every 20 to 30 minutes, which for these tests was sufficient to track the changes in concentration. Details of the procedure are found in Appendix A. Trial measurements using the 4 minute monitoring procedure showed excellent correlation to standard measurements taken after 3.5 hours when the cell was not flushed out after the 4 minute measurement.

#### 3.4.2.2 Off-Gas Collection and Analysis

The Work Plan calls for collection of the off-gas for analysis rather than periodic grab sampling as was done for the radon monitoring. To achieve this, the test furnace was designed so it could be sealed to the atmosphere. Gas sample bags were connected to the outlet of the furnace. As the furnace was heated and as off-gas was evolved during the melt, gases were forced from the furnace and collected in the sample bag. The sample bag was left open for the duration of the melt. Just before shutting off the furnace after holding at the melt temperature, the sample bag was closed to prevent the collected off-gases from being drawn back into the furnace as the

furnace cooled. A small sample was taken for mass spectrometric analysis. The samples were analyzed for CO<sub>2</sub>, Ar, O<sub>2</sub>, N<sub>2</sub>, CO, He, H<sub>2</sub>, CH<sub>4</sub>, NO<sub>x</sub>, and SO<sub>2</sub>.

3.4.2.3 Condensate Collection and Analysis

The condensate obtained from cooling the off-gas was collected for analysis. A shell and tube heat exchanger was used to cool the off-gas immediately upon exiting the furnace. Condensed liquid from each run was collected in a polyethylene bottle and removed and refrigerated at less than 4°C immediately upon completion of the run. A portion of the condensate from each run was transferred to a 40 mL volatile organic analytes (VOA) vial with zero head space, and the vial along with the remaining condensate was shipped in a refrigerated container for analysis. The volumes of condensate collected were much less than that required to carry out the analyses called for in the Work Plan. A few of the analytes which could be determined with the volumes obtained were identified. These included radon, lead, total sulfur, total thorium, total uranium, and gamma spectral analysis. This issue is discussed further in Section 3.6.

3.4.2.4 Glass Sampling and Analysis

After cooling to ambient temperature, the crucible was broken into pieces to remove the glass for analysis. The glass was fractured, removed from the crucible, and divided into the amounts required for the various analyses. In the cases where a salt layer or nodule was formed, these were removed prior to analysis. Although not a desirable outcome from a processing standpoint, the formation of the salt layer or reduced metal nodule observed in some of the melts was not expected to significantly affect the properties of the glass which were being measured; therefore, results from these glasses should be representative of similar glasses resulting from further glass development. In the Sequence C melts, the crucible was corroded somewhat by the melt, and small alumina pieces had spread into the edges of the melt; therefore, glass samples from Sequence C also contained a small fraction of small alumina pieces.

Portions of the glass were sent to various labs to perform the required analyses. The TCLP was performed on about 100 g of glass from each melt, about 300 g were separated for the full TCLP analysis, and about 200 to 450 g of glass were used to perform the PCT and the conductivity and viscosity measurements. The radon emanation measurements used 10 to 20 g of the glass, and the rest of the glass remained attached to the crucible.

3.5 DATA MANAGEMENT

The data from the vitrification treatability study was acquired in accordance with the PNL Vitrification Plan WTC-060 as presented in Appendix C. Laboratory notebooks were used for this project. All laboratory notebooks are uniquely numbered and permanently bound with sequentially numbered pages. The notebook is project specific and assigned to the individuals working on the project. Daily laboratory activities associated with the project were recorded in the project-specific notebook. At the conclusion of the project, the treatability laboratory will provide a records turnover package which contains all raw data generated during the vitrification

project, all calculations performed, plus all documentation specified in the above mentioned Quality Assurance Program Plan (QAPP).

3.6 DEVIATIONS FROM THE WORK PLAN

Inherent in experimental work is the occurrence of unexpected results not foreseen in the planning stages. Nevertheless, the work was successfully carried out with very few deviations from the stated plan. The deviations discussed below deal with the process system, the waste analysis, the condensate analysis, and the procedures included for a few of the measurements.

3.6.1 Process System

The system diagrams included in the Work Plan were initial conceptual ideas of a potential system configuration not the diagrams of the actual system to be used in the treatability study. A part of the treatability study project was to design and fabricate a system that would meet the requirements of the Work Plan. The final system design was significantly different from the initial concepts developed. An example was the use of a shell and tube heat exchanger to cool the off-gas rather than discharging the off-gas underneath the surface of a pool of water. This modification minimized the pressure in the furnace when collecting the off-gas in the closed system, thereby reducing possible leakage from the system. Additionally, during system shakedown and testing, further modifications were required as the actual function of the system was tested. An example of this was the addition of delay chambers into the off-gas system after significant concentrations of radon-220 (thoron) were detected. The inclusion of delay chambers allowed the radon-220 to decay prior to monitoring.

3.6.2 Waste Analysis

The screening tests were carried out as planned with only minor changes in the list of analytes. The Work Plan specifies that the purpose of the chemical analysis data from the screening tests was to assist in the assessment of the feasibility of vitrifying the analyzed wastes. Table 4.1 of the "Operable Unit 4 Treatability Study Work Plan for the Vitrification of Residues from Silos 1, 2, and 3" lists the elements to be determined in the inorganic chemical analysis. Chlorine and fluorine were excluded from this list in our testing. These are not oxide-forming materials and should not have been included in the anion list. Additionally, the anion list in Table 4.2 of the Work Plan included sulfate, sulfide, and sulfite. Only sulfate is reported in the results of this study. Distinguishing between the different states of sulfur would be very difficult since procedures to prepare solid samples for analysis will change the oxidation state of the sulfur. Even if this could be done, the results would not contribute significantly to the stated purpose of assessing the feasibility of vitrifying the wastes.

3.6.3 Condensate Analysis

The Work Plan called for a very large list of analytes for the condensate removed from the off-gas. Since the condensate (or a portion thereof) is potentially a secondary waste stream, this

requirement is reasonable under the proper conditions. However, at the scale of the tests carried out here, the condensate collected was a fraction of that needed to perform the required analyses (100 to 250 mL obtained, 6000 mL required). The analyte list was modified as previously described to reflect the actual volumes collected. It should be realized that the condensate from these treatability tests may not reflect that which is produced in a full-scale melter because of the differences in the systems. The type of off-gas equipment will influence the condensate composition. The off-gas from the batch system used in these tests undergoes very different thermal conditions from those encountered in a continuous system. Additionally, in these tests, the melt surface was exposed completely without any cold cap, leading to increased potential for volatilization. Reliable, quantitative conclusions regarding the condensate or off-gas composition of a continuous melter are not possible using the data collected in these batch tests. The data are useful in providing qualitative information about the condensate and off-gas expected from a full-scale vitrification system.

#### 3.6.4 Procedures

While carrying out the tests, it became necessary to modify some of the procedures included as part of the Work Plan in order to obtain the desired data. Specifically, the procedure for monitoring the radon emanation during vitrification was extensively modified when it was observed that quantitative measurements could not be obtained by following the existing procedure. This was discussed in detail in Section 3.6.3.

Additionally, the procedure for monitoring the radon emanation from the glass was changed. The initial procedure called for monitoring the radon concentration flowing past a sample of the vitrified residue. The radon emanation rate was so low that no significant increase in counts above the background was measurable. Therefore, the procedure was changed to use a closed system in which the radon concentration was allowed to build up to equilibrium (30 days). This method is much more sensitive and allows the measurement of much lower emanation rates. The disadvantage is that 30 days are required to reach equilibrium instead of the few hours required in the open system. This modification allowed the radon emanation from the vitrified waste to be determined successfully.

## 4.0 RESULTS AND DISCUSSION

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### 4.1 SCREENING TESTS

The screening tests provided physical and chemical data on the K-65 and Silo 3 wastes to assist in determining the applicability of vitrification to these waste streams. The results of these tests are presented and discussed below.

#### 4.1.1 Physical Properties

Table 4.1 presents a general description of the waste materials as observed during the screening tests. There are two points of interest. First, no rocks of any kind were found in any of the samples. The K-65 material used during previous testing contained about 20 percent by weight pea-sized rock, which was removed prior to vitrification testing (Janke and Chapman, 1991). It has been suggested that the material used in the previous testing was possibly taken from the top surface of the silos, and as such, may have included debris dumped into the silo after the silo was filled. The rock and other debris found with the K-65 material in previous tests may be only a local phenomena confined to the surface of the waste. The absence of rocks or pebbles of any kind through all zones of the silos supports this hypothesis.

A second point of interest is that visual differences between the zones of Silos 1 and 2 correlated with measured differences in the physical properties. The physical properties of the three zones of Silo 1 are similar except for the moisture content. The measured densities (most notably the specific gravity) are very consistent. On the other hand, the visual observations of the material from Silo 2 showed noticeable differences in color and texture, not only from Silo 1, but also among the zones of Silo 2. The measured densities for Silo 2 also showed more variation, as did the wetting behavior of the material during the measurements.

The measured physical properties determined in the screening tests are reported in Tables 4.1 to 4.3. Measurements were made from three different sample cans for each zone, and the average of the three measurements is reported in the tables. There was some concern that the samples may have dried significantly during shipping and storage; however, estimates based on the reported initial weight of the sample prior to shipping did not show significant loss. The bulk density is reported as either the wet, compacted density or the crushed, dry settled density. The wet, compacted density was determined by packing a known mass of wet material into a graduated cylinder until no further compaction was observed, while the crushed, dry settled density was determined by filling a graduated cylinder with a known mass of dried, crushed material and tapping the cylinder on the bench-top until no further settling was observed. The wet, compacted density is thought to be the most representative estimate of the material density as it is found in the silos; therefore, this value is used to calculate the volume reduction achieved through vitrification of the waste material. Different values for the bulk density are obtained if the measurement is made using another basis, such as wet, uncompacted density or dry, unsettled density. Several other density measurements were made but are not reported here. The specific gravity of the materials represents the actual density of the particles making up the

waste. As previously discussed, differences in the appearance of the material correlate with differences in the measured densities, indicating possible chemical variation in the wastes.

Table 4.1. General Description of the Waste from Silos 1, 2, and 3

<u>Sample</u>	<u>Description</u>
Silo 1 Zone A	The material was grayish brown when wet, pale brown when dry. No rocks of noticeable size were observed. The material was in many clumps which broke apart easily. Material does not appear excessively wet. When dry, the clumps break into a fine, ash-like powder. The dry material wets readily.
Silo 1 Zone B	The material is similar in color and texture to Zone A. No rocks of noticeable size were observed. Material was in bigger clumps than Zone A, perhaps a little wetter. The dry material wets readily.
Silo 1 Zone C	The material is similar in color and texture to Zone A. No rocks of noticeable size were observed. The material was in very big clumps, almost one big ball, and was noticeably wetter than Zones A and B. The dry material wets readily.
Silo 2 Zone A	The material is dark brown, much darker than Silo 1. No rocks of noticeable size were observed. Material was clumpy and not excessively wet. Some reddish material was observed in distinct pieces spread throughout the sample. The dry material is more powdery than Silo 1 and is much more difficult to wet.
Silo 2 Zone B	The material is light brown, not as dark as Silo 2A and not as light as Silo 1. No rocks of noticeable size were observed. The material is much wetter than Silo 2A, very large clumps. The dry material is fine and powdery and is more difficult to wet than Silo 1.
Silo 2 Zone C	The material is a dark greenish-gray. Very wet, almost like clay. Material readily clumps together. Much coarser than Silo 2A and 2B, more gritty or sandy. Pressure causes the material to flow like a fluid.
Silo 3 Zones ABC	The material is medium brown with a reddish tint, definite rust color when wet. Very fine and powdery, like talc. Material pours readily. Appears very dry. No clumps or rocks observed.

Table 4.2. Physical Properties of the K-65 and Silo 3 Material

Physical Properties	Silo 1			Silo 2			Silo 3
	Zone A	Zone B	Zone C	Zone A	Zone B	Zone C	Zones ABC
moisture content (%)	26.9	35.3	35.9	27.8	35.6	29.7	4.8
bulk density (g/cm <sup>3</sup> )							
wet, compacted	1.81	1.67	1.70	1.87	1.71	1.92	0.92
crushed dry, settled	1.00	0.91	0.90	1.16	0.92	1.13	0.88
specific gravity	2.79	2.77	2.74	2.72	2.57	2.81	2.86

Table 4.3 reports the measured radon emanation rates for the K-65 material. These values are substantially less than the 52,400 pCi/m<sup>2</sup>/s reported in previous testing (Janke and Chapman, 1991). This difference is attributable to the smaller sample size in the present work. Janke and Chapman used approximately 1000 g of dry K-65 material for the measurement of radon emanation, while the current work used samples of 125 to 150 g. The difference between the emanation rates measured in the current test and the previous test illustrates the necessity of using a comparable basis when reporting radon emanation rates. The most useful basis for the measurements made in these tests is the mass of dry material, since in the absence of other effects the radon emanation should be proportional to the amount of radium in the sample. The emanation rate based on the area of the sample surface or the absolute rate of pCi/hr is useful only for comparison among measurements made on identical amounts of material in identical geometric arrangements. The value of most significance in Table 4.3 is, therefore, the specific emanation rate based upon grams of dry material.

Table 4.3. Radon Emanation from Untreated K-65 Material

Sample	pCi/hr	pCi/m <sup>2</sup> /s	pCi/g/hr
Silo 1A	78,311	2683	525
Silo 1B	198,126	6788	1457
Silo 1C	213,466	7314	1711
Silo 2A	61,360	2102	416
Silo 2B	171,629	5880	1297
Silo 2C	57,933	1985	533

Variation in the measured emanation rate per unit mass among the different samples does not correlate with differences in radium content. A possible cause of the observed variations is the different moisture contents in each zone. Radon emanation rates from solids have been found to depend greatly on the moisture content of the material (Nazaroff and Nero, 1988; Stranden et al., 1984; Strong and Levins, 1982). Chemical differences in the wastes also may play a part, since the fraction of radon escaping from the solid matrix can vary if the radium is distributed differently within the solid matrix (Nazaroff and Nero, 1988). Using the data from Table 4.3 and the measured radium-226 content of the samples (reported below), the emanation coefficient of the K-65 material is found to vary from 0.19 to 0.66. These values are consistent with reported values for similar materials (Nazaroff and Nero, 1988). The data from these

measurements of radon emanation from the K-65 material gives an approximate range of emanation rates to be expected from the material. Conservative estimates of radon emanation from the material can be made using this data. Accurate predictions would require more extensive measurements under carefully controlled conditions to determine the variation of the emanation rate with moisture content for samples from each of the zones.

#### 4.1.2 Chemical Analysis

The inorganic composition of the Silo 1, 2, and 3 material as determined in the screening tests is presented in Tables 4.4 to 4.6. The elemental composition was determined by ICP unless otherwise noted. The oxidation state assumed for each of the oxides is given by the oxide formula in the tables. The composition of the material from each zone of Silos 1 and 2 was measured along with the material from Silo 3. Additionally, data is presented for a composite sample from both Silos 1 and 2 made from equal dry masses of material from the different zones within each silo. The tables also report both the average and the range of the measurements within each silo.

For Silos 1 and 2, a comparison of the composite values to the average of the zones provides an indicator of analytical error. Since the composite is made from equal amounts of each zone, the values should be identical. The comparison for Silo 1 shows good agreement for all components, while for Silo 2, the agreement is good for all components except for silica. Since silica is often difficult to completely dissolve when preparing samples for ICP analysis, silica concentrations determined by ICP are often low. Therefore, the silica values for zones 2A and 2C may be lower than the true value.

Comparing the range to the average provides an indicator of differences in composition between the zones. For Silo 1, the range is close to the average for all components except carbonate and sodium. This indicates a fairly consistent composition throughout the silo, which agrees with observations from the physical properties determination as previously mentioned. For Silo 2, however, a wide range about the average is observed for several components (barium, magnesium, iron, lead) where good analytical precision was indicated by the composite analysis. This indicates actual differences in composition between the zones, which also agrees with the observations from the measurement of the physical properties. There was no distinction between zones for the Silo 3 samples; all the samples analyzed were assumed to have similar compositions. A comparison of the range of values to the average composition for Silo 3 indicates that this assumption is valid to the extent that the samples analyzed in these tests are representative of the overall variation which is actually present in the silo.

Table 4.4. Inorganic Composition of Silo 1 Samples (dry wt%)

Component in waste	Notes	Zone A	Zone B	Zone C	Composite	Average A,B,C	Range A,B,C
SiO <sub>2</sub>		52	48	48	49	50	48 - 52
PbO		10	13	13	13	12	10 - 13
BaO		6.0	6.1	6.8	6.3	6.3	6.0 - 6.8
CO <sub>2</sub>	a	1.4	3.5	4.6	na	3.2	1.4 - 4.6
Al <sub>2</sub> O <sub>3</sub>		2.6	2.7	2.6	2.6	2.6	2.6 - 2.7
Fe <sub>2</sub> O <sub>3</sub>		2.7	2.3	2.4	2.6	2.5	2.3 - 2.7
SO <sub>3</sub>	b	1.9	1.8	1.6	na	1.8	1.7 - 1.9
Na <sub>2</sub> O		1.0	2.2	2.2	1.8	1.8	1.0 - 2.2
MgO		1.2	1.2	1.1	1.2	1.2	1.1 - 1.2
P <sub>2</sub> O <sub>5</sub>		0.93	0.46	0.48	0.65	0.62	.46 - .93
K <sub>2</sub> O		0.72	0.72	0.60	0.60	0.68	.60 - .72
MoO <sub>2</sub>		0.69	0.27	0.34	0.47	0.43	.27 - .69
CaO		0.62	0.28	0.22	0.45	0.37	.22 - .62
La <sub>2</sub> O <sub>3</sub>		0.65	0.31	0.29	0.41	0.42	.29 - .65
NiO		0.29	0.51	0.45	0.41	0.42	.29 - .51
Ce <sub>2</sub> O <sub>3</sub>		0.64	0.32	0.27	0.35	0.41	.27 - .64
N <sub>2</sub> O <sub>5</sub>	c	0.23	0.42	0.21	0.24	0.29	.21 - .42
TiO <sub>2</sub>		0.35	0.24	0.25	0.28	0.28	.24 - .35
Nd <sub>2</sub> O <sub>3</sub>		0.30	0.15	0.13	0.20	0.19	.13 - .30
CoO		0.17	0.22	0.19	0.18	0.19	.17 - .22
SrO		0.075	0.089	0.084	0.081	0.082	.07 - .09
Cl	c	0.062	0.10	0.076	0.072	0.079	.06 - .10
V <sub>2</sub> O <sub>3</sub>		0.064	0.063	0.057	0.060	0.061	.06 - .06
CuO		0.053	0.063	0.055	0.052	0.057	.05 - .06
ZrO <sub>2</sub>		0.059	0.036	0.058	0.047	0.051	.04 - .06
SeO <sub>2</sub>		0.035	0.056	0.049	0.042	0.047	.04 - .06
Cr <sub>2</sub> O <sub>3</sub>		0.029	0.015	0.015	0.022	0.019	.01 - .03
MnO		0.016	0.012	0.014	0.014	0.014	.01 - .02
BeO		0.0056	0.0069	0.0056	0.0056	0.0060	.01 - .02
F	c	0.0035	0.0070	0.0040	0.0040	0.0048	.00 - .01
As <sub>2</sub> O <sub>3</sub>		ND	ND	ND	ND	ND	---
CdO		ND	ND	ND	ND	ND	---
SnO <sub>2</sub>		ND	ND	ND	ND	ND	---
ThO <sub>2</sub>		ND	ND	ND	ND	ND	---
UO <sub>2</sub>		ND	ND	ND	ND	ND	---
ZnO		ND	ND	ND	ND	ND	---
total		85	86	86	81	86	

## Notes:

- (a) Determined from the difference between total carbon and total organic carbon, expressed as carbonate.
- (b) Sulfate was determined as total sulfur using ICP and expressed as sulfate.
- (c) Determined by IC on a leachate from the sample leached in distilled water. "na" signifies "not analyzed"; ND - indicates less than detection limits. ICP results are valid to a maximum of 2 significant figures. Typical precision is  $\pm 10\%$ .

Table 4.5. Inorganic Composition of Silo 2 Samples (dry wt%)

Component in waste	Notes					Average	Range
		Zone A	Zone B	Zone C	Composite	A,B,C	A,B,C
SiO <sub>2</sub>		49	57	46	58	51	46 - 57
PbO		4.9	7.2	6.4	6.6	6.2	4.9 - 7.2
Fe <sub>2</sub> O <sub>3</sub>		8.4	3.4	6.4	5.8	6.1	3.4 - 8.4
Al <sub>2</sub> O <sub>3</sub>		3.7	3.2	3.2	3.4	3.4	3.2 - 3.7
CO <sub>2</sub>	a	3.3	3.5	3.3	na	3.4	3.3 - 3.5
BaO		1.5	3.7	3.8	3.1	3.0	1.5 - 3.8
CaO		3.1	2.2	2.2	2.7	2.5	2.2 - 3.1
MgO		2.3	1.1	1.6	1.7	1.7	1.1 - 2.3
SO <sub>3</sub>	b	1.4	0.87	2.7	na	1.7	.87 - 2.8
Na <sub>2</sub> O		0.61	0.98	1.0	0.93	0.88	.61 - 1.0
K <sub>2</sub> O		0.72	0.60	0.72	0.84	0.68	.60 - .72
P <sub>2</sub> O <sub>5</sub>		0.70	0.73	0.61	0.68	0.68	.61 - .73
N <sub>2</sub> O <sub>5</sub>	c	0.66	0.63	0.57	0.67	0.62	.57 - .66
UO <sub>2</sub>		0.45	0.51	0.45	0.51	0.47	.45 - .51
NiO		0.31	0.46	0.33	0.38	0.36	.31 - .46
TiO <sub>2</sub>		0.36	0.30	0.32	0.36	0.33	.30 - .36
Ce <sub>2</sub> O <sub>3</sub>		0.31	0.40	0.29	0.35	0.33	.29 - .40
La <sub>2</sub> O <sub>3</sub>		0.27	0.36	0.23	0.30	0.29	.23 - .36
ZrO <sub>2</sub>		0.12	0.12	0.18	0.28	0.14	.12 - .18
Nd <sub>2</sub> O <sub>3</sub>		0.16	0.19	0.13	0.23	0.16	.13 - .19
CoO		0.18	0.25	0.20	0.22	0.21	.18 - .25
CuO		0.068	0.084	0.10	0.083	0.084	.07 - .10
Cr <sub>2</sub> O <sub>3</sub>		0.120	0.037	0.10	0.080	0.083	.04 - .12
MoO <sub>2</sub>		0.040	0.120	0.079	0.077	0.080	.04 - .12
SrO		0.035	0.078	0.072	0.064	0.062	.03 - .08
As <sub>2</sub> O <sub>3</sub>		0.033	0.033	0.079	0.053	0.048	.03 - .08
SeO <sub>2</sub>		0.042	0.042	0.042	0.042	0.042	.04 - .04
MnO		0.031	0.030	0.036	0.035	0.032	.03 - .04
V <sub>2</sub> O <sub>3</sub>		0.078	0.077	0.088	0.022	0.081	.08 - .09
ZnO		0.011	0.011	0.012	0.017	0.011	.01 - .01
Cl	c	0.0080	0.0030	0.0030	0.0040	0.0047	.00 - .01
F	c	0.0030	0.0050	0.0050	0.0040	0.0043	.00 - .01
BeO		ND	ND	ND	ND	ND	ND
CdO		ND	ND	ND	ND	ND	ND
SnO <sub>2</sub>		ND	ND	ND	ND	ND	ND
ThO <sub>2</sub>		ND	ND	ND	ND	ND	ND
total		83	88	81	87	84	

## Notes:

- (a) Determined from the difference between total carbon and total organic carbon, expressed as carbonate.
- (b) Sulfate was determined as total sulfur using ICP and expressed as sulfate.
- (c) Determined by IC on a leachate from the sample leached in distilled water. "na" signifies "not analyzed"; ND - indicates less than detection limits. ICP results are valid to a maximum of 2 significant figures. Typical precision is  $\pm 10\%$ .

Table 4.6. Inorganic Composition of Silo 3 Samples (dry wt%)

Component in waste	Notes	#1	#2	#3	#4	Average #1 - #4	Range #1 - #4
SO <sub>4</sub>	a	15	15	15	15	15	
SiO <sub>2</sub>		14	13	13	16	14	13 - 16
MgO		11	9.6	9.9	10	10	9.6 - 11
P <sub>2</sub> O <sub>5</sub>		10	8.4	9.5	9.2	9.3	8.4 - 10
Fe <sub>2</sub> O <sub>3</sub>		8.0	8.1	7.5	8.6	8.0	7.5 - 8.6
N <sub>2</sub> O <sub>5</sub>		6.0	6.1	6.3	6.1	6.1	6.0 - 6.3
Na <sub>2</sub> O	b	na	5.9	5.7	6.2	5.9	5.7 - 6.2
CaO		5.2	4.1	5.0	4.5	4.7	4.1 - 5.2
Al <sub>2</sub> O <sub>3</sub>		4.3	5.8	4.6	6.4	5.3	4.4 - 6.4
CO <sub>2</sub>	a	1.9	1.9	1.9	1.9	1.9	
K <sub>2</sub> O		1.8	2.3	1.8	1.2	1.8	1.2 - 2.3
MnO		0.65	0.70	0.62	0.72	0.67	.62 - .72
Li <sub>2</sub> O		0.45	0.51	0.46	na	0.47	.45 - .51
NiO		0.47	0.57	0.43	0.59	0.52	.43 - .59
V <sub>2</sub> O <sub>3</sub>		0.35	0.65	0.36	0.64	0.50	.35 - .65
ThO <sub>2</sub>		0.34	0.34	0.34	0.23	0.31	.23 - .34
UO <sub>2</sub>		0.23	0.34	0.34	0.45	0.34	.23 - .45
CuO		0.36	0.46	0.34	0.46	0.41	.34 - .46
CoO		0.36	0.36	0.32	0.39	0.36	.32 - .39
As <sub>2</sub> O <sub>3</sub>		0.18	0.33	0.23	0.40	0.29	.18 - .40
TiO <sub>2</sub>		0.25	0.21	0.22	0.21	0.22	.21 - .25
PbO		0.18	0.21	0.16	0.22	0.19	.16 - .22
MoO <sub>2</sub>		0.15	0.22	0.12	0.23	0.18	.12 - .23
F		0.077	0.090	0.10	0.053	0.079	.05 - .10
Cr <sub>2</sub> O <sub>3</sub>		0.086	0.089	0.075	0.082	0.083	.08 - .09
ZnO		0.059	0.069	0.055	0.082	0.066	.06 - .08
BaO		0.037	0.030	0.036	0.028	0.033	.03 - .04
Y <sub>2</sub> O <sub>3</sub>		0.036	0.044	0.036	na	0.039	.04 - .04
SrO		0.025	0.028	0.024	0.028	0.026	.02 - .03
ZrO <sub>2</sub>	b	na	0.018	0.020	0.014	0.017	.01 - .02
Cl		0.013	0.021	0.017	0.013	0.016	.01 - .02
Ce <sub>2</sub> O <sub>3</sub>		0.0000	0.023	0.012	0.035	0.018	.00 - .04
La <sub>2</sub> O <sub>3</sub>		0.0082	0.010	0.0088	0.018	0.011	.01 - .02
Nd <sub>2</sub> O <sub>3</sub>		ND	0.012	0.0082	0.017	0.0124	.00 - .02
BeO		ND	0.0056	0.0056	0.0069	0.0060	.00 - .01
CdO		0.0011	0.0043	0.0046	0.0074	0.0044	.00 - .01
SeO <sub>2</sub>		na	na	na	0.028	0.028	
SnO <sub>2</sub>		na	na	na	ND	ND	
total		81	85	84	90	87	

## Notes:

- (a) Sulfate and carbonate were determined from a single sample separate from these analyses.
- (b) Only the Na<sub>2</sub>O<sub>2</sub> fusion was performed, so values for Na and Zr could not be obtained. "na" signifies "not analyzed"; ND - indicates less than detection limits. ICP results are valid to a maximum of 2 significant figures. Typical precision is ±10%.

Values for several of the analytes should be used with caution. Some were frequently close to the detection limits (As, Be, Cr, Se, Th, U, Zn). For Silos 1 and 2, the value for sulfur (from which the sulfate is derived) was not only near detection limits, but usually was above detectable limits in only one of the two fusions. Since the ICP analyses from the two fusions are averaged, sulfate values could be higher than reported. The nitrate, chloride, and fluoride values were obtained by IC of a deionized water extraction from the waste material. This method measures only what is dissolved in the water. Although most salts of these materials are soluble, it is not likely that analytes were quantitatively extracted from the sample. This is most significant for the nitrate, which is present at the highest concentrations. Again, values reported here for these anions should be used with caution. Organic carbon levels as found in the total carbon analysis were low. For Silos 1 and 2, the organic carbon weight percent ranged from 0.3 percent to 1.2 percent, while for Silo 3 it was less than 0.1 percent.

The total weight percent for all samples analyzed was less than 100 percent. The values from these analyses range from 81 percent to 90 percent. Some of this discrepancy is due to absence of data for some of the samples (sodium for Silo 3 #1, carbonate and sulfate for the composites of Silos 1 and 2). Some may result from failure to completely solubilize the sample being analyzed. Some undissolved particles were observed in the fusions for the ICP analyses, and for the IC analyses, the water leach is not likely to quantitatively extract the anions of interest. Considering these factors, the agreement between the totals for each silo is very good. Finally, all water bound in the sample may not have been removed by drying the samples at 160°C. Chemically bound water remaining in the samples would cause the total weight percent to be less than 100 percent.

#### 4.1.3 Radiochemical Analysis

The isotopic analysis of the silo materials was determined using gamma energy analysis. Results are presented in Tables 4.7 to 4.9. These values are in reasonable agreement with results previously reported for the K-65 material (Janke and Chapman, 1991). A comparison between the composite values and an average derived from the three zones in Silos 1 and 2 shows good agreement for most isotopes, although for Silo 1, there appears to be some degree of analytical error based upon the difference between the average of the three zones and the composite analysis. Additionally, the thorium-230 values for Silos 1C and 2A are questionable. For Silo 1C, no thorium-230 was detected, although the measured value for the composite sample (which includes part of the Silo 1C material) seems to indicate that there is thorium-230 in all the samples. For Silo 2A, the reported thorium-230 value is much higher than in the other zones of the silo, although the composite sample for Silo 2 indicates that the thorium-230 level is about equal in all three zones. Difficulty with the thorium-230 results is likely a result of the low energy gamma peak of thorium-230 being the only peak not subject to interferences, and therefore suitable for determination of the thorium-230. Since the lower gamma energies are subject to the greatest errors, the thorium-230 results are the most likely to have significant error.

The results for Silo 3 show significant differences between sample 4 and the other three samples. These differences are likely due to the use of two different counting methods for the Silo 3 material. Samples 1 to 3 were to be dissolved and the resulting solution counted; however, the samples could not be dissolved completely. Both the liquid and the solids were counted separately, and the results were averaged based upon the mass of sample in each form. Sample 4 was counted as a solid. This is the same method that was used for the Silo 1 and 2 gamma energy analysis. The results from sample 4 are believed to be the most accurate.

Table 4.7. Isotopic Content of Silo 1 Material (nCi/g)

<u>Isotope</u>	<u>Zone A</u>	<u>Zone B</u>	<u>Zone C</u>	<u>Average</u>	<u>Composite</u>
Bi-214	368	414	441	408	439
Pb-214	368	414	438	407	437
Ra-226	368	414	441	408	439
Pb-210	212	327	316	285	292
Th-230	45	69	ND	38	54
Pb-211	18	14	19	17	19
Ra-223	15	16	16	15	14
Rn-219	14	12	15	14	15

Notes:

Isotopes other than those listed are likely to be present.

ND - signifies the isotope was not detected. Additionally, Ac-227, Pa-231, Po-210, Ra-224, Ra-228, Th-228, Th-232, U-234, U-235, and U-238 were not detected.

Table 4.8. Isotopic Content of Silo 2 Material (nCi/g)

<u>Isotope</u>	<u>Zone A</u>	<u>Zone B</u>	<u>Zone C</u>	<u>Average</u>	<u>Composite</u>
Bi-214	176	259	242	226	230
Ra-226	176	259	242	226	230
Pb-214	178	253	246	226	229
Pb-210	182	236	247	222	233
Th-230	184	25	35	81	32
Ra-223	7	10	8	8	8
Rn-219	5	9	8	7	7
Pb-211	unresolved	8	8	8	7

Notes:

Isotopes other than those listed are likely to be present.

Ac-227, Pa-231, Po-210, Ra-224, Ra-228, Th-228, Th-232, U-234, U-235, and U-238 were not detected.

"Unresolved" indicates the isotope was present but could not be resolved due to interferences.

Table 4.9. Isotopic Content of Silo 3 Material (nCi/g)

Isotope	#1	#2	#3	#4
Th-230	51.0	64.5	51.3	142.0
U-238	2.7	1.3	2.3	ND
Pb-210	1.8	3.0	2.1	9.8
Pb-214	1.0	1.1	1.1	4.6
Ra-226	0.8	0.8	0.9	4.7
Bi-214	0.8	0.8	0.9	4.7
Pb-211	0.6	0.6	unresolved	ND
Ra-223	0.5	0.7	0.4	unresolved
Pa-231	0.5	1.0	0.7	ND
Ra-224	0.4	0.3	0.4	0.4
Th-232	0.3	0.3	0.3	0.3
Rn-219	ND	ND	ND	0.7
U-235	unresolved	unresolved	unresolved	unresolved

**Notes:**

Isotopes other than those listed are likely to be present.

ND - signifies isotope was not detected; additionally, Ac-227, Po-210, Ra-228, Th-228, and U-234 were not detected.

"Unresolved" indicates the isotope was present, but could not be resolved due to interferences.

A comparison of the Silo 3 thorium content from the inorganic analysis and from the gamma energy analysis shows good agreement. Dividing the measured activity for thorium-232 (0.3 nCi/g) by the specific activity of thorium-232 (110 nCi/g) gives a value of 0.27 weight percent for the thorium content, which is in good agreement with the 0.31 weight percent average for total thorium from the inorganic analysis. Other isotopes of thorium have much higher specific activities and do not contribute significantly to the mass fraction in the sample.

The fact that many isotopes were below detection limits can be attributed to the isotopes' presence in only very small amounts, their lack of significant gamma emissions, or the obscurity of their emission peaks by interferences. Accurate and quantitative measurement of all the isotopes requested would require analytical techniques which were beyond the scope of these screening studies. The gamma energy analysis was successful in determining the isotopes present in the most significant amounts.

**4.1.4 Conclusions**

The primary purpose of the screening tests was to provide data to support the treatability vitrification study. Specifically, sufficient data were required to determine if the material from the different zones should be combined into a single mix for the tests, to assist in determining appropriate glass formulations, and to allow calculation of the reduction in volume and radon

emanation. Based upon results from the chemical analysis, it was determined that the K-65 material could be combined into a single mix for the tests. The observed variability in composition was within acceptable limits for glass formulations. The Silo 3 material also was found to be uniform. The chemical and physical property data were sufficient to allow formulation of the glasses. This was especially important for the Silo 3 material, which is very low in glass-forming elements and high in phosphate, sulfate, and nitrate. The glass formulation for Silo 3 alone, therefore, was much different than that for the K-65 material.

#### 4.2 REMEDY SCREENING SEQUENCE ZERO TESTS (100 GRAM MELTS)

The Sequence Zero tests consisted of numerous small melts of the waste material and appropriate additives. Based upon the results from the screening tests, the K-65 material that was received as separate samples from each zone of Silos 1 and 2 was combined into a single mix. The Silo 3 material also was combined in a similar fashion. Combining these materials allowed all of the melts to be performed using waste material of the same composition. Multiple melts were carried out for each of the waste combinations (Sequences A through D). Samples of glasses from each sequence which were judged appropriate by the previously described criteria in Section 3.4 and were sent to a subcontracted laboratory for modified TCLP analysis.<sup>1</sup> Results from the Sequence Zero tests were used to define the formulations for use in the bench-scale melts.

##### 4.2.1 Sequence A

The melts for Sequence A consisted of the K-65 material mixed with sodium carbonate and carbon in the proportions indicated in Table 4.10. The projected composition for each of the melts, as well as the melt temperature, are also indicated in the table. Sodium carbonate was added in amounts necessary to give an estimated content of sodium oxide in the final glass ranging from 5 percent to 20 percent. The effect of the sodium is not only to reduce the melting temperature, but to prevent crystallinity in the glass. Empirical rules for lead glasses predict a sodium oxide content of between 15 percent and 20 percent will provide the optimum balance between devitrification at too low a content and loss of durability at too high a content (Volf, 1984).

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<sup>1</sup>The modified TCLP, as it applies to the identified vitrification tests, is defined as analysis of the vitrified product for leachability of the following heavy metals: Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver. Based on the available EP toxicity data (Buelt, 1989) from the previous vitrification test, all of the heavy metals from the EP toxicity list, with the exception of lead, were below the regulatory limits.

Table 4.10. Glass Formulations and Projected Compositions (wt% oxide) for Sequence A 100 g Tests

Element	Melt Number 100A/								
	1.1	1.2	2.1	2.2	3.1	3.2	3.3	3.4	4.1
Si	51.1	54.3	57.5	60.7	57.5	57.5	57.5	57.5	54.3
Na	20.2	15.1	10.1	5.1	10.1	10.1	10.1	10.1	15.1
Pb	10.0	10.6	11.2	11.8	11.2	11.2	11.2	11.2	10.6
Ba	5.1	5.4	5.7	6.1	5.7	5.7	5.7	5.7	5.4
Fe	3.9	4.1	4.4	4.6	4.4	4.4	4.4	4.4	4.1
Al	3.0	3.2	3.4	3.5	3.4	3.4	3.4	3.4	3.2
Mg	1.4	1.5	1.6	1.7	1.6	1.6	1.6	1.6	1.5
Ca	1.2	1.3	1.3	1.4	1.3	1.3	1.3	1.3	1.3
K	0.71	0.75	0.80	0.84	0.80	0.80	0.80	0.80	0.75
P	0.68	0.73	0.77	0.81	0.77	0.77	0.77	0.77	0.73
Ce	0.41	0.44	0.47	0.49	0.47	0.46	0.47	0.47	0.44
La	0.40	0.42	0.45	0.47	0.45	0.45	0.45	0.45	0.42
Ni	0.40	0.42	0.45	0.47	0.45	0.45	0.45	0.45	0.42
Mo	0.33	0.35	0.37	0.39	0.37	0.37	0.37	0.37	0.35
Ti	0.31	0.33	0.35	0.37	0.35	0.35	0.35	0.35	0.33
Co	0.20	0.22	0.23	0.24	0.23	0.23	0.23	0.23	0.22
Nd	0.20	0.21	0.22	0.23	0.22	0.22	0.22	0.22	0.21
U	0.18	0.19	0.20	0.21	0.20	0.20	0.20	0.20	0.19
Zr	0.08	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.09
Sr	0.08	0.08	0.08	0.09	0.08	0.08	0.08	0.08	0.08
V	0.07	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.07
Cu	0.07	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.07
Se	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Cr	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mn	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02
As	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Zn	0.004	0.004	0.005	0.005	0.005	0.005	0.005	0.005	0.004
Be	0.004	0.004	0.004	0.005	0.004	0.004	0.004	0.004	0.004
total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Glass Formulation (g dry additive/g dry waste)									
Na <sub>2</sub> CO <sub>3</sub>	0.316	0.215	0.128	0.049	0.128	0.128	0.128	0.128	0.216
C	0.000	0.000	0.000	0.000	0.001	0.002	0.004	0.008	0.002
melt T (°C)									
	1150	1150	1350	1350	1350	1350	1350	1350	1350

Note: Cd, Sn, and Th were below detection limits.

The first melts (100A/1.1 and 100A/1.2) were carried out at 1150°C, which is similar to conditions of the previous test melts (Janke and Chapman, 1991). The resulting glasses were black and glossy with some crystalline inclusions up to about 1/8 inch (0.32 cm) in diameter. On top of the glass was a solidified salt layer about 1/32 inch (0.08 cm) to 1/16 inch (0.16 cm) thick. This layer was assumed to be composed largely of sulfate salts, and later analysis of a similar layer showed the major component of the salt layer to be sodium sulfate.

The next two melts (100A/2.1 and 100A/2.2) were performed at 1350°C and included smaller amounts of soda. Additionally, melt 100A/1.2 was remelted at the higher temperature. Upon remelting 100A/1.2, the salt layer disappeared with only traces of yellow crystal material spread in spots on the surface of the glass. The glass itself was almost completely free of crystalline inclusions. Melt 100A/2.1 also formed a homogeneous and glossy black glass with some crystal inclusions and similar yellow spotting on the surface. Melt 100A/2.2 had large white inclusions in the black glass and also some yellow patches.

The next four melts at 1350°C (100A/3.1 to 100A/3.4) were all at a sodium content of about 10 percent oxide with varying amounts of carbon added to eliminate the yellow spotting on the surface of the glass. The glass in all the melts was similar: black and very glossy with some white inclusions up to 1/4 inch (0.64 cm) in diameter. Some of the inclusions were rounded and reddish colored on the surface. All the melts were essentially free of salts on the surface. The surfaces of 100A/3.2 and 3.4 were completely clear, while 100A/3.1 had a thin film (like frost on a window) and 100A/3.3 had some small, yellow spots. It appeared that the reduction of the residual sulfate was achieved as effectively with the smaller amounts of carbon as it was with the larger amounts.

The final melt (100A/4.1) was carried out at 1350°C with the same composition as 100A/1.2, but with a small carbon addition to reduce the residual sulfate. The resulting glass was very homogeneous and glossy with only a few scattered white crystals. The surface was completely free from any salt residue as evidenced by a very glossy appearance.

An important observation from these melts is that the higher melt temperature (1350°C versus 1150°C) greatly reduces the formation of a salt layer on the surface of the melt. With the addition of small amounts of carbon, the salt layer is completely eliminated. No reduced metal nodule was observed in any of these melts. Another observation is that the melts with higher sodium contents tended to have fewer of the large, crystalline inclusions.

The TCLP for metals was performed on glass samples from the melts 100A/2.1 and 100A/4.1. Results from these analyses are presented in Table 4.11. Both glasses passed the test with leachate concentrations below regulatory limits. The choice of the formulation for the bench-scale tests was therefore based upon other factors. Although the waste loading for 100A/2.1 was slightly higher, the final formulation chosen was 100A/4.1. This choice was based mainly upon the observation of fewer crystalline inclusions in the glass at the higher sodium content.

Table 4.11. TCLP Results from the Sequence A 100 g Melts  
(all values are in mg/L)

Analyte	100A/2.1			100A/4.1	
	Regulatory Limit	Detection Limit	Results	Detection Limit	Results
Arsenic	5.0	0.01	<0.01	0.01	<0.01
Barium	100.0	1.0	<1.0	0.05	0.20
Cadmium	1.0	0.002	<0.002	0.05	<0.05
Chromium	5.0	1.0	<1.0	0.05	<0.05
Lead	5.0	0.003	0.05	0.05	0.22
Mercury	0.2	0.0004	<0.0004	0.0004	<0.0004
Selenium	1.0	0.01	<0.01	0.01	<0.01
Silver	5.0	1.0	<1.0	0.05	<0.05

#### 4.2.2 Sequence B

The melts for Sequence B consisted of an equal dry weight mixture of the K-65 and BentoGrout material combined with sodium carbonate and carbon in the proportions listed in Table 4.12. The projected compositions for each of the melts as well as the melt temperature are also indicated in the table. The composition of the K-65/BentoGrout mixture is quite similar to the K-65 material alone. This waste mixture for Sequence B has a higher alumina content and a lower lead content than Sequence A. The composition is similar enough that the same formulations used for Sequence A were used for Sequence B. The sodium content of the final glass was varied from 10 percent to 20 percent, and a small carbon addition was made to reduce the sulfates. The glass from 100B/1.1 was very glossy and homogeneous with very few crystalline inclusions. The crystals were white and similar to those in the Sequence A melts. Melt 100B/1.2 was similar to 100B/1.1 but had significantly more crystalline inclusions. The white crystals tended to be located near the surface of the glass. The Sequence B glasses had more of the white, crystalline inclusions than the Sequence A glasses. The last melt (100B/1.3) did not make a glass of sufficient quality. The surface of the melt was pitted and large gas bubbles were found throughout the melt. Some crystals were also observed. An expected effect of the BentoGrout addition was an increase in the melting temperature result from an increase in the alumina content. This was indeed found as evidence by the incomplete melting of 100B/1.3.

Table 4.12. Glass Formulations and Projected Compositions  
(wt% oxide) for Sequence B 100 g Tests

Element	Melt Number		
	100B/1.1	100B/1.2	100B/1.3
Si	53.0	56.3	59.6
Na	20.1	15.1	10.1
Al	8.2	8.7	9.3
Pb	4.9	5.2	5.5
Fe	3.4	3.7	3.9
Mg	3.4	3.6	3.8
Ba	2.5	2.7	2.8
Ca	1.3	1.4	1.5
P	0.94	1.0	1.1
K	0.68	0.72	0.76
Ti	0.26	0.28	0.29
Ce	0.20	0.21	0.23
La	0.20	0.21	0.22
Ni	0.19	0.21	0.22
Mo	0.16	0.17	0.18
Co	0.10	0.11	0.11
Nd	0.10	0.10	0.11
U	0.09	0.09	0.10
Zr	0.04	0.04	0.05
Sr	0.04	0.04	0.04
Mn	0.04	0.04	0.04
V	0.03	0.04	0.04
Cu	0.03	0.04	0.04
Se	0.02	0.02	0.02
Cr	0.02	0.02	0.02
As	0.01	0.01	0.01
Zn	0.002	0.002	0.002
Be	0.002	0.002	0.002
total	100.0	100.0	100.0
Glass Formulation (g dry additive/g dry waste)			
Na <sub>2</sub> CO <sub>3</sub>	0.308	0.207	0.117
C	0.001	0.001	0.001
melt T (°C)			
	1350	1350	1350

Note: Cd, Sn, and Th were below detection limits.

The TCLP for metals was performed on glass samples from the melts 100B/1.1 and 100B/1.2. Results from these analyses are presented in Table 4.13. Both glasses passed the test with leachate concentrations of metals below regulatory limits. The choice of the formulation for future tests was therefore based upon other factors. Although there were fewer crystalline inclusions in melt 100B/1.1, the composition chosen for the bench-scale tests was that of melt 100B/1.2. The major factor in this choice was that this formulation was the same as that chosen for Sequence A. During retrieval of the K-65 material, the waste composition is expected to range from pure K-65 material to a mixture of K-65 and BentoGrout. Ideally, this range of variation would be encompassed by a single formulation.

Table 4.13. TCLP Results from the Sequence B 100 g Melts  
(all values are in mg/L)

<u>Analyte</u>	<u>Regulatory</u>	<u>Detection</u>	<u>Result</u>	
	<u>Limit</u>	<u>Limit</u>	<u>100B/1.1</u>	<u>100B/1.2</u>
Arsenic	5.0	0.01	<0.01	<0.01
Barium	100.0	0.05	0.39	0.22
Cadmium	1.0	0.05	<0.05	<0.05
Chromium	5.0	0.05	<0.05	<0.05
Lead	5.0	0.05	0.11	0.11
Mercury	0.2	0.0004	<0.0004	<0.0004
Selenium	1.0	0.01	<0.01	<0.01
Silver	5.0	0.05	<0.05	<0.05

#### 4.2.3 Sequence C

The melts for Sequence C consisted of the Silo 3 material and various additives as indicated in Table 4.14. The projected compositions for each of the melts, as well as the melt temperatures, are also indicated in the Table 4.14. Because the composition of the Silo 3 material is not typical of glass-forming wastes, investigation of potential glass formulations was conducted prior to the 100 g melts. Using simple simulants in a nonradioactive laboratory, it was determined that additions of alumina and either silica or boric acid formed homogeneous melts at high waste loadings and reasonable temperatures. With boron added as additional glass former, the melt was very glossy, while with silica added, the melt was homogeneous, but crystalline. Melts with the actual Silo 3 material using the old furnace confirmed the results of the simulant tests on a qualitative basis. Silo 3 material alone was also melted and formed a nonhomogeneous, crystalline melt.

Using the information from these simulant tests, the 100 g melts were carried out. The proportions of added silica and boric acid were varied in different melts in order to investigate a range of compositions. The amount of alumina added was also varied. The first set of melts was carried out at 1250°C. Melt 100C/1.1 was the composition which gave a very glossy product in the test melts previously conducted. The product of melt 100C/1.1 was a very homogeneous melt; however, the melt was devitrified and crystalline rather than glossy as was

observed in the previous test melts. Apparently, the slower cooling of the glass in the new system compared to the previous test melts resulted in devitrification of the melt. There were no visible crystals. This formulation, as many of the others with the Silo 3 material, foamed significantly so that some of the glass spilled into the tray holding the crucibles. Melt 100C/1.2 included additions of alumina and boric acid only. The melt was glossy but had some large, slag-like inclusions. The melt attacked the crucible wall and foamed significantly. Corrosion of the crucible wall in this melt is likely a result of the low glass viscosity which would be expected with the high content of boria and low silica content of this glass composition. Melts 100C/1.3 and 100C/1.4 were variations of 100C/1.1, substituting silica for boric acid or reducing the alumina content. Both glasses were very similar to 100C/1.1 in appearance and behavior. The glass was very homogeneous and crystalline, and both foamed. Melt 100C/1.3, which had more silica and less boric acid, appeared to foam less than the other melts.

The second set of melts was carried out at 1350°C. Melt 100C/2.1 was with additions of silica and alumina only. It foamed some but did not overflow. The glass was homogeneous and devitrified with a metallic luster along the breakage plane. Melt 100C/2.2 was the same as 100C/2.1 but with a little boric acid substituted for some of the silica. The glass was again homogeneous and devitrified. No foaming was observed. Melt 100C/2.3 was the same as 100C/2.2 except for a higher alumina content. The surface of the glass was uneven and slaggy in appearance. Melt 100C/2.4 was similar to 100C/2.2, but with more boric acid substituted for silica. Significant corrosion of the crucible was observed, again a likely result of a low viscosity melt.

The foaming observed in most of these melts was a problem for the bench-scale tests, since foaming would result in a loss of glass from the crucible and reduce the amount of glass available for analysis. Therefore, for these tests, a formulation which eliminated foaming was sought. While the foaming observed was a problem for the purposes of these tests, it does not necessarily indicate a problem in a full-scale melter. A crucible melt typically produces conditions favorable to foaming which are not encountered in a joule-heated melter. When performing crucible melts in a furnace, the batch in the crucible will melt from the outside in, often forming a viscous melt on the outer surface which prevents the escape of gases generated inside. Additionally, the geometry of the crucible (narrow walls compared to a large melter) often contributes to the stability of a foam. The foaming observed in these melts apparently results from the decomposition of sulfate in the melt. Adjusting the composition can potentially reduce the foaming by changing the viscosity of the melt at the temperature at which the gas is generated. This was apparently observed in these melts, since the melts which were higher in silica (hence, more viscous) exhibited reduced or no foaming. Assessing potential problems with foaming for the Sequence C glass must continue into the pilot-scale testing during the remedy design phase of this work.

The TCLP for metals was performed on glass samples from the melts 100C/1.2 and 100C/2.2. Results from these analyses are presented in Table 4.15. Although both glasses passed the test with leachate concentrations below the limits, the formulation used for melt 100C/2.2 was chosen for the bench-scale tests, since foaming was not observed for this formulation.

Table 4.14. Glass Formulations and Projected Compositions (wt% oxide)  
for Sequence C 100 g Tests

Element	Melt Number 100C/							
	1.1	1.2	1.3	1.4	2.1	2.2	2.3	2.4
Si	20.0	11.0	29.9	20.0	35.0	30.0	30.0	25.0
Al	20.0	20.0	20.0	15.0	20.0	20.0	25.0	20.0
Mg	7.9	7.9	7.9	9.1	10.2	10.2	9.1	10.2
P	7.3	7.3	7.3	8.3	9.4	9.4	8.3	9.4
Fe	6.3	6.3	6.3	7.2	8.1	8.1	7.2	8.1
Na	4.7	4.7	4.7	5.3	6.0	6.0	5.3	6.0
B	25.0	33.9	15.0	25.0	0.03	5.0	5.0	10.0
Ca	3.7	3.7	3.7	4.2	4.7	4.7	4.2	4.7
K	1.4	1.4	1.4	1.6	1.8	1.8	1.6	1.8
Mn	0.53	0.53	0.53	0.61	0.68	0.68	0.60	0.68
Ni	0.41	0.41	0.41	0.46	0.52	0.52	0.46	0.52
V	0.39	0.39	0.39	0.45	0.50	0.50	0.45	0.50
Li	0.37	0.37	0.37	0.43	0.48	0.48	0.42	0.48
Cu	0.32	0.32	0.32	0.37	0.41	0.41	0.36	0.41
Co	0.28	0.28	0.28	0.32	0.36	0.36	0.32	0.36
U	0.27	0.27	0.27	0.31	0.34	0.34	0.31	0.34
Th	0.25	0.25	0.25	0.28	0.32	0.32	0.28	0.32
As	0.22	0.22	0.22	0.26	0.29	0.29	0.26	0.29
Ti	0.17	0.17	0.17	0.20	0.22	0.22	0.20	0.22
Pb	0.15	0.15	0.15	0.17	0.19	0.19	0.17	0.19
Mo	0.14	0.14	0.14	0.16	0.18	0.18	0.16	0.18
Cr	0.07	0.07	0.07	0.07	0.08	0.08	0.07	0.08
Zn	0.05	0.05	0.05	0.06	0.07	0.07	0.06	0.07
Y	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.04
Ba	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Se	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03
Sr	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.03
Ce	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
Zr	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
La	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Nd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Be	0.004	0.004	0.004	0.004	0.005	0.005	0.004	0.005
Cd	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.004
total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Glass Formulation (g dry additive/g dry waste)								
SiO <sub>2</sub>	0.113	0.000	0.240	0.082	0.207	0.157	0.194	0.108
Al <sub>2</sub> O <sub>3</sub>	0.201	0.201	0.201	0.114	0.146	0.146	0.226	0.145
H <sub>3</sub> BO <sub>3</sub>	0.563	0.766	0.338	0.493	0.000	0.088	0.099	0.176
melt T (°C)	1250	1250	1250	1250	1350	1350	1350	1350

Note: The waste for Sequence C consists of the Silo 3 material alone.

Table 4.15. TCLP Results from the Sequence C 100 g Melts  
(all values are in mg/L)

Analyte	Regulatory	Detection	Result	
	Limit	Limit	100C/1.2	100C/2.2
Arsenic	5.0	0.01	0.016	0.099
Barium	100.0	0.05	<0.05	<0.05
Cadmium	1.0	0.05	<0.05	<0.05
Chromium	5.0	0.05	<0.05	<0.05
Lead	5.0	0.05	0.05	<0.05
Mercury	0.2	0.0004	<0.0004	<0.0004
Selenium	1.0	0.01	<0.01	<0.01
Silver	5.0	0.05	<0.05	<0.05

The observations of the different melts for Sequence C are indicative of the greater difficulty in formulating a glass for the Silo 3 material. However, the results of these melts show that a durable, vitrified product can be made from the Silo 3 material alone. Also significant is the absence of problems with a salt layer in these melts. The glass formulation apparently promotes the decomposition of the sulfates in the waste without requiring the addition of a reducing agent. Another important observation is that the glasses appeared to be very similar over a wide range of compositions. This suggests that a formulation for Silo 3 may be able to effectively tolerate wide ranges in composition. The chosen formulation is very different from typical glass compositions, but it yields a homogeneous product which has passed a TCLP for metals.

#### 4.2.4 Sequence D

The melts for Sequence D consisted of a 70:30 dry weight percent mixture of K-65 and Silo 3 material along with appropriate additives as indicated in Table 4.16. The projected compositions for each of the melts, as well as the melt temperature, are also indicated in the table. Several approaches to develop formulations for this glass were tried. One approach was to make the glass similar to the Sequence A and B glasses by adding soda. Another approach involved making the glass similar to the Sequence C glass by adding alumina. Finally, a combination of the two approaches was tried. Additional melts further developed these initial attempts.

Melt 100D/1.1 consisted of the K-65/Silo 3 mixture with only carbon as an additive. The resulting melts contained many crystalline inclusions and gas bubbles throughout the glass. The addition of sodium to a final composition of 10 weight percent oxide along with carbon was tried in 100D/1.2. The resulting melt was very glossy with some white crystalline inclusions on the surface. The melt also foamed over some. Alumina and carbon were added in 100D/1.3 to a final amount of 10 weight percent alumina in the glass. The melt was crystalline and fairly homogeneous, similar to the Sequence C glasses, but with a larger crystal structure. No foaming was evident. Melt 100D/1.4 included both sodium and alumina as additives. The product had many crystalline inclusions in the glass and some bubbles.

Table 4.16. Glass Formulations and Projected Compositions (wt% oxide)  
for Sequence D 100 g Tests

Element	Melt Number 100D/									
	1.1	1.2	1.3	1.4	2.1	2.2	2.3	3.4	3.1	3.2
Si	52.4	49.3	49.6	43.1	57.0	56.9	44.2	50.7	56.9	56.8
Na	3.6	9.5	3.4	9.5	9.6	14.8	3.1	6.8	14.8	14.8
Pb	9.2	8.6	8.7	7.6	7.0	5.9	7.8	8.9	5.9	5.9
Fe	6.8	6.4	6.4	5.6	5.2	4.4	5.7	6.6	4.4	4.4
Mg	5.3	5.0	5.0	4.4	4.0	3.4	4.5	5.1	3.4	3.4
Al	4.8	4.6	9.9	15.2	3.7	3.1	14.6	4.7	3.1	3.1
Ba	4.7	4.4	4.4	3.9	3.6	3.0	3.9	4.5	3.0	3.0
P	4.3	4.1	4.1	3.6	3.3	2.8	3.7	4.2	2.8	2.8
Ca	3.0	2.8	2.8	2.4	2.3	1.9	2.5	2.9	1.9	1.9
K	1.4	1.3	1.3	1.1	1.0	0.9	1.1	1.3	0.88	0.88
Ni	0.57	0.53	0.54	0.47	0.43	0.37	0.48	0.55	0.37	0.37
Ce	0.39	0.36	0.36	0.32	0.29	0.25	0.32	0.37	0.25	0.25
Mo	0.37	0.35	0.35	0.31	0.28	0.24	0.31	0.36	0.24	0.24
Ti	0.37	0.35	0.35	0.31	0.28	0.24	0.31	0.36	0.24	0.24
La	0.37	0.35	0.35	0.30	0.28	0.24	0.31	0.36	0.24	0.24
Co	0.33	0.31	0.31	0.27	0.25	0.21	0.28	0.32	0.21	0.21
U	0.30	0.28	0.28	0.24	0.23	0.19	0.25	0.29	0.19	0.19
Mn	0.29	0.27	0.27	0.24	0.22	0.19	0.24	0.28	0.19	0.19
V	0.26	0.25	0.25	0.22	0.20	0.17	0.22	0.26	0.17	0.17
Cu	0.23	0.21	0.21	0.19	0.17	0.15	0.19	0.22	0.15	0.15
Li	0.19	0.18	0.18	0.16	0.14	0.12	0.16	0.18	0.12	0.12
Nd	0.18	0.17	0.17	0.15	0.14	0.12	0.15	0.18	0.12	0.12
As	0.13	0.12	0.12	0.11	0.10	0.08	0.11	0.13	0.08	0.08
Th	0.13	0.12	0.12	0.10	0.10	0.08	0.11	0.12	0.08	0.08
Zr	0.08	0.08	0.08	0.07	0.06	0.05	0.07	0.08	0.05	0.05
Sr	0.08	0.07	0.08	0.07	0.06	0.05	0.07	0.08	0.05	0.05
Cr	0.07	0.07	0.07	0.06	0.06	0.05	0.06	0.07	0.05	0.05
Se	0.05	0.05	0.05	0.04	0.04	0.03	0.04	0.05	0.03	0.03
Zn	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.02
Y	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
B	0.011	0.011	0.011	0.009	0.009	0.007	5.3	0.011	0.007	0.007
Be	0.005	0.005	0.005	0.004	0.004	0.003	0.005	0.005	0.003	0.003
Cd	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.002	0.001	0.001
total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Glass Formulation (g dry additive/g dry waste)										
SiO <sub>2</sub>	0.000	0.000	0.000	0.000	0.169	0.268	0.000	0.000	0.268	0.267
Na <sub>2</sub> CO <sub>3</sub>	0.000	0.082	0.000	0.102	0.115	0.247	0.000	0.043	0.247	0.247
Al <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.043	0.102	0.000	0.000	0.093	0.000	0.000	0.000
H <sub>3</sub> BO <sub>3</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.083	0.000	0.000	0.000
C	0.002	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.010	0.005
melt T (°C)	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350

Note: Sn was below detection limits.

For the second set of melts, the compositions were made to be much closer to the successful formulations used in the previous sequences. Silica and soda were added to the waste in 100D/2.1 and 100D/2.2 in amounts to bring the silica and sodium levels in the glasses to a level similar to that of the Sequence A glass. Melt 100D/2.1 foamed significantly, but 100D/2.2 did not foam. The lack of foaming in melt 100D/2.2 was likely a result of the salt layer which formed on the surface of the melt. The glass under the salt layer was glossy with very few crystalline inclusions.

Melt 100D/2.3 included additions of alumina and boric acid to give a glass composition similar to the Sequence C glasses. The resulting melt resembled natural obsidian with some degree of crystallinity. There were no large crystalline inclusions, nor was foaming observed. Of equal interest was the absence of a salt layer, even without the addition of carbon. Melt 100D/2.4 foamed significantly. The final two melts were carried out using the composition of 100D/2.2, but included different carbon additions. Both 100D/3.1 and 100D/3.2 were homogeneous and glossy. The salt layer was absent, but there were more crystalline inclusions than in 100D/2.2.

The TCLP for metals was performed on glass samples from the melts 100D/2.3 and 100D/3.1. Results from these analyses are presented in Table 4.17. Both glasses passed the test with leachate concentrations below the limits. The composition used for 100D/3.1 was chosen for the bench-scale melts. This selection was based on the observation of the very homogeneous and glossy product and the observed ability to decompose the salt layer by addition of carbon with the mix. There was greater confidence that the glossy product would perform well in leachability tests. Further glass development should include an investigation of the composition used in 100D/2.3, since it appears that this formulation may avoid the formation of a salt layer without the need of added reductant.

Table 4.17. TCLP Results from the Sequence D 100 g Melts  
(all values are in mg/L)

Analyte	Regulatory	Detection	Result	
	Limit	Limit	100D/2.3	100D/3.1
Arsenic	5.0	0.01	<0.01	0.024
Barium	100.0	0.05	0.20	0.82
Cadmium	1.0	0.05	<0.05	<0.05
Chromium	5.0	0.05	<0.05	<0.05
Lead	5.0	0.05	0.29	<0.05
Mercury	0.2	0.0004	<0.0004	<0.0004
Selenium	1.0	0.01	<0.01	<0.01
Silver	5.0	0.05	<0.05	<0.05

#### 4.2.5 Conclusions

The Sequence Zero tests were successful in identifying formulations for the Sequences A through D which passed the TCLP for metals. A significant amount of data regarding different

formulations was obtained; the formulations selected for further investigation in the bench-scale tests are listed in Table 4.18. It must be realized that the selection of these formulations was based on very simple criteria (visual appearance and leach resistance) and did not consider other important criteria such as conductivity, viscosity, and phase stability. These glass formulations, therefore, demonstrate the ability to vitrify the different waste streams considered and are a measure of the performance that can be obtained with the vitrified waste form. Further development is necessary, however, to arrive at formulations appropriate for processing in a continuous system.

#### 4.3 BENCH-SCALE TESTING SEQUENCE A TO D TESTS (1000 GRAM MELTS)

Sequence A to D testing was carried out as previously described using the formulations chosen in the Sequence Zero testing also previously described. The Sequence Zero testing allowed the 1000 g melts to be carried out with reasonable confidence that the glass product would meet the objectives of the treatability testing. During the Sequence Zero testing, the system operation and test procedures were tested and modified as required. The Sequence A to D tests were carried out by mixing the appropriate formulation in an alumina crucible, sealing the crucible in the furnace, and then heating the crucible through the appropriate temperature profile. During the test, monitoring or collection of the off-gas was carried out as appropriate. The temperature of the furnace was increased from ambient temperature to 1350°C at the rate of 200°C per hour, held at 1350°C for 2 hours, and then shut off. The melt then cooled at approximately the same rate as the furnace interior (1020°C after 1 hour, 870°C after 2 hours, 630°C after 4 hours, 390°C after 8 hours). After cooling, the melt was removed from the furnace, the gamma dose was rate measured, the crucible was broken up, and the glass samples were collected. General observations from the tests are discussed below, followed by a report of specific test data.

##### 4.3.1 General Observations from the Sequence A to D Melts

The open system tests were carried out as described in the test plan. One observation regarding the operation of the system was a tendency for the off-gas flow rate to drop at the higher temperatures. Because of this, it was necessary to frequently monitor and adjust the flow to keep it constant. The cause of the unsteadiness in the off-gas flow is thought to be related to condensation which was observed in the off-gas lines downstream and upstream of the pump. Apparently, the heat exchanger at the furnace outlet did not remove enough moisture from the off-gas to prevent condensation in the off-gas lines. The radon monitoring procedure developed during the Sequence Zero tests worked very smoothly. The glasses produced in the 1000 g melts were similar to those produced in the Sequence Zero tests, although some differences were observed. The glass from the first melt of Sequence A had some yellow patches on its surface, assumed to be unreduced sulfate. Including additional carbon in the formulation was successful in eliminating the yellow patches in the second melt for Sequence A. A small (about 7 g), reduced metal nodule was observed in the bottom of the open system melt for Sequence A. The Sequence C melt foamed over slightly, which had not been observed in the 100 g melts for the formulation used. In the Sequence D tests a significant salt layer formed on the surface of the melt despite the addition of carbon.

Table 4.18. Glass Formulations and Projected Compositions (wt% oxide) to be Used in the Sequence A to D Tests

<u>Element</u>	<u>Sequence A</u>	<u>Sequence B</u>	<u>Sequence C</u>	<u>Sequence D</u>
Si	54.28	56.32	30.01	56.87
Na	15.15	15.07	5.98	14.76
Pb	10.58	5.18	0.19	5.94
Fe	4.14	3.65	8.11	4.38
Mg	1.49	3.59	10.18	3.43
Al	3.16	8.75	20.01	3.13
Ba	5.42	2.65	0.03	3.03
P	0.73	1.00	9.36	2.80
Ca	1.27	1.43	4.71	1.91
K	0.75	0.72	1.79	0.88
Ni	0.42	0.21	0.52	0.37
Ce	0.44	0.21	0.02	0.25
Mo	0.35	0.17	0.18	0.24
Ti	0.33	0.28	0.22	0.24
La	0.42	0.21	0.01	0.24
Co	0.22	0.11	0.36	0.21
U	0.19	0.09	0.34	0.19
Mn	0.02	0.04	0.68	0.19
V	0.07	0.04	0.50	0.17
Cu	0.07	0.04	0.41	0.15
Li	0.00	0.00	0.48	0.12
Nd	0.21	0.10	0.01	0.12
As	0.02	0.01	0.29	0.08
Th	0.00	0.00	0.32	0.08
Zr	0.09	0.04	0.02	0.05
Sr	0.08	0.04	0.03	0.05
Cr	0.05	0.02	0.08	0.05
Se	0.05	0.02	0.03	0.03
Zn	0.004	0.002	0.07	0.02
Y	NA	NA	0.04	0.01
B	NA	NA	5.0	0.01
Be	0.004	0.002	0.005	0.003
Cd	ND	ND	0.004	0.001
total	100.0	100.0	100.0	100.0
<u>Glass Formulation (g dry additive/g dry waste)</u>				
SiO <sub>2</sub>	0.000	0.000	0.157	0.268
Na <sub>2</sub> CO <sub>3</sub>	0.216	0.207	0.000	0.247
Al <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.146	0.000
H <sub>3</sub> BO <sub>3</sub>	0.000	0.000	0.088	0.000
C	0.002	0.001	0.000	0.010
melt T (°C)	1350	1350	1350	1350

Note: Sn is below detection limits for all sequences.

NA - signifies not analyzed. ND - indicates less than detection limits.

The closed system melts were identical in composition to the open system melts except, in some cases, for differences in the amount of carbon added. The surface of the closed system melt for Sequence A was glossy and free from any salt layer. Upon breaking the crucible and examining the glass, a crystalline nodule of about 30 g in mass was found on the bottom of the crucible, significantly larger in size than the nodule observed in the open system test. Based on its appearance and density, the nodule appears to be lead sulfide. Apparently, the additional carbon which was included to remove the yellow patches observed on the surface in the open system melt, along with the less oxidizing atmosphere in the closed system, led to the formation of reduced metal sulfides. The Sequence C melt again foamed over slightly. Additionally, during the Sequence C test, power to the furnace was temporarily lost. As a result, the temperature dropped several hundred degrees just before the soak period of the temperature profile. When power was restored, the temperature was ramped back up and held at the melt temperature for 2 hours. The main result of this temperature drop was more corrosion of the crucible than occurred in the open system test. For the Sequence D closed system melt, the carbon addition was decreased. It was thought that the reducing atmosphere of the sealed furnace would be sufficient to decompose the salt layer. This was not the case and a salt layer was again formed.

The formation of a salt layer from sulfates in the waste appears to be an issue with the melts containing K-65 material. The presence of molten salts can have both positive and negative effects. Molten salts can accelerate melting and enhance the release of gases from the melt. However, the molten salt layer is typically more corrosive to refractories than is the glass. A salt phase which continually increases in size would lead to processing problems. Finally, if the molten salt exits the melter with the glass product, the waste form quality could be compromised. Two means for dealing with the salt layer have been demonstrated in these tests; one is to decompose the sulfate through appropriate additives, and the other is to devise a glass formulation in which the salt layer does not form. Decomposing the sulfate by adding carbon to the formulation presents the difficulty of possibly overreducing the melt, leading to the formation of reduced metal phases. The formation of a reduced metal phase is not desirable unless a means of dealing with this secondary waste form (both in processing and disposal) is included in the treatment plan. Nevertheless, the addition of carbon to the formulation may be a viable means of dealing with the sulfates. Developing a glass formulation which prevents the formation of a salt layer without requiring the addition of carbon is another option for dealing with sulfates in the waste. Melts from Sequence C showed that certain formulations did not form a salt layer, even with a sulfate content of up to 15 percent in the waste, while the 100 g melts from Sequence D demonstrated that the formation of a salt layer in the absence of a carbon addition could be avoided through changes to the formulations. Such a formulation would not have a problem with reduced metal phases brought about by the addition of carbon to the glass formulation.

#### 4.3.2 Glass Formulation Data

Table 4.19 reports the formulation data for each of the eight tests. The mass of material as well as the measured moisture content of all components of the formulations are reported. Additionally, various masses are reported. The total dry weight is the mass of dry material

before vitrification. The total glass is the measured mass of material in the crucible after vitrification. The total oxide from formers is the calculated mass present in the final glass that came from the nonwaste additives. The total oxide from waste is calculated as the difference between the mass of the glass and the mass of the oxide from formers. The waste loading is defined as the mass fraction of waste material in the final waste product. It is obtained by dividing the total amount of oxide from the waste by the total amount of glass. Expressed as a percent, the waste loading ranges from 66 percent for Sequence C to 89 percent for Sequence B.

Table 4.19. Glass Formulation Data for Sequence A through D Bench-Scale Melts

Component	% H <sub>2</sub> O	Test Number							
		AO.1	BO.1	CO.1	DO.1	AC.1	BC.1	CC.1	DC.1
Weight in grams:									
K-65	(a)	1518	741	---	887	1509	756	---	908
Silo 3	(a)	---	---	1045	283	---	---	1045	283
BentoGrout	8.1	---	577	---	---	---	577	---	---
Na <sub>2</sub> CO <sub>3</sub>	6.4	247	233	---	229	247	233	---	229
SiO <sub>2</sub>	0.3	---	---	159	193	---	---	159	193
Al <sub>2</sub> O <sub>3</sub>	0.1	---	---	147	---	---	---	147	---
H <sub>3</sub> BO <sub>3</sub>	---	---	---	88	---	---	---	88	---
Carbon	4.7	2	2	---	9	5	2	---	4
total		1767	1553	1439	1601	1761	1568	1439	1617
% Water In <sup>(a)</sup> :									
K-65 Mix		28.6	28.5	---	28.2	28.2	29.9	---	29.9
Silo 3 Mix		---	---	3.5	3.6	---	---	3.5	3.6
Weights in grams:									
total dry weight		1317	1280	1402	1325	1319	1280	1402	1320
total glass <sup>(b)</sup>		1117	1109	1038	1104	1102	1111	1032	1113
oxide from formers		135	127	355	317	135	127	355	317
oxide from waste		982	982	683	787	967	984	677	796
Waste Loading		0.88	0.89	0.66	0.71	0.88	0.89	0.66	0.72

Notes:

- (a) The moisture content of the waste material was measured before the various runs.  
 (b) This is the mass of glass actually produced from the melt.

#### 4.3.3 Radon Emanation During Vitrification

Figure 4.1 shows the measured radon concentration profiles in the vitrification off-gas during the vitrification tests. Superimposed on the figure is the approximate temperature profile during the tests. The temperature profile and the radon concentration profiles may not exactly correspond because of mixing in the furnace volume and in the delay chambers. The peaks in radon concentration are also broadened because of this mixing of the off-gas. Table 4.20 compares the total activity released during the course of vitrification to the theoretical maximum

radon activity initially present in the waste. These measurements indicate that essentially all the radon initially present in the waste is released during vitrification.

Table 4.20. Radon Released During Vitrification of OU4 Material ( $\mu\text{Ci}$ )

<u>Sequence</u>	<u>Measured Rn-222 Activity<sup>(a)</sup></u>	<u>Maximum Rn-222 Activity<sup>(b)</sup></u>
A	320	363
B	151	178
C	5	5
D	199	215

Notes:

- (a) Obtained by integrating the emanation profile from the open system run and multiplying by the flow rate.  
 (b) Equal to the Ra-226 activity in the waste being vitrified.

The observation that all of the radon in the sample is released during vitrification is not unexpected. Typically, only a fraction of the radon in soil escapes from the material. Radon must escape from the solid grains and then diffuse out of the pore space. During vitrification, a convective flow from the pores will occur due to gas expansion, greatly enhancing radon transport from the pore volume. Additionally, gases are generated during the melting process, first from vaporization of water and then from decomposition of the solid material (carbonates, nitrates, sulfates). This will provide an added convective flow, further enhancing radon transport from the solid material. The shape of the emanation profile seems to indicate that convective transport from the generation of gases is the most significant factor.

The shape of the emanation profiles is distinctly bimodal, with the first peak at about 300°C and the second peak at about 800°C to 900°C. The first peak is thought to result from water vapor being driven from the material and carrying with it radon from the pore spaces. The second peak is centered at the temperatures where significant glass-forming reactions begin to take place. The structure of the solid material begins to break up freeing much of the radon previously trapped within the solid matrix. These reactions also generate significant volumes of gas from the carbonates, nitrates, and sulfates present in the material. The generation of gases, along with the changing solid structure during melting, is thought to be the cause of the second peak.

A comparison of the radon emanation from the initial waste with the radon emanation from the molten material shows that they are approximately equal, indicating that radon release from the molten material is not enhanced relative to the nonvitrified residue.

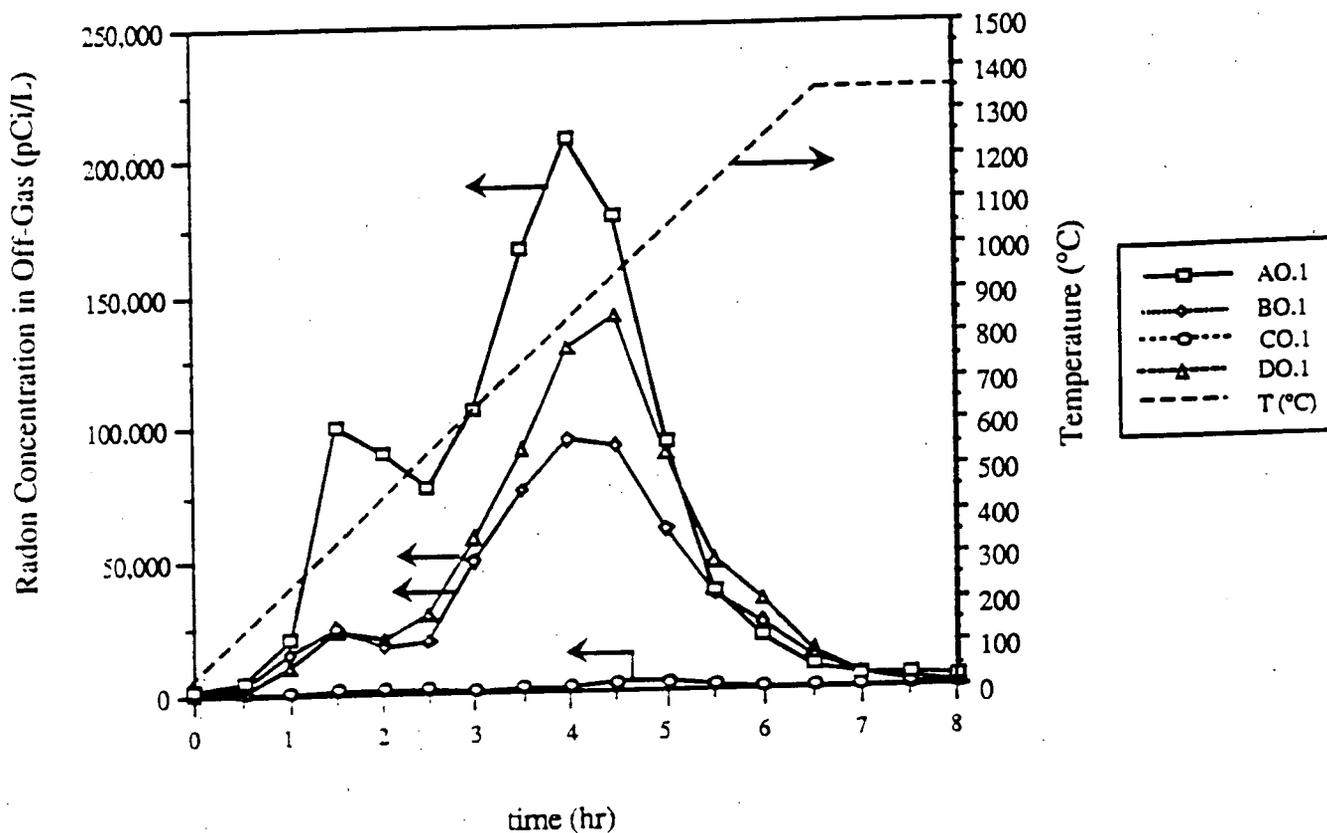


Figure 4.1. Radon Emanation Profiles During Bench-Scale Vitrification of OU-4 Material (Off-Gas Flow Rate of 9.4 L/min)

Three important conclusions can be drawn from this data. First, the design value for the maximum radon concentration in the off-gas should be based upon the maximum theoretical amount of radon present in the material determined from the radium-226 content of the waste. Second, once the material is retrieved, it should be fed to the melter as soon as possible to minimize the overall radon generation in the process. This assumes that retrieving and conveying the material will release a significant fraction of the radon contained in the material. This radon release must be captured and controlled. If the material is then stored at another location for several days, the radon concentration will again build to equilibrium levels, and when the material is moved or vitrified, the radon will be released again. If the material is fed to the melter soon after retrieval, less radon will be contained in the sample since equilibrium levels will not have been reached, and release from the vitrification process will be reduced. Finally, these tests indicate that radon emanation from the molten waste material is not enhanced relative to the untreated residue.

#### 4.3.4 Radon Emanation from the Vitrified Waste

Table 4.21 reports the radon emanation measured from the vitrified waste. The total activity in equilibrium with the glass sample is reported along with the radon emanation rate. The glass used in the emanation measurements is from the fraction which passed through a 0.16 inch (4 mm) screen and was retained on a 0.09 inch (2.4 mm) screen. The surface area was estimated by assuming all the particles were spherical with a diameter of 0.16 inch (4 mm). The area calculated in this manner is a conservative minimum value, since most particles are not spherical (hence have more area for a given volume of glass) and since the largest particle which could pass through the screen was assumed to be the size of all particles. Using the minimum surface area of the sample to calculate the radon emanation rate results in a conservative estimate of the maximum rate.

Table 4.21. Radon Emanation from Vitrified Waste

Test Number	Sample Mass (g)	Estimated Area (m <sup>2</sup> )	Radon Activity (pCi) at:		Radon Emanation Rate (pCi/m <sup>2</sup> /s) at:	
			7 days	30 days	7 days	30 days
AO.1	12.7	0.0068	79.4	190.5	0.025	0.059
AC.1	14.3	0.0077	86.4	148.4	0.024	0.041
BO.1	9.6	0.0051	34.3	59.3	0.014	0.024
BC.1	18.0	0.0096	27.5	41.3	0.006	0.009
DO.1	10.4	0.0056	42.6	78.9	0.016	0.030
DC.1	21.5	0.0115	69.7	109.0	0.013	0.020

It is important to note that the 7-day measurements reported here are likely to be somewhat lower than the true 7-day value. The 7-day values were obtained by circulating air from the sample container through the monitor in a closed system until equilibrium was reached. There were indications of loss of radon, possibly through either absorption in the system or leakage. The 30-day measurements eliminated this problem by using a grab-sampling monitoring method

to measure the concentration that had built up in the closed sample container. The 30-day values are therefore felt to be the most accurate measurement of the radon emanation rate.

The emanation rates measured here are an order of magnitude lower than those measured in previous tests (Janke and Chapman, 1991). Previous tests measured the radon emanation from the crucible containing the vitrified residue using a once through flow system assuming the cross sectional area of the crucible was the emanating area. In a crucible melt, as the material begins to slump and reduce in volume, some amount of material typically remains on the walls of the crucible. Since this material is separated from the bulk of the glass melt, it often never fully vitrifies. Additionally, the walls of the crucible become coated with glossy glaze. The greater emanation observed in the previous tests is thought to result from this partly-vitrified material that remains on the crucible walls.

Vitrification of the K-65 waste is shown to result in a significant reduction in the radon emanation rate. A direct comparison is difficult, since emanation from the waste is dependent on the volume of material present, while for the vitrified residue, the emanation depends upon the exposed surface. A qualitative comparison using data from test AO.1 shows a reduction from about 30,000 pCi/m<sup>2</sup>/s prior to vitrification to 0.059 pCi/m<sup>2</sup>/s for the vitrified residue (at 30 days), a decrease of more than 500,000 times. A large measure of the reduction is due to the monolithic nature of the vitrified waste. The vitrified waste traps the radon within the glass volume allowing only radon generated at the surface to escape. An additional mechanism for reduction in the radon emanation rate is a more uniform distribution of radium through the waste. A current hypothesis is that radium is concentrated on the surfaces of soil particles and is not uniformly distributed throughout the material (Nazaroff and Nero, 1988). The emanation from a soil particle would therefore be greater than from a particle of vitrified waste in which the radium was uniformly distributed.

The measured emanation rates from the vitrified residue are two to three orders of magnitude less than the EPA limit of 20 pCi/m<sup>2</sup>/s for emanation from mill tailings. Also of interest is the fact that the observed radon emanation rates from the vitrified K-65 residue are similar in magnitude to emanation rates from normal building materials such as brick or concrete, despite a radium content as much as 1,000,000 times higher. Typical emanation rates for walls or slabs of concrete range from 0.015 to 0.225 pCi/m<sup>2</sup>/s and for brick range from 0.015 to 0.038 pCi/m<sup>2</sup>/s (Nazaroff and Nero, 1988).

#### 4.3.5 Waste Volume Reduction

Table 4.22 reports the specific gravity of the vitrified waste along with the calculated volume reduction. The volume reduction is based upon the difference between the volume of the final glass product (including additives) and the initial volume of the waste in its current state. The waste volume was calculated using the wet, compacted density, which is assumed to be the most representative of the material in its current state. Significant volume reductions ranging from 50 percent to 68 percent are achieved through vitrification of the waste. In other words, the

final waste volume ranged from 32 percent of the initial waste volume at best to only 50 percent at the worst.

Table 4.22. Waste Volume Reduction Achieved through Vitrification

<u>Test Number</u>	<u>Volume of Waste (mL)</u>	<u>Specific Gravity of Glass</u>	<u>Mass of Glass (g)</u>	<u>Volume of Glass (mL)</u>	<u>% Volume Reduction</u>
AO.1	857.4	2.87	1116.6	389.1	54.6
AC.1	852.7	2.84	1102.2	388.1	54.5
BO.1	916.0	2.69	1109.1	412.4	55.0
BC.1	924.3	2.68	1111.1	415.1	55.1
CO.1	1135.8	2.86	1037.5	363.0	68.0
CC.1	1135.8	2.84	1032.2	363.3	68.0
DO.1	808.7	2.75	1104.1	401.9	50.3
DC.1	820.9	2.75	1113.9	404.3	50.7

#### 4.3.6 Modified TCLP Data

A 100 g sample of glass from each of the tests was used in performing a modified TCLP<sup>2</sup> for metals. Table 4.23 presents results from these analyses. The purpose of these analyses was to provide an initial confirmation of the durability of the glass product prior to carrying out further analyses. The leachate concentrations of the TCLP metals were below regulatory limits for all the glasses. Lead and barium were the two metals consistently detected in the leachate from the K-65 glasses (Sequences A, B, D), and arsenic was the only detectable analyte in the leachate from the Silo 3 glasses (Sequence C). The presence of chromium indicated in the leachate from AO.1 is thought to result from transposition of the result for lead at the analytical laboratory contracted to perform these tests; however, although the laboratory rechecked the data, no error could be found. Chromium was below detection limits for all other samples analyzed (including the 100 g tests) and is only present in trace amounts in the initial waste, while the absence of lead in the leachate is inconsistent with previous results.

<sup>2</sup>The modified TCLP, as it applies to the identified vitrification tests, is defined as analysis of the vitrified product for leachability of the following heavy metals: Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver. Based on the available EP toxicity data (Buel, 1989) from the previous vitrification test, all of the heavy metals from the EP toxicity list, with the exception of lead, were below the regulatory limits.

Table 4.23. Modified TCLP Results from the Bench-Scale Melt Glasses  
(all values are mg/L)

Analyte	Regulatory Limit	Test Number							
		AO.1	AC.1	BO.1	BC.1	CO.1	CC.1	DO.1	DC.1
Arsenic	5.0	0.06	ND	ND	ND	0.20	0.09	0.01	0.01
Barium	100.0	1.15	0.10	ND	0.24	ND	ND	0.36	0.51
Cadmium	1.0	ND	ND	ND	ND	ND	ND	ND	ND
Chromium	5.0	0.20	ND	ND	ND	ND	ND	ND	ND
Lead	5.0	ND	0.10	ND	0.28	ND	ND	0.15	0.24
Mercury	0.2	ND	0.0008	ND	ND	ND	ND	ND	ND
Selenium	1.0	ND	ND	ND	ND	ND	ND	ND	ND
Silver	5.0	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND - indicates less than detection limits which are: arsenic, 0.01; barium, 0.05; cadmium, 0.05; chromium, 0.05; lead, 0.05; mercury, 0.0004; selenium, 0.01; silver, 0.05.

#### 4.3.7 Full TCLP

A sample of the vitrified product from the Sequence A through D bench-scale melts was crushed and sieved to a particle size of less than 0.16 inch (4 mm) in diameter and sent to an independent analytical laboratory where the TCLP was performed and the leachate analyzed. Table 4.24 reports the average leachate concentrations for the sequence A through D glasses. The results presented are the average of the two glasses from each sequence. While the absolute leachate concentrations are useful for determining compliance with regulatory limits for the specific metals to which the test applies (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver), the fractional release is a more significant measure of the leaching of the glass, since it relates the leachate concentration of each element to its initial concentration in the glass. The fractional release is the total amount of an element leached from the sample divided by the total amount of that element initially present in the sample. Table 4.25 reports the fractional release from the Sequence A through D glasses.

Table 4.24. TCLP Leachate Concentrations from the Bench-Scale Melt Glasses

<u>Element (mg/L)</u>	<u>Sequence A</u>	<u>Sequence B</u>	<u>Sequence C</u>	<u>Sequence D</u>
Ag	ND	ND	ND	ND
Al	0.155	0.285	0.397	0.126
As	0.004	0.016	0.628	0.052
B	0.017	0.029	1.281	0.009
Ba	0.779	0.495	0.051	1.780
Be	ND	ND	0.003	ND
Ca	0.295	0.683	8.590	1.218
Cd	ND	ND	0.009	ND
Co	0.024	0.011	0.112	0.028
Cr	ND	ND	ND	ND
Cu	0.029	0.030	0.381	0.085
Hg	ND	ND	ND	ND
K	0.248	0.249	0.685	0.272
Li	ND	ND	0.382	ND
Mg	0.144	0.360	11.910	0.587
Mn	0.006	0.035	0.991	0.039
Mo	0.037	0.032	0.261	0.036
Na	ND	ND	ND	ND
Ni	0.052	0.078	ND	0.060
P	0.070	0.450	9.535	0.860
Pb	1.003	0.425	0.018	0.538
Sb	ND	ND	ND	ND
Se	ND	ND	ND	ND
Si	1.750	1.295	2.645	1.585
Th	0.040	0.003	0.001	0.005
U	0.038	0.026	0.285	0.034
V	ND	0.009	0.380	0.028
Zn	0.054	0.072	0.049	0.048
<hr/>				
<u>Radionuclides (pCi/L)</u>				
Pb-210	3470	1690	55	2170
Ra-226	4415	2553	45	2145
Th-230	502	123	17	125
Th-232	ND	ND	ND	ND
U-238	ND	ND	95	11

Note: ND - indicates the leachate concentration was below detection limits.

Table 4.25. TCLP Fractional Release from the Bench-Scale Melt Glasses  
(expressed as %)

<u>Element</u>	<u>Sequence A</u>	<u>Sequence B</u>	<u>Sequence C</u>	<u>Sequence D</u>
Ag	ND	ND	ND	ND
Al	0.018	0.012	0.007	0.015
As	0.059	0.444	0.576	0.162
B	ND	ND	0.165	ND
Ba	0.032	0.042	0.341	0.131
Be	ND	ND	0.151	ND
Ca	0.051	0.121	0.507	0.169
Cd	ND	ND	ND	ND
Co	0.028	0.027	0.078	0.033
Cr	ND	ND	ND	ND
Cu	0.099	0.211	0.232	0.145
Hg	ND	ND	ND	ND
K	0.036	0.038	0.074	0.037
Li	ND	ND	0.344	ND
Mg	0.032	0.033	0.388	0.057
Mn	0.065	0.238	0.377	0.054
Mo	0.028	0.050	0.310	0.038
Na	ND	ND	ND	ND
Ni	0.031	0.096	ND	0.042
P	0.044	0.206	0.467	0.141
Pb	0.020	0.018	0.016	0.019
Sb	ND	ND	ND	ND
Se	ND	ND	ND	ND
Si	0.014	0.010	0.038	0.012
Th	ND	ND	0.001	0.015
U	0.046	0.064	0.188	0.040
V	ND	0.078	0.221	0.050
Zn	3.007	8.272	0.172	0.580
Pb-210	0.031	0.030	0.017	0.034
Ra-226	0.030	0.034	0.029	0.026
Th-230	0.017	0.008	0.0003	0.004
Th-232	ND	ND	ND	ND
U-238	ND	ND	0.136	0.050

Note: ND - indicates leachate concentration was below detection limits or the initial concentration of the element was not known.

The TCLP test was developed as a means of determining the toxicity characteristic of a material in order to classify materials as hazardous or nonhazardous prior to disposal in a landfill. The TCLP leachate concentrations presented in Table 4.24 show that the vitrified material in all cases tests nonhazardous by the TCLP, meaning the leachate concentrations of the TCLP metals were below regulatory limits. Previous testing of the K-65 and Silo 3 material by the Extraction Procedure (EP) Toxicity Test (precursor to the TCLP) have found the leachate concentrations of lead from the K-65 material, and arsenic, cadmium, chromium, and selenium from the Silo 3 material, to exceed the regulatory limits (Janke and Chapman, 1991; U.S. DOE, 1990). A comparison of the data from the untreated and vitrified residue shows that lead concentration in the leachate is reduced about 500 times for the K-65 residue, arsenic concentration in the leachate is reduced about 100 times for the Silo 3 material, and cadmium, chromium, and selenium concentrations are reduced to near or less than detection limits. The vitrified product effectively immobilizes the hazardous elements and reduces their release to levels less than the regulatory limits.

The results from these 1000 g melts confirm the previous results obtained from the 100 g test melts; however, a general difference is noted between the results from the two tests. The concentration of elements present in significant amounts (lead, barium, and arsenic) in the leachate of the 1000 g melt samples was generally 2 to 4 times greater than the concentration of the same elements in the leachate from the corresponding 100 g melt. The probable cause of the observed differences is related to the size to which the sample was crushed. The glass samples from the 1000 g test melts were crushed at the treatability laboratory to a size of less than 0.16 inch (4 mm) prior to TCLP testing (a factor of two less than the maximum size limit of 0.37 inch (9.5 mm) required by the TCLP procedure), while the samples from the 100 g tests were crushed to meet the 0.37 inch (9.5 mm) size limit at the laboratory performing the tests. The surface area of the 100 g melt samples was therefore greater than that of the 1000 g melt samples by at least a factor of 2. Thus, the difference in particle size appears to account for the observed differences between the TCLP results of the 100 g and 1000 g melts. Results from previous TCLP testing of vitrified K-65 material closely agree with the results obtained from the TCLP testing of the 100 g melts in the current tests (Janke and Chapman, 1991).

The fractional release data presented in Table 4.25 normalizes the leachate concentration of an element based on its initial concentration in the TCLP sample, providing a basis for comparing the leach rate of different elements. The fractional release of elements present in the glass at concentrations greater than 0.1 weight percent for the Sequence A and B glasses generally ranges from about 0.01 percent to 0.1 percent. The fractional release is in this same range for some of these elements in the Sequence C and D glasses, while for other elements, the fractional release is an order of magnitude higher, indicating that some elements (mainly Mg, Ca, Ba, and P for both sequences, and a number of other elements for Sequence C) were leached at greater rates. The radionuclides (including radium-226) were observed to leach at the lower rates for all the glasses. Although some elements appeared to be leached at higher rates from the Sequence C and D glasses, the ability of the glasses to retain the hazardous constituents was not compromised. Radionuclides (including radium-226) were leached from the glass at the lower rate comparable to silica, alumina, and lead.

The fractional release for elements present in the glass in small amounts typically shows a great degree of variation, since a small change in the leachate concentration results in a large change in the fractional release rate. Most notable for the results presented here is the fractional release observed for zinc. A likely contamination source for zinc was the brass screens through which the material was sieved. A small amount of contamination would result in a large fractional release for Sequence A and B glasses because of the extremely low concentration of zinc in the glass, while the effect is much less for Sequence C and D glasses because of their higher zinc content. Contamination from the brass screens could also have affected the fractional release values for copper, although not as significantly because copper is present in higher concentrations.

The TCLP was also performed on untreated samples of K-65 material from each zone of Silos 1 and 2 and on untreated samples of Silo 3 material. The leachate from each test was analyzed for radionuclides. Table 4.26 reports leachate concentrations for untreated K-65 and Silo 3 materials. The values for each zone of the K-65 material were averaged to give a composite leachate concentration representative of leaching from the mix of K-65 material that was used in the treatability tests. The leachate concentrations from each zone were averaged in proportion to the amount of the material from each zone in the mix of K-65 material. Table 4.27 reports the fractional release of several radionuclides from the untreated waste. Only a few radionuclides are listed because initial concentrations of the other radionuclides in the waste were not known.

Table 4.28 presents a comparison of the leachate activity from the untreated wastes to the leachate activity from the vitrified wastes. A wide variation in reduction in leaching of the various radionuclides achieved through vitrification is observed. While leaching of actinium-227 from the untreated waste is reduced by a factor of thousands of times through vitrification, leaching of some radionuclides is unchanged. The low ratios observed do not necessarily indicate a failure of the glass to immobilize some of the radionuclides. The ratios show that some radionuclides are not leached as readily as others from the untreated waste. This is demonstrated clearly by the data in Table 4.27. While nearly 9 percent of the lead-210 in the K-65 material is leached from the untreated waste, only 0.45 percent of the radium-226 and 0.01 percent of the thorium-230 are leached. Such differences can arise because of differences in solubility among the various elements at the conditions encountered in the leachate (Reimus et al., 1988; Strachan et al., 1985). The leaching of radium-226 will be considered as an example of how solubility limitations affect the leaching results.

Table 4.26. TCLP Leachate Concentrations from Untreated OU4 Material

<u>Radionuclides (pCi/L)</u>	<u>K-65</u>	<u>Silo 3</u>
Ac-227	5474	15
Pa-231	(a)	(a)
Pb-210	763,694	(b)
Po-210	79,796	119
Ra-226	53,194	1954
Ra-228	48	(a)
Th-228	60	3
Th-230	285	17
Th-232	6	(a)
U-234	1063	85
U-235/236	50	4
U-238	1089	87
<hr/>		
<u>Elements<sup>(c)</sup> (mg/L)</u>		
Pb	630	
Ba	0.76	

## Notes:

- (a) Leachate concentration was less than detection limits.  
 (b) Pb-210 concentration in blank leachate was greater than in the leachate from Silo 3; assume zero concentration.  
 (c) Data for Pb and Ba for K-65 material are from Janke and Chapman (1991).

Table 4.27. TCLP Fractional Release from the Untreated OU4 Material (expressed as %)

<u>Element</u>	<u>K-65</u>	<u>Silo 3</u>
Pb-210	8.6	ND
Ra-226	0.45	0.87
Th-230	0.01	0.0003
U-238	ND	0.09
Pb	15	ND
Ba	0.03	ND

Note: Values for Pb and Ba are based upon data from Janke and Chapman (1991).

ND - Not detected.

Table 4.28. Ratio of the Activity in the Leachate from the Untreated Waste to the Activity in the Leachate from the Vitrified Waste

<u>Radionuclide</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Ac-227	3655	> 2737	> 10	1856
Pb-210	229	226	ND	246
Po-210	186	137	15	217
Ra-226	12	12	44	18
Ra-228	4	2	ND	1
Th-228	12	20	2	17
Th-230	1	1	2	2
Th-232	> 3	> 3	ND	> 4
U-234	90	52	1	68
U-235/236	> 50	> 15	1	> 34
U-238	89	75	1	70

Note: ND - indicates activity in leachate from glass was less than detection limits.

Radium sulfate has limited solubility in aqueous solution ( $K_{sp} = 4 \times 10^{-15}$  in cold water, although the solubility is likely to be somewhat different from this value at the conditions of the TCLP leachate), so only very small amounts of radium can be in solution when the leachate contains significant amounts of sulfates. At a sulfate concentration of 50 mg/L, the maximum radium concentration in a water solution is about 2000 pCi/L. If more radium were added to a solution at these conditions, the additional radium would precipitate as radium sulfate, and the solution concentration of radium would remain unchanged. Therefore, if the concentration of radium in the leachate from a material is limited by the solubility of radium sulfate, the radium concentration will not reflect the extent of the dissolution of the waste.

A comparison of the concentrations of radium and barium in the leachate from the untreated and vitrified residues indicates that the radium concentration in the TCLP leachate is likely to be solubility limited in the case of untreated waste, while from the vitrified residue, the radium concentration appears to be limited by the leaching of radium from the glass. The ratio of the molar concentration of barium to radium in the leachate from the untreated waste is approximately 23,000, while the ratio of the solubility product of barium sulfate to that of radium sulfate is about 29,000. The similarity of these two numbers, along with the observation that the sulfate concentration is sufficiently high (estimated at 50 mg/L) to approach the solubility limits of these two elements, indicates that the solution is saturated with radium and barium. Therefore, the radium concentration in solution will not be proportional to the amount of solid which has dissolved. In contrast, the ratio of the molar concentration of barium to radium in the leachate from the vitrified K-65 residue is 262,000, an order of magnitude higher than the ratio of the solubility products, indicating that the radium concentration in solution is not limited by the solubility of radium sulfate. The leachate concentration of radium should therefore be proportional to the degree of dissolution of the vitrified material, as was observed.

Consideration of solubility limitations explains the large variations observed in the fractional release from the untreated K-65 material. The relatively high sulfate concentration in the leachate prevented additional radium and barium from entering solution once the saturation limit was reached, while the more soluble lead sulfate was leached into solution to a much greater extent. For the vitrified waste, the fractional releases of radium, barium, and lead from the glass were approximately equal, indicating the absence of solubility limitations. The absence of solubility limitations would be expected since both radium and sulfate concentrations in the leachate from the vitrified waste are at least an order of magnitude lower than from the untreated waste.

Although the above discussion is somewhat qualitative, it provides an explanation based upon the available data for the observed leaching behavior of radium-226 from the vitrified and untreated K-65 material. Solubility limitations are likely to be a factor for other radionuclides also, explaining the wide range of values presented in Table 4.28.

The TCLP results for the vitrified wastes demonstrated the effectiveness of glass as a waste form for the OU4 wastes. Leachate concentrations of hazardous metals were below regulatory limits for all of the glasses made in these tests. The TCLP leachate concentration of lead from the vitrified residue is about 500 times less than from the untreated waste. Radionuclides (in particular, radium-226) were found to leach from the glasses at the same rate as the major glass constituents, indicating the absence of selective leaching of radionuclides. A comparison of TCLP data from the untreated and vitrified residues indicates that leaching of radium (and probably other radionuclides) from the untreated waste is limited by solubility constraints, resulting in a relatively low concentration of radium in the leachate from the untreated waste.

#### 4.3.8 Product Consistency Test (PCT)

Leach testing was also performed on samples from each of the melts using the PCT. The PCT is a 7-day static leach test developed for the high-level waste vitrification program. The test uses deionized water at 90°C to leach a glass sample which has been crushed and sieved to a size fraction of -100/+200 mesh. The PCT leach test was performed at the treatability laboratory on samples of the vitrified product from the Sequence A through D bench-scale melts. The leachates obtained from these tests were sent to an independent laboratory for analysis. Table 4.29 presents the measured PCT leachate concentrations for the Sequence A through D glasses (average of the two glasses from each sequence).

Table 4.29. PCT Leachate Concentrations for the Bench-Scale Melt Glasses

Elements ( $\mu\text{g/L}$ )	Sequence			
	A	B	C	D
K	1620	561	1383	1605
Na	124,983	40,650	7132	59,800
Si	69,867	34,633	14,850	58,467
Li	ND	ND	689	242
B	144	77.4	2052	151
U	0.9	11.2	14.7	2.1
Th	ND	ND	7.1	4.0
<b>Radionuclides (pCi/L)</b>				
Ra-226	7810	1445	<1323	2520

Note: ND - indicates the leachate concentration was less than detection limits.

The absolute leachate concentrations reported above are not an accurate measure of the leach rate of the glass. The leachate concentration is greatly dependent on the surface area to volume ratio of the sample material, the duration of the leach test, and the initial concentration of the element in the sample. For this reason, leach rates are typically expressed as grams of an element leached per square meter of surface per day, normalized based upon the initial concentration of the element in the sample. Therefore, the normalized leach rate for each element represents the rate at which the glass would be leached if the glass as a whole were leached at the same rate as that element. Table 4.30 reports the normalized leach rates determined using the data from Table 4.29.

Table 4.30. Normalized Leach Rates for 7-day PCT Leaching of Bench-Scale Melt Glasses ( $\text{g/m}^2/\text{day}$ )

Element	A	B	C	D
K	0.019	0.007	0.007	0.016
Na	0.079	0.026	0.011	0.039
Si	0.020	0.009	0.008	0.016
Li	(a)	(a)	0.022	0.031
B	(a)	(a)	0.009	(a)
U	(b)	0.0010	0.0003	0.0001
Th	(a)	(a)	0.0002	0.0004
Ra-226	0.0019	0.0007	(b)	0.0011

## Notes:

- (a) Initial concentration in glass is not known.  
 (b) Leachate concentration was less than the detection limit.

The normalized leach rates reported above indicate that all of the glass formulations tested exhibit exceptional durability comparable to glasses developed for the vitrification of high-level wastes. The normalized leach rates for the Sequence A to D glasses are an order of magnitude less than the Defense Waste Processing Facility Environmental Assessment (EA) glass leach rates (Jantzen et al., 1992) and are comparable to those measured for simulated high-level waste glasses (Piepel et al., 1989). Leach rates for the EA glass were found to be 0.28 g/m<sup>2</sup>/d for silica and 0.97 g/m<sup>2</sup>/d for sodium, while for simulated waste glasses, typical values were 0.03 g/m<sup>2</sup>/d for silica and 0.07 g/m<sup>2</sup>/d for sodium. The EA glass is designed to be a standard representing the maximum acceptable leach rate for high-level waste glasses; therefore, the Sequence A to D glasses are substantially more durable than the minimum standard for high-level waste glasses. The leaching of radionuclides in the PCT was one to two orders of magnitude less than leaching of the major elemental constituents of the glass. These low values are likely to be a result of solubility limitations in the leachate.

A comparison of the PCT data to the TCLP data is difficult, if not impossible. The tests are carried out at very different conditions, and wide variations in the results are possible. Past experience has shown that a glass which is durable under neutral conditions is often attacked under acidic conditions, and vice versa (Chick et al., 1981). Absolute concentrations in the leachate from the two tests are not comparable, nor is a fractional release rate, because the surface area of the sample in the PCT is as much as a factor of 50 higher than the area of the TCLP sample. PCT data are normalized to a leach rate per unit surface area of the sample, while the lack of a well defined surface area prevents an accurate presentation of TCLP data on this basis; however, a normalized leach rate can be crudely estimated for the TCLP by estimating the surface area of the sample.

Using the most conservative estimate of the surface area for the TCLP (assuming all particles are spherical with a diameter of 0.16 inch (4 mm), giving the minimum surface area for leaching and hence the maximum leach rate), the estimated leach rates observed in the TCLP tests are in the range of 0.2 to 1 g/m<sup>2</sup>/d (except for the previously identified elements selectively leached from the Sequence C and D glasses). The TCLP appears to leach the glass more aggressively than the PCT; however, the points discussed above must be considered. The difference between the acid conditions of the TCLP and the neutral to basic conditions of the PCT can result in great differences in the leaching behavior. Additionally, most particles are smaller than the mesh size through which they pass and substantial quantities of very fine particles are generated during crushing of the TCLP sample; therefore, the actual surface area of the TCLP sample is likely to be greater than the value estimated above, resulting in an inflated value of the normalized leach rate.

The results of leaching the Sequence A through D glasses by the PCT have shown these glasses to be very durable on a comparable basis to glasses developed for the disposal of high-level waste. A semiquantitative comparison of the PCT results to the TCLP results indicates that the glasses may be more aggressively leached by the TCLP. Nevertheless, the PCT leach testing has demonstrated a high degree of durability for the vitrified OU4 wastes.

#### 4.3.9 Viscosity and Electrical Conductivity

The viscosity and electrical conductivity of the glasses from the Sequence A to D tests were measured as a function of temperature. Measurements were made using 100 to 140 g of glass from the open system melts. Figures 4.2 and 4.3 present results of these measurements, which are plotted as the logarithm of the viscosity versus inverse temperature. Straight lines indicate that the viscosity data demonstrate typical temperature dependence for glass melts (Kingery, 1976). Using curve fitting techniques, the viscosity and conductivity of the glasses were predicted every 100°C over the range from 1150°C to 1450°C. Tables 4.31 and 4.32 report these values. Only the glass from Sequence A was measured over this entire temperature range. Samples from Sequences B and D were not measured at the higher temperatures because of reboil of the glass at temperatures above about 1375°C. For the Sequence C glass, the viscosity was below the measurement limits of the test apparatus above about 1400°C. These extrapolated values should be used with caution.

Table 4.31. Glass Viscosity as a Function of Temperature (Pa•s)

<u>Sequence</u>	<u>Temperature (°C)</u>			
	<u>1150</u>	<u>1250</u>	<u>1350</u>	<u>1450</u>
A	76.5	29.6	12.9	6.2
B	351.1	131.7	55.7	26.0
C	200.3	22.0	3.2	0.6
D	125.6	43.3	17.0	7.5

Note: The values at 1150°C and 1450°C are extrapolated from the measured data for all sequences except Sequence A.

Table 4.32. Glass Conductivity as a Function of Temperature ((ohm•cm)<sup>-1</sup>)

<u>Sequence</u>	<u>Temperature (°C)</u>			
	<u>1150</u>	<u>1250</u>	<u>1350</u>	<u>1450</u>
A	0.135	0.191	0.258	0.336
B	0.108	0.150	0.199	0.257
C	0.033	0.063	0.111	0.183
D	0.121	0.169	0.228	0.297

Note: The values at 1150°C and 1450°C are extrapolated from the measured data for all sequences except Sequence A.

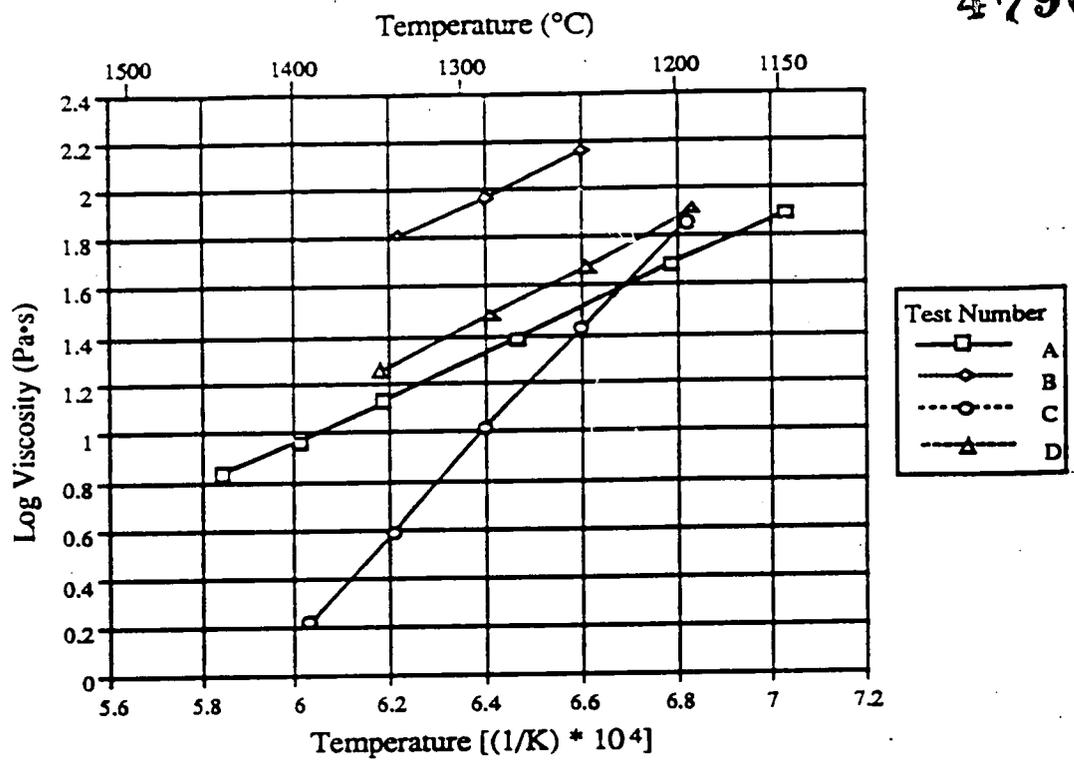


Figure 4.2. Viscosity of Fernald Glasses as a Function of Temperature

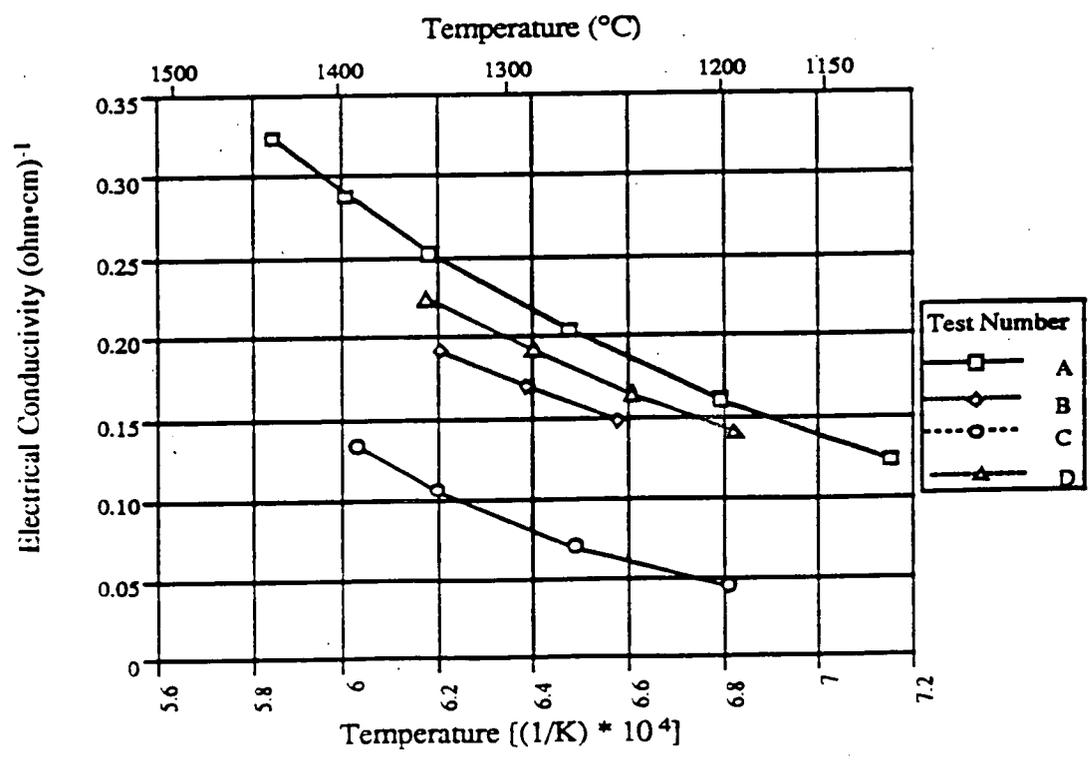


Figure 4.3. Electrical Conductivity of Fernald Glasses as a Function of Temperature

The viscosity data show the glass from Sequences A, C, and D to have reasonable viscosities for processing (about 2 to 15 Pa•s) within the temperature range reported, while the glass from Sequence B was too viscous in this temperature range. The higher viscosity for the Sequence B glass results from the high alumina content in the BentoGrout. The viscosity for Sequence B could be brought within acceptable ranges by increasing the fluxing additives or reducing the BentoGrout content of the waste mixture.

The viscosity of the Sequence C glass is much more dependent on temperature than the other glasses. At higher temperatures, the glass is therefore much less viscous. This could be a cause of the observed attack on the crucible for the Sequence C tests. Another observation during the viscosity measurements on the Sequence C glass was an increase in viscosity at constant temperature at all temperatures except the highest measured, indicating crystal growth in the melt.

The conductivity values for all the glasses are near typical ranges for glass processing (about 0.1 to 0.5 (ohm•cm)<sup>-1</sup>). The conductivity data all show a similar dependence on temperature. For the Sequence A, B, and D glasses, the conductivity at a given temperature is lower for the more viscous glasses. The Sequence C glass, while showing a similar dependence on temperature, is substantially lower in conductivity than the other glasses despite a generally lower viscosity. The lower conductivity of the Sequence C glass is likely to result from a lower alkali content and a higher alumina content relative to the other glasses.

The conductivity of the glass primarily affects the power system design. A higher conductivity requires more current and less voltage, while the opposite is true for a lower conductivity. If two different glass formulations are to be processed in the same equipment, it will be necessary to assure that both are compatible with the system design.

The results presented above show that the K-65 and Silo 3 wastes can be made into glasses with reasonable conductivity and viscosity for processing in a joule-heated ceramic melter; however, it is also evident that further development of these glass formulations is needed.

#### 4.3.10 Off-Gas Composition

Table 4.33 reports the composition of the off-gas samples collected during the closed system vitrification tests. The entire off-gas was collected using a closed system as required by the Work Plan. As a result, these measurements are useful only for qualitative evaluation of the off-gases generated during vitrification. Quantitative evaluation is not possible since the off-gas generated from the melt is diluted and mixed with the atmosphere initially present in the furnace. Additionally, the composition of the gas in the furnace at the end of the run will be different from the composition of the gas collected during the run. More quantitative results would be obtained by using an open system and performing periodic grab-sampling of the off-gas throughout the test.

Table 4.33. Composition of the Off-Gas Collected in the Closed System Tests  
(mole %)

<u>Component</u>	<u>AC.1</u>	<u>BC.1</u>	<u>CC.1-1</u>	<u>CC.1-2</u>	<u>CC.1-3</u>	<u>DC.1</u>
N <sub>2</sub>	75.6	66.4	77.6	77.3	77.0	66.8
O <sub>2</sub>	19.4	13.8	19.6	19.5	17.7	13.5
CO <sub>2</sub>	4.11	19.0	1.5	2.2	4.4	19.0
Ar	0.89	0.76	0.95	0.91	0.88	0.79
CO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NO <sub>x</sub>	<0.01	<0.01	<0.01	0.02	0.05	0.01
He	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
H <sub>2</sub>	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CH <sub>4</sub>	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SO <sub>2</sub>	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Notes: The off-gas for sequence C was collected over three temperature intervals. The first interval was from start to 500°C, the second from 500°C to 1100°C, and the third from 1100°C to 1350°C.

During the open system tests, the off-gas was observed to change color in certain temperature ranges. From about 600°C to 1100°C, the off-gas became red-orange in Sequence C and D melts. At about 1100°C, the off-gas became a milky white in all the melts. During Sequence C, the off-gas was therefore collected over three temperature ranges to investigate the observed color changes.

The off-gas compositions mainly show significant generation of carbon dioxide for all the melts, in part because of the addition of sodium carbonate as a flux for Sequences A, B, and D. Carbonate in the waste is also a source. Nitrogen oxides were found in the off-gas from the Sequence C and D melts. The absence of sulfur dioxide in all the off-gas samples was unexpected. Significant amounts of sulfur, however, were found in the condensate from the open system tests, indicating that sulfur in the off-gas was removed before collection of the off-gas in the sample bag. The red-orange gas observed in the off-gas is believed to be nitrogen oxides generated from the decomposition of nitrates in the waste. This coloring of the off-gas was observed only with Silo 3 glasses, since the levels of nitrates in the Silo 3 material are 10 times higher than those in the K-65 material. The cause of the milky white color is unknown.

#### 4.3.11 Condensate Composition

The off-gas from the vitrification tests was cooled in a shell and tube heat exchanger and the condensate collected for analysis. Table 4.34 presents results of these analyses. Quantitative analysis is not possible. The amount of condensate, and thus the concentration of the analytes, is not a controlled variable. Results are presented only for the open system tests since no condensate was obtained from the closed system tests. Without a convective flow through the

furnace, water vapor apparently diffused to cooler areas of the furnace and condensed in the interior of the furnace.

Table 4.34. Condensate Analysis from Bench-Scale Melts

Radionuclides:	Test Number			
	AO.1	BO.1	CO.1	DO.1
Radium-226 (pCi/L)	30	36	377	7
Radon-222 (pCi/L)	13,233	145	20	8471
<b>Inorganic Analysis:</b>				
Lead (mg/L)	4.5	4.3	7.1	11.1
Sulfur (mg/L)	2530	2020	29,700	3720
Total Thorium (mg/L)	1.0	1.0	2.6	1.1
Total Uranium (mg/L)	<0.001	<0.001	<0.001	<0.001

Most interesting of these results is the high sulfur levels. Sulfur was found in the condensate at a level of 3 weight percent for Sequence C and about 0.3 weight percent for the other sequences. Apparently, the sulfur oxides from the decomposition of the sulfate were readily absorbed by the condensate. The results also show the volatilization of some metals as evidenced by the lead, thorium, and radium. The radon concentrations show a wide variation. The level for Sequence C is expected to be lower because of the much lower radium content of the waste. The level for Sequence B is very low compared to Sequences A and D. Levels of radon in the off-gas during Sequence B were comparable to those of Sequences A and D, so the difference must result from sampling, handling, or analytical methods.

4.3.12 Gamma Dose Rate from the Vitrified Waste

Table 4.35 presents the gamma dose rate from the vitrified waste. It was measured along the crucible axis at the specified distance from the bottom of the crucible. The usefulness of this data is limited since the gamma dose rate is dependent upon the amount of material present. In order to predict the gamma dose rate for other geometries and amounts of material, it is necessary to know the concentration of gamma-producing nuclides in the glass. Existing models can then be used to estimate dose rates for any geometry and size.

4.4 COMPARISON TO TEST OBJECTIVES

The general objectives of these tests were successfully met. The data generated allow the performance of vitrification technology to be compared to other technologies based upon the criteria identified in the treatability study Work Plan. Specifically, these criteria were the leachability of the waste form, the volume reduction achieved through treatment, and the reduction in radon emanation from the waste. Specific objectives for the tests which were identified in the Work Plan are discussed below.

Table 4.35. Gamma Dose Rate from the Vitrified Waste (mR/hr)

4796

Test Number	Distance from Crucible Bottom (in.)			
	0	6	12	24
AO.1	7.2	0.5	0.2	0.0
AC.1	5.3	0.5	0.2	0.0
BO.1	6.5	0.8	0.2	0.0
BC.1	2.6	0.2	0.1	0.0
CO.1	0.0	0.0	0.0	0.0
CC.1	0.3	0.1	0.0	0.0
DO.1	3.2	0.1	0.0	0.0
DC.1	3.8	0.4	0.1	0.0

The chemical and physical properties of the wastes were determined and used in developing the glass formulations for the tests. Each of the waste streams identified in the Work Plan (Sequences A through D) was successfully vitrified using the developed glass formulations. Various analyses were carried out on the glass in support of the test objectives. The TCLP data for each of the glasses allows comparison of the leachability to other waste forms based upon a standard procedure. Radon emanation from the vitrified product was measured, and the volume reduction was calculated based upon measurements of the specific gravity of the vitrified waste. The total radon released during vitrification was determined for use in design of capture systems. Finally, the composition of the off-gas and condensate from these tests was determined, providing a qualitative indication of the species to be expected during continuous melter operation.

4.5 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

The vitrification tests, the PCT, and the modified TCLP were all carried out in accordance with the PNL Vitrification QA Plan WTC-060 as presented in Appendix C. Laboratory notebooks were used for this project in which the daily laboratory activities were recorded. The full TCLP and the analysis of the leachate from the PCT were performed by others following standard QA/QC protocol in the QAPP and Volume 4 of the RI/FS Work Plan.

4.6 COSTS/SCHEDULE FOR PERFORMING THE TREATABILITY STUDY

The overall costs associated with the performance of the vitrification treatability studies are summarized as follows:

Develop Approved Work Plan	\$ 85,000
Conduct Vitrification Treatability Studies	\$ 537,300
FERMCO Prepare/Submit Final Report	\$ <u>20,000</u>
<b>TOTAL ESTIMATED COST</b>	<b>\$ 642,300</b>

Figure 4.4 represents the baseline schedule from which the performance of the treatability study is measured. 4.796

#### 4.7 KEY CONTACTS

Personnel involved in the management of the overall RI/FS process include: J. R. Craig, DOE-Fernald Office (DOE-FN) Project Director; R. B. Allen, DOE-FN Operable Unit 4 Branch Chief; D. J. Carr, FERMCO RI/FS Contracting Officer Technical Representative; S. B. Rhyne, IT Operable Unit 4 Manager; W. S. Pickles, FERMCO CRU4 Project Director; and D. A. Nixon, FERMCO CRU4 Environmental Department Manager.

The principal parties included in the management of the Operable Unit 4 Vitrification Treatability Study are DOE-FN, FERMCO, IT, and PNL. Personnel involved in the specific management of the Operable Unit 4 Vitrification Treatability Study include: R. B. Allen, DOE-FN Operable Unit 4 Branch Chief; W. S. Pickles, FERMCO CRU4 Project Director; D. A. Nixon, FERMCO CRU4 Environmental Department Manager; R. L. Vogel, FERMCO Senior Environmental Engineer; L. A. Heckendorn, Theta Technologies, Inc. Senior Environmental Engineer; C. C. Chapman, PNL, Manager of Operable Unit 4 Vitrification Testing Program; and D. S. Janke, PNL, responsible for FERMCO Operable Unit 4 Vitrification Testing and Reporting.

ACTIVITY ID	REM DUR	PCT	EARLY START	EARLY FINISH	1991					1992					1993												
					J	JUL	AUG	S	OCT	N	DEC	JAN	F	MAR	APR	MAY	JUN	JUL	AUG	S	OCT	N	DEC	JAN	F	MAR	APR
4E00E70305	0	100	17JUN91A	30JUL91A																							PREPARE TS WORK PLAN - VIT (4205W31305)
4E00E70320	0	100	31JUL91A	31JUL91A																							SUBMIT TS WORK PLAN TO WEMCO - VIT (4205W31320)
4E00E70325	0	100	1AUG91A	29AUG91A																							WEMCO REVIEW OF TS WORK PLAN - VIT (4205W31325)
4E00E70330	0	100	30AUG91A	2OCT91A																							INCORPORATE WEMCO COMMENTS - VIT (4205W31330)
4E00E70402	0	100	14SEP91A	10OCT91A																							SHIP RESIDUE TO SUBCONTRACTOR (4205W31402)
4E00E70340	0	100	3OCT91A	3OCT91A																							SBMT REV TS WP TO DOE/WEMCO/ASI-VIT (4205W31340)
4E00E70345	0	100	4OCT91A	21OCT91A																							DOE/WEMCO/ASI RVW REVISED WP - VIT (4205W31345)
4E00E70350	0	100	22OCT91A	11NOV91A																							INCORP COMMENTS TO REVISED WP - VIT (4205W31350)
4E00E70355	0	100	12NOV91A	12NOV91A																							SBMT REVISED TS WP TO DOE/WEMCO-VIT (4205W31355)
4E00E70360	0	100	13NOV91A	13NOV91A																							SUBMIT TS WORK PLAN TO EPA - VIT (4205W31360)
4E00E70370	0	100	14NOV91A	30DEC91A																							EPA REVIEW OF TS WORK PLAN - VIT (4205W31370)
4E00E70380	0	100	31DEC91A	24JAN92A																							INCORPORATE EPA COMMENTS - VIT (4205W31380)
4E00E70385	0	100	28JAN92A	29JAN92A																							DOE/WEMCO RVW OF FINAL TS WP-VIT (4205W31385)
4E00E70390	0	100	29JAN92A	29JAN92A																							SUBMIT FINAL WORK PLAN TO EPA - VIT (4205W31390)
4E00E70395	0	100	30JAN92A	11MAR92A																							EPA REVIEW OF FINAL TS WORK PLAN (4205W31395)
4E00E70405	0	100	24FEB92A	14AUG92A																							CONDUCT TREATABILITY STUDY - V
4E00E70666	0	100	12MAR92A	14MAR92A																							RESOLVE USEPA COMMENTS
4E00E70400	0	100	6APR92A	6APR92A																							EPA APPROVAL OF TS WORK PLAN - VIT (4205W314
4E00E70401	0	100	24APR92A	24APR92A																							SUBMIT REVISED PROCEDURES TO USEPA
4E00E70410	0	100	24SEP92A	7OCT92A																							COMPILE TEST RESULTS FROM TS - VIT (4205W3141
4E00E70415	0	100	8OCT92A	5NOV92A																							PREPARE TS REPORT - VIT (4205W31415)
4E00E70417	0	100	6NOV92A	6NOV92A																							TRANSMIT TS REPORT TO WMCO - VIT (4205W31417)
4E00E70420	0	100	9NOV92A	29JAN93A																							WMCO REVIEW OF TS - VIT (4205W31420)

74

0087

4295

Plot Date 9MAR93  
 Data Date 1MAR93  
 Project Start 1OCT90  
 Project Finish 14JUL93

Activity Bar/Early Dates  
 Critical Activity  
 Progress Bar  
 Milestone/Flag Activity

PNL1

Sheet 1 of 2

FERMCO / CRU4  
 CURRENT SCHEDULE  
 PNL VITRIFICATION STUDY

FERNALD ENVIRONMENTAL RESTORATION MGMT CORP

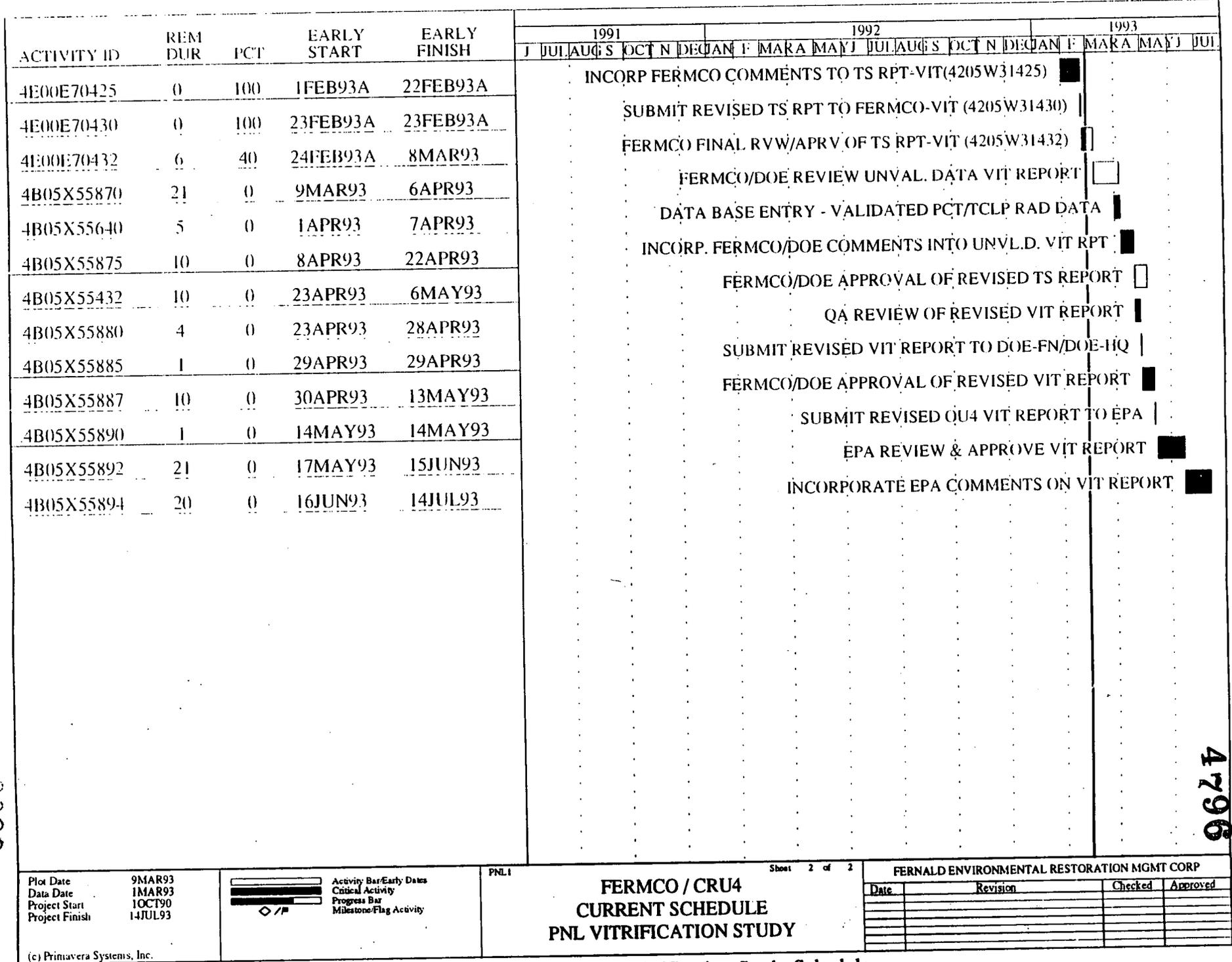
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Figure 4.4 DNT Vitrification Study Schedule

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Plot Date 9MAR93  
 Data Date 1MAR93  
 Project Start 1OCT90  
 Project Finish 14JUL93

Activity Bar/Early Dates  
 Critical Activity  
 Progress Bar  
 Milestone/Flag Activity

PNL1 Sheet 2 of 2

**FERMCO / CRU4  
 CURRENT SCHEDULE  
 PNL VITRIFICATION STUDY**

FERNALD ENVIRONMENTAL RESTORATION MGMT CORP			
Date	Revision	Checked	Approved

Figure 4.4. PNL Vitrification Study Schedule

## 5.0 REFERENCES

- Chapman, C. C. and J. L. McElroy. 1989. "Slurry-Fed Ceramic Melter - A Broadly Accepted System to Vitrify High-Level Waste." High Level Radioactive Waste and Spent Fuel Management, Vol. II, ASME Book No. 10292B.
- Chick, L. A., G. F. Piepel, G. B. Mellinger, R. P. May, W. J. Gray, C. Q. Buckwalter. 1981. The Effect of Composition on Properties in an 11-Component Nuclear Waste Glass System. PNL-3188, Pacific Northwest Laboratory, Richland, Washington.
- Janke, D. S. and C. C. Chapman. 1991. Characteristics of Fernald's K-65 Residue Before, During, and After Vitrification. FMPC/Sub--035, U. S. Department of Energy, Oak Ridge, Tennessee.
- Jantzen, C. M., N. E. Bibler, and D. C. Beam. 1992. Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material (U). WSRC-TR-92-346, Westinghouse Savannah River Co., Aiken, South Carolina.
- Kingery, W. D., et al. 1976. Introduction to Ceramics. John Wiley and Sons, New York.
- Nazaroff, W. W. and A. V. Nero, Jr., ed. 1988. Radon and Its Decay Products in Indoor Air, John Wiley and Sons, New York.
- Piepel, G. F., T. E. Jones, D. L. Eggett, and G. B. Mellinger. 1989. Product Consistency Test Round Robin Conducted by the Material Characterization Center - Summary Report. PNL-6967, Pacific Northwest Laboratory, Richland, Washington.
- Reimus, M. A. H., G. F. Piepel, G. B. Mellinger, and L. R. Bunnell. 1988. West Valley Glass Product Qualification Durability Studies, FY 1987-1988: Effects of Composition, Redox State, Thermal History, and Groundwater. PNL-6723, Pacific Northwest Laboratory, Richland, Washington.
- Strachan, D. M., L. R. Pederson, and R. O. Lokken. 1985. Results from the Long-Term Interaction and Modeling of SRL-131 Glass with Aqueous Solutions. PNL-5654, Pacific Northwest Laboratory, Richland, Washington.
- Stranden, E., A. K. Kolstad, and B. Lind. 1984. "The Influence of Moisture and Temperature on Radon Exhalation." *Radiat. Prot. Dosim.*, 7, 55.
- Strong, K. P. and D. M. Levins. 1982. "Effect of Moisture Content on Radon Emanation from Uranium Ore and Tailings." *Health Phys.*, 42, 27.

U. S. Department of Energy. 1990. Remedial Investigation Report for Operable Unit 4,  
Task 6 Report. FMPC-0406-5, Oak Ridge, Tennessee.

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Volf, M. B. 1984. Chemical Approach to Glass (Glass Science and Technology; Vol. 7),  
Elsevier, New York.

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APPENDIX A  
OU4 TREATABILITY STUDY PROCEDURES

PNL PROCEDURES FOR  
VITRIFICATION OF OPERABLE UNIT 4 WASTES

## I. INTRODUCTION

The following describes the procedures which will be used by PNL in support of the treatability study for the vitrification of operable unit 4 wastes. This information is provided to allow the quality of the data generated to be evaluated. The following sections discuss the test instruments and calibration, the test apparatus, and the procedures for measuring the physical properties of both untreated and treated waste, radon emanation of the treated and untreated wastes, radon emanation during vitrification, gamma dose rate from the vitrified material, and the modified TCLP for metals.

The determination of the physical properties (moisture content, density, specific gravity) will be carried out on three samples from each sample group received by PNL. A sample group is defined as the set of cans containing material from the same location (i.e., Silo 2 Zone B). The material from each sampling location was shipped in anywhere from 8 to 24 containers. Radon emanation and gamma dose rates will be monitored continuously and will not require replication. TCLP will be performed on a single sample from a given test run. All work performed in this study will be done in accordance with NQA-1 Impact Level 2 as detailed in the treatability study work plan.

## II. TEST INSTRUMENTATION AND CALIBRATION

Following is a list of the instruments to be used for these tests:

- Mettler BB240 - Electronic balance with 240 g capacity, 0.001 g readability with  $\pm 0.002$  g linearity.
- Mettler PJ6000 - Electronic balance with 6000 g capacity, 0.1 g readability with  $\pm 0.1$  g linearity.
- Mettler LJ16 - Moisture analyzer with 300 g capacity, scale readability of 0.001 g, moisture analysis readability of 0.01% (0.1% for sample < 10g) and reproducibility of result of 0.03% (0.3% for sample < 10g).
- Eberline RGM-3 Radon Gas Monitor - Calibrated to an accuracy of  $\pm 5\%$  from background up to a maximum concentration of  $10^6$  pCi/L
- Pylon AB-5 Portable Radon Monitor with Pylon Model 300A Lucas Cell - The 300A cell has an accuracy of 0.3% at 50,000 cps (about 36,000 pCi/L), while the AB-5 monitor has an accuracy of 0.3% at 1,000,000 cps.
- Hanford Cutie Pie (CP) - A portable, air-filled ionization chamber ratemeter for measuring gamma dose rate. Four linear ranges of operation (0-5, 0-50, 0-500, 0-5000 mR/hr) with a linearity of  $\pm 5\%$  of full-scale.
- Dwyer Ratemaster Rotameters - Various sizes, with a  $\pm 5\%$  accuracy.

Calibration of the balances, moisture analyzer, rotameters, and Hanford CP are performed by the on-site Westinghouse or PNL calibration services, while the radon monitors were calibrated by the

manufacturers at their calibration labs. Calibration is consistent with the QA/QC requirements of the project.

### III. TEST APPARATUS

Physical properties measurements will be performed in a laboratory hood using standard laboratory glassware and the balances listed previously. Description of the procedures are provided below.

Vitrification and radon emanation measurements will be performed in the system shown in Figure 1. The control and electrical systems power silicon carbide heaters which heat the furnace to as high as 1500 °C, melting the sample in a refractory crucible. Radon from the waste is carried away by air which is continually drawn through the system by internal pumps in the radon monitors. The air is filtered to remove ambient radon before being drawn through the furnace. The off-gas (air sweep plus radon and other gases generated during vitrification) passes out of the furnace directly into a shell and tube heat exchanger where it is cooled, condensing out moisture present in the waste or generated during vitrification. The off-gas is then heated to a maximum of 50 °C before entering the radon monitors in order to prevent condensation in the monitoring cell. The off-gas passes through the monitors, through rotameters, and is vented to the hood.

Besides allowing monitoring of the off-gas during vitrification, the system also provides the ability to monitor the radon emanation from a sample of waste (treated or untreated). This monitoring system is isolated from the off-gas monitoring and can be carried out at any time, even during a vitrification run. The sample is placed inside the sealed, sample monitoring chamber and filtered air is again drawn into the vessel by the monitor's internal pump. Radon generated in the waste is carried away by the constant flow of air, the concentration is measured by the monitor, and the air stream is vented to the hood.

### IV. DETAILED PROCEDURES

#### A. Moisture Analysis.

The moisture analysis is automatically carried out by the Mettler LJ16. The sample to be measured is placed in a tared, aluminum drying pan and heated by infrared radiation at a user-defined temperature (up to 160°C). The analyzer measures the weight loss and calculates and displays the percent moisture of the sample (mass lost divided by the original sample mass times 100%). It is believed, however, that some loss of moisture has occurred from the samples during shipping and storage. To quantify the loss previous to the moisture analysis, the original moisture content will be estimated based on the current total sample weight compared to the initial sample weight as recorded on the original container. This value will provide an upper bound for the moisture content, while the measured value from the moisture analyzer will give a lower bound. The sample size specified for this procedure (30 - 40 g) is fixed by the amount of dry material required for the bulk and apparent density measurements; the moisture analysis only requires a few grams or less.

#### Procedure

1. Turn on the moisture analyzer and verify that the appropriate settings have been made. These settings are infinite drying time, 160 °C drying temperature, and the calculation mode set to percent moisture.
2. Measure and record the mass of a sample can, contents, and lid.

3. Tare the moisture analyzer. Place an aluminum drying pan in the moisture analyzer and record its mass. Re-tare the moisture analyzer.
4. Open the sample can and thoroughly mix the sample until the moisture content appears to be uniform. Evenly distribute about 30 to 40 g of sample into the aluminum pan. Record the mass of the sample portion added.
5. Close the lid of the moisture analyzer and press the START key.
6. Set the display to show weight loss. Allow the sample portion to dry until the observed change in mass is less than 0.001 g/min. Record the measured weight loss and the calculated percent moisture.
7. Set the dried sample portion aside for use in dry density measurements.

#### Calculations

$$\% \text{moisture in sample (calculated by the analyzer)} = 100\% * (\Delta m) / (m_i) \quad (1)$$

where:

$\Delta m$  = weight loss of sample portion

$m_i$  = initial mass of sample portion

#### B. Bulk Density.

The bulk density can be measured in several different ways for either the wet or dry material, i.e., uncompacted, compacted, or settled. This procedure will allow measurement of the bulk density for several conditions. The wet material is measured both in the *uncompacted and compacted* form. The uncompacted density is representative of the material after it is retrieved (i.e., the density as is in the sample container), while the compacted density is more representative of the material in the silos, with void spaces removed. The dry material density is measured as *unsettled (uncompacted)* or settled for the material both as is (with clumps) and with the clumps broken up. The density most representative of the dry material would depend on the drying method (if it produced a clumpy material or ground up the clumps) and the handling method (whether or not the material settles).

#### Procedure

1. Measure and record the mass of a 50 mL graduated cylinder.
2. Place between 45 and 50 mL of wet solid from the sample can into the graduated cylinder. Measure and record the mass of the cylinder and sample.
3. Tap the cylinder three times on the table top and record the observed volume of material.
4. Pack and compact the sample in the cylinder, breaking up clumps and voids in the material. A piece of metal rod is useful for this. When the sample is compacted and void spaces eliminated (as much as possible), measure and record the observed volume of compacted material.
5. Measure and record the mass of another 50 mL graduated cylinder.

6. Take the sample which was dried in the moisture analysis (about 20 - 30 g dry) and break up any large clumps so that the largest chunks are about 2 to 4 mm in diameter.
7. Place the sample in the cylinder and measure the mass of the cylinder with added sample.
8. Tap the cylinder three times and record the initial volume of material. Then, tap the cylinder on the table-top until no further settling is observed. Record the volume of settled material.
9. Remove the material from the cylinder and crush all clumps until the material is fairly powdery. Then repeat steps 7 and 8 for the crushed material. When finished, set the material aside for use in the determination of apparent density.

### Calculations

For all of the above measurements, the density is calculated as follows:

$$\text{bulk density} = m / V \quad (2)$$

where:

m = mass of the sample (wet, dry, crushed dry) in the cylinder  
 V = measured volume of the sample (initial, compacted, settled)

### C. Apparent Density.

The apparent density (or specific gravity) is the actual density of the particles of material. To measure the apparent density, the volume actually occupied by the solid material must be determined (as opposed to the interstitial volume between the particles). This method is different for the untreated waste (finely divided particles) versus the vitrified waste (large, solid pieces).

The apparent density of the untreated waste is measured by intimately mixing a portion of the solid with water in a flask whose volume is known very precisely. The mass of water can be measured through weighing and converted to a volume if the temperature of the water is known. Since the volume of the flask is known, the volume occupied by the solid can be obtained by difference. Knowing the mass of solid in the flask then allows calculation of the apparent density.

The apparent density of the vitrified waste is determined by measuring the buoyant force exerted on a sample of the vitrified residue. The buoyant force allows the mass, and thereby the volume, of water displaced to be calculated. The volume of water displaced is equal to the volume of the sample, and the density can then be calculated.

### Procedure - Untreated

1. Measure and record the mass of an empty 100 mL volumetric flask (ASTM class A  $\pm 0.08$  mL).
2. Add the dry sample which remains from the bulk density determinations (about 20 - 30 g dry) and measure and record the mass of the flask plus sample.
3. Fill the flask with water to the volumetric mark. This should be done by filling the flask partially with distilled water and swirling until the material is completely wet, then filling the remainder of the way. If a foam forms on top, then the foam must be removed and the mass of solids removed as part of the foam determined. The mass of solids is determined

by drying the foam and determining the mass of the residue. After the foam is removed, add water to the volumetric mark if required. Measure and record the mass of the flask, sample, and water.

4. Measure and record the temperature of the water in the flask. Then discard the material.

#### Calculation - Untreated

$$\text{apparent density} = (m_{fs} - m_f - m_{sinf}) / [V_f - (m_{fsw} - (m_{fs} - m_{sinf})) / \text{density}] \quad (3)$$

where:

$m_f$  = mass of empty flask

$m_{fs}$  = mass of flask and dry sample

$m_{fsw}$  = mass of flask, sample, and water

$m_{sinf}$  = mass of sample removed with the foam

density = density of water at the measured temperature

$V_f$  = volume of the volumetric flask

#### Procedure - Vitrified

1. Place a 2000 mL beaker about three-fourths full of water on the electronic balance and tare. Suspend a stainless steel mesh basket from a fine wire (or fishing line) with a well defined mark to which the basket can be consistently submerged. Submerge the basket to this mark and tare the scale.
2. Lift the basket out of the water. Keep it over the beaker so any water which drips off the basket remains in the beaker.
3. Place a known mass of vitrified sample (about 50 to 100 g) into the basket. The pieces must be large enough so as to be retained in the basket.
4. Submerge the basket to the same point as step 1. Record the mass; this is the buoyant force.
5. Measure the temperature of the water in the beaker.

#### Calculation - Vitrified

$$\text{apparent density} = m_s / (F_b / \rho) \quad (4)$$

where:

$m_s$  = mass of the vitrified sample submerged

$F_b$  = buoyant force (the mass measured in step 4)

$\rho$  = density of water at the measured temperature

#### D. Volume Reduction.

The volume reduction is calculated from the bulk density and initial mass of the waste and the apparent density and final mass of the glass, so there is not a procedure by which it is determined, only a calculation using previously determined values. The volume reduction can have several values, depending on the initial density on which it is based. The general formula is given below

in terms of initial and final densities. The calculated value would be reported along with the specification of the original basis (i.e., wet uncompact density, dry settled density, etc.)

#### Calculation

$$\text{volume reduction\%} = 100\% * [1 - (m_f * \rho_i) / (m_i * \rho_f)] \quad (5)$$

#### E. Gamma Dose Rate of Vitrified Waste.

The gamma dose rate will be measured directly from the crucible containing the vitrified waste using the Hanford CP. Measurements will be taken along the axis of the cylindrical block of vitrified waste at contact with the crucible bottom and 6", 12", and 24" from the bottom of the crucible. The CP instrument will be operated, and all appropriate corrections to the measured dose rate made, as detailed in PNL-MA-562 Section CP.

#### Procedure

1. Measure the background dose rate using the CP at the location where the measurements are to be made. This location should be away from the hood, sample storage, and other sources of radiation which would lead to a high background reading. The background reading should be taken just before each measurement on the vitrified waste.
2. When the crucible has cooled after vitrification (about 24 hrs), remove the crucible to the measurement location.
3. Place the window of the CP in contact with the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate.
4. Repeat step 3 with the CP window at distances of 6", 12", and 24" from the bottom of the crucible and record the dose rates.

#### Calculation

The CP reads the dose rate directly (mR/hr). The only calculations required will be to multiply the measured dose rate by appropriate correction factors as detailed in PNL-MA-562. These may include corrections for photon energy dependence, temperature, and source-to-window distance.

#### F. Radon Emanation from K-65 Waste (untreated).

Radon emanation from the untreated wastes will be measured in the system shown in Figure 1. The sample to be measured will be placed in a can, and the can placed inside the sample monitoring chamber. The internal pump in the monitor will draw air through the sample chamber and into the monitor at a constant flow rate until a steady-state concentration is reached. The air inlet is filtered through a charcoal filter to remove ambient radon. Knowing the air flowrate and the concentration of radon in the gas stream the radon emanation rate can be calculated.

Radon emanation from the untreated waste will be measured using the Eberline RGM-3 radon monitor which operates at a flowrate of approximately 8 Lpm. The steady-state concentration under these conditions is estimated to be about 3,000 pCi/L.

### Procedure

1. Open valves V6 and V8 and close valve V7. Flush the radon monitor with clean air and measure the background counts due to the plateout of radon daughters in the sample monitoring cell according to the manufacturer supplied operating instructions.
2. Place a known mass (100 to 200 g) of untreated or vitrified residue into a sample can of known diameter (hence, known cross-sectional area). Distribute the material evenly in the can.
3. Place the sample can into the sample monitoring chamber and seal the lid. Open valve V7 and close valve V6.
4. Set the monitor so that the data collected is output to the printer as it is generated. Start the monitor and record the flow rate in the system. Monitor the radon levels until the concentration reaches a steady state.

### Calculations

$$\text{radon emanation (pCi/m}^2\text{/hr)} = C * Q / A_{xs} \quad (6)$$

$$\text{radon emanation (pCi/kg/hr)} = C * Q / m_s \quad (7)$$

where:

C = measured concentration in pCi/L

Q = measured flowrate in L/hr

$A_{xs}$  = cross sectional area of the sample can in  $m^2$

$m_s$  = sample mass in kg

### G. Radon Emanation During Vitrification.

Radon emanation from the K-65 waste during vitrification will be measured using the system shown in Figure 1. During the entire melting process, from before any heating to completion of the melt, the vacuum pump will be on. Air will be drawn into the furnace at a rate of 20 scfh. This will provide a continuous flow through the system and will maintain the composition of the gas in the off-gas lines approximately equal to that in the furnace. The standard position of the valves to the Pylon radon monitor will be closed for the valve between the off-gas line and the monitor and open for the air bleed valve into the monitor. These positions will be periodically reversed to sample and measure the radon concentration in the off-gas.

The Pylon monitor will be set to run in the continuous mode with one minute interval lengths. The flowmeter will be adjusted full open and the pump on the monitor will be set to run at the maximum flow rate (>5 scfh). The pump will be on at all times during the run, most of the time flushing ambient air through the cell.

Off-gas will be circulated through the system overnight to allow the radon concentration to reach a steady state value prior to beginning the test. Measurements will be taken with this initial level prior to start-up of the furnace. Following furnace start-up, the measurements will be taken about every 30 minutes for the duration of the test.

Procedure

- a. Make sure the valve to the off-gas (V5) is closed, the air bleed (V4) is open, and the pump in the monitor is on.
- b. Press start. Monitor the cell background for two, one minute intervals.
- c. After two intervals, close the air bleed (V4) and open the valve to the off-gas (V5).
- d. Count for two more intervals.
- e. Immediately close the valve to the off-gas (V5) and open the air bleed valve (V4).
- f. Press stop to halt the monitoring (but leave the pump running).
- g. Repeat every 30 minutes or as required to obtain the desired number of data points.

Calculation

$$\text{Radon conc. (pCi/L)} = \text{NCPM/S*} \quad (8)$$

where:

NCPM = net count per minute of the fourth one minute interval  
 S\* = cell sensitivity (cpm/pCi/L) determined for this procedure

This monitoring scheme attempts to measure the counts before appreciable buildup of radon daughters has occurred and then to flush the cell before significant buildup of background has occurred. At the maximum flowrate of the monitor, the concentration in the cell is estimated to be greater than 99% of the actual off-gas concentration after one minute of flushing; therefore, measurements after one minute of flushing should reflect the actual radon concentration in the off-gas. The counts for the second one minute interval should reflect the activity of the radon plus daughters. The buildup of daughter activity in this time period is fairly small, estimated to be a maximum of about 20% of the radon activity. A calibration using a known radon concentration will give a sensitivity factor for this modified procedure which will allow the radon concentration to be calculated. Immediate flushing with ambient air will prevent the buildup of daughter products and will allow additional measurements to be taken within the time scale of the melting test.

H. Radon Emanation from the Vitrified Waste.

The radon emanation from the vitrified waste is determined by sealing a sample of the glass into a container and allowing the radon concentration build up. After seven days, the sample container is connected to a Pylon AB-5 monitor with a Lucas 300A scintillation cell in a closed loop system. The gas from the sample container is circulated through the system until well mixed, and then monitored for radon concentration following the standard procedures of the instrument. The sample container is then sealed up again and the concentration allowed to build up to equilibrium levels (greater than 30 days). Since part of the radon from the sample container is lost during this monitoring procedure (i.e., remains in the monitor and tubing), more than 23 days are required to reach the 30-day level after the seven day measurement. The additional time required can be calculated based upon the decay constants of radon. The measurement procedure is repeated again after the 30-day level is reached.

Procedure

1. Place a sample of glass which has been sieved to a -5/+8 fraction (using standard mesh screens) into the sample chamber and seal it. Record the amount of glass, the date and the time.
2. Monitor the radon concentration after 7 days using the following grab sampling procedure:
  - a. Set the monitor for 10 minute intervals and count the cell background for 3 intervals.
  - b. With the pump at the maximum flow rate, start the pump and run for 3 minutes while continuing to monitor. Shut off the pump after three minutes.
  - c. Continue monitoring for 4 1/2 hours.
  - d. Close the valves to the monitoring chamber and flush out the cell.
3. Allow the sample to sit until the 30-day level is reached; then repeat the measurement.

Calculation

$$\text{radon concentration (pCi/L)} = (\text{NCPM} * C) / (S * A) \tag{9}$$

where:

- NCPM = net count per minute in the six intervals from 3.5 hours to 4.5 hours
- C = 1.00378 (correction factor for decay during the 6 ten minute intervals)
- S = cell sensitivity (cpm/pCi/L)
- A = 0.97394 (correction for decay up to the start of monitoring)

$$\text{radon activity (pCi)} = \text{measured concentration} * \text{system volume} \tag{10}$$

$$\text{system volume} = 0.991 \text{ L}$$

$$\text{radon emanation rate (pCi/m}^2\text{/s)} = \text{activity} * \lambda / A \tag{11}$$

where:

- activity = measured activity (pCi)
- $\lambda$  = decay constant for radon (s<sup>-1</sup>)
- A = surface area of the glass (m<sup>2</sup>)

I. Modified TCLP.

The modified TCLP (or TCLP for metals only) will be performed by CEP Labs according to the Method 1311 included in the Work Plan. The analysis will require about a 100 g sample of vitrified waste. Metals analyzed for will include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

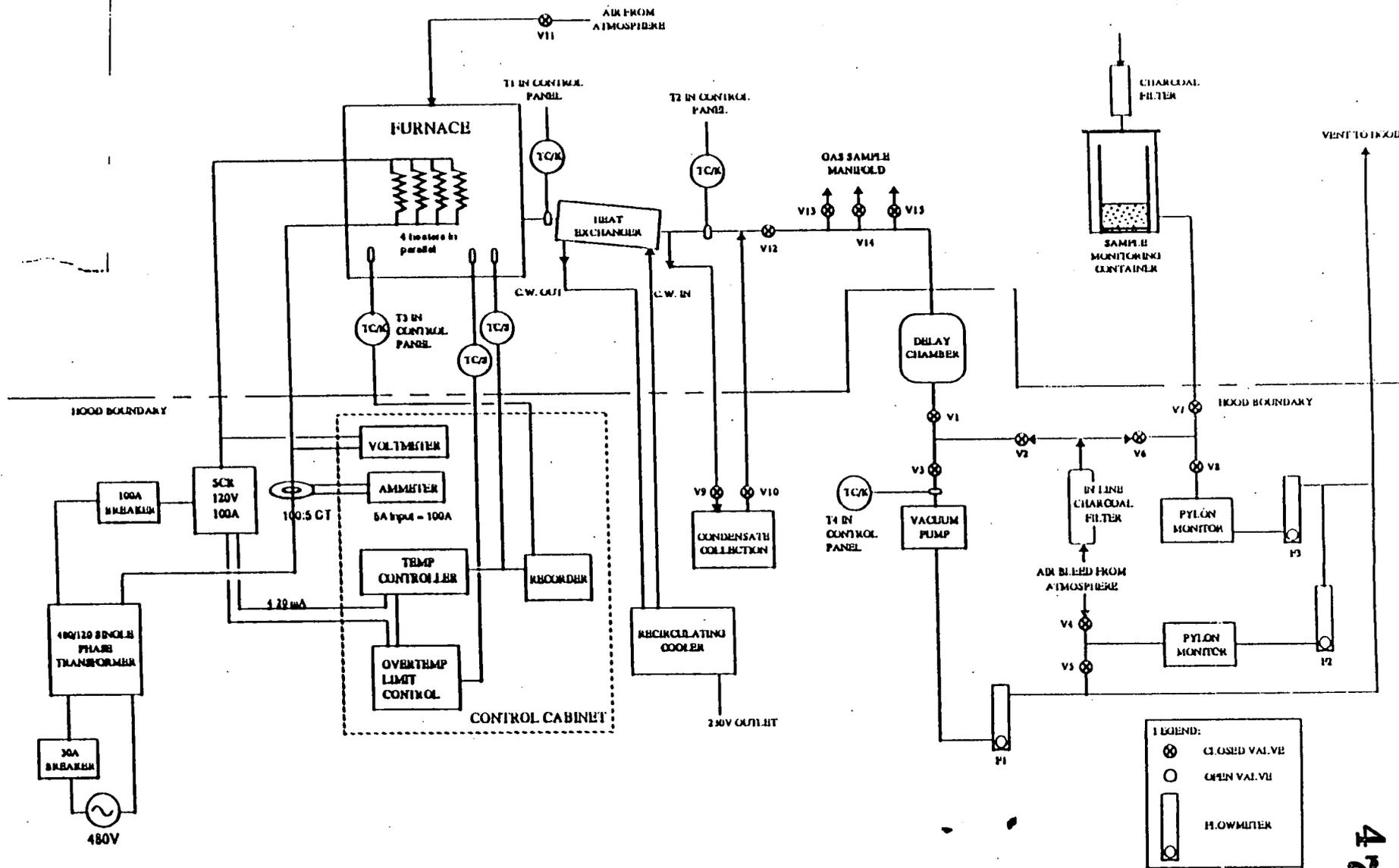


Figure 1. Bench Scale Test System for Vitrification of Operable Unit 4 Wastes

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APPENDIX B  
OU4 TREATABILITY TEST PLAN

TEST PLAN FOR THE BENCH SCALE VITRIFICATION TESTING  
OF FEMP'S OPERABLE UNIT FOUR - SILOS 1,2, AND 3

### INTRODUCTION

The Fernald Environmental Management Project (FEMP) is a contractor-managed federal facility once used for the production of purified uranium metal. The FEMP has been segregated into five operable units. Operable unit 4 is defined as a geographic area that contains Silos 1 and 2 (K-65 silos), Silo 3 (metal oxide silo), and the unused Silo 4. Silos 1 and 2 were used for the storage of radium-bearing residues formed as by-products of uranium ore processing. The residues contain uranium, uranium daughter products, and some heavy metals (primarily lead). Silos 3 and 4 were designed to receive dry materials only. Silo 3 contains calcinated residues of various metal oxides while Silo 4 was never used.

Vitrification studies will be performed on the K-65 material by itself, the K-65 material with Bento-grout added, the metal oxide by itself, and a mixture of K-65 material and metal oxide material. The objectives of these studies are as follows; determine the composition of the off-gas generated during vitrification, determine the radon emanation rate both during vitrification and from the vitrified K-65 wastes, determine the volume reduction resulting from vitrification, determine the gamma dose rates of the vitrified wastes, and finally; determine the leachability of the vitrified wastes. The primary goal of these treatability tests is to develop a stable waste form with minimal leachability of all contaminants, including radionuclides and with reduced radon emanation.

### TEST DESCRIPTION

The purpose of these tests is to provide a quantitative evaluation of the performance of the vitrification treatment option. As stated in the 'Operable Unit 4 Treatability Study Work Plan for the Vitrification of Residues from Silos 1, 2, and 3', four different sequences of material (A-D) will be tested. Sequence A consists of the K-65 material by itself. Sequence B consists of the K-65 material with Bento-grout added. Sequence C consists of the silo 3 (metal oxide) material by itself. Lastly, sequence D consists of a mixture of the K-65 material and the metal oxide material.

The first run for each of the above sequences will be performed using an open equipment set-up. This allows for continuous monitoring of the radon emanation during the vitrification process. The open system will be as shown in Figure 1 with valves V1, V3, V11, and V12 open.

The second test run for each of the sequences will be performed with a closed system set-up. This allows for collection of off-gas to determine its chemical composition. The closed system will also be as shown in Figure 1, but with valves V1 and V11 closed. Valves V13, V14, and V15 will be opened one at a time depending on which gas sample bag is being filled.

During both the open and closed system runs, the valves on the various flow meters will be fully open unless otherwise stated. These flow meters are for measurement rather than control of flow.

After an initial pre-test waste composite preparation, 100 g test melts (or Sequence 0 melts) will be completed. The results of these test melts will help predict the required compositions for the Sequence A-D tests. As described below, two phases will be required to complete each test within Sequences A-D. When running the Sequence A-D tests, all of the open system runs will be done first. Once the open system run from each sequence has passed a modified TCLP test, the closed system run for that sequence will be completed.

Phase I: During the first phase of the test, the material will be melted in a bench-scale furnace. Either an open or closed system will be used, depending on whether the radon emanation is being monitored or the off-gas is being collected. Condensate will also be collected for analysis.

Phase II: During this phase, the vitrified material will be analyzed for radon emanation at 7 and 30 days, volume reduction (based on the specific gravity of the glass), TCLP leachate results, conductivity, viscosity, and gamma dose rate.

### HAZARDOUS MATERIALS AND WASTES

All materials used and wastes produced will be handled in accordance with the Waste Technology Center Chemical and Waste Management Plan and PNL-MA-8. All waste produced will be low-level, unmixed waste. Such waste will include gloves, paper cloths, glassware, and cleaning supplies. SDAR # 15-11-1B-0301 (latest revision) will be used for waste disposal. All unused and vitrified test material will be returned to Fernald. All containers will be labeled appropriately, MSDS's will be available, and personnel will be informed of the hazards present.

### SAFETY

Activities associated with the tests will be in accordance with the Waste Technology Center Environmental, Safety, and Health (ES&H) Plan and all applicable Standard

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Operating Procedures (SOP's) and Radiation Work Permits (RWP's). All personnel performing activities are required to understand the safety requirements for the work at hand.

Hazards associated with this work are the high temperature furnace and the associated electrical power, and radiation. The furnace will be continuously manned and all combustibles will be removed from the area during furnace operation. All staff will be formally trained in radiation protection and will be familiar with all applicable RWP's.

### QUALITY ASSURANCE

Testing is to be conducted as Impact Level II work and will be in accordance with QA Plan WTC-060 Rev 1. Analyses of samples will be obtained through Analytical Request Forms for PNL services or through a Statement of Work for off-site services.

The procedures for the two phases of tests follow. Data sheets, which need to be initialed and dated as each step is completed, are included within this test plan. Log entries will be made directly into the laboratory notebook (BNW 53877). These are for recording a general log of the test and actions taken, observations that are either unanticipated or which may influence the results of the test, and speculative notes. Printouts and other data outputs will be entered in the laboratory notebook. The data sheets will be entered into the project files. Any exceptions to this test plan that, due to unanticipated events, may be required to achieve the test objectives, will need to be approved by the project manager (Dan Janke). Any major changes to this test plan will be approved by WEMCO. Once the modifications have been approved, they will be noted in the following data sheets and/or logged in the laboratory notebook.

Each test will be given a number that corresponds to the sequence it is under, whether it is using the open or closed system, the run number, and the start date for the test. An example test number is: AO.1-mm.dd.yy. The 'A' is for Sequence A, the 'O' is for an open system run, the '1' is for the first run, and the 'mm.dd.yy' is the start date format. During each test run various items (such as crucibles, condensate bottles, gas sample bags, and sample cans) will be labeled with the test number and an explanation of the vessel's contents.

0105

I. PRE-TEST PREPARATION

## A. K-65 Composite

PNL has been provided with samples of the K-65 material from three zones (A, B, and C) within each silo. This results in a total of six separate samples of K-65 material. Vitrification will be performed on a composite K-65 sample made from a mixture of the above six samples. To complete all the required vitrification sequences, approximately 8 kg of composite K-65 material is required.

The required wet weight quantities from each zone will be calculated based on their moisture contents. This data will be recorded in the laboratory notebook. The proper amount from each zone will then be added to a metal can labeled 'K-65 Composite'. The exact amount added from each zone will also be recorded in the notebook. This composite will be mixed thoroughly to ensure a homogeneous mixture.

## B. Silo 3 Composite

PNL received 34 cans containing the Silo 3 (metal oxide) material. To complete all the required vitrification sequences, approximately 7 kg (dry weight) of composite Silo 3 material is required. Material will be combined from enough of the 34 cans until 7 kg has been mixed.

The required wet weight quantity will be calculated from the moisture content of the Silo 3 material. This data and the amount added from each can will be recorded in the laboratory notebook. The material will be added to a metal can labeled 'Silo 3 Composite'. This composite will be mixed thoroughly to ensure a homogeneous mixture.

## C. Sequence 0 Tests

Up to three 100 g test melts will be conducted for each sequence A-D. The glass forming composition will be varied in these melts until a reasonable composition is found for use in the sequence A-D tests. The various compositions used and the results of these test melts will be recorded in the laboratory notebook.

During these 100 g test runs, the furnace will be operated as stated in SOP #81, the Standard Operating Procedure for laboratory furnaces.

II. PHASE I - Vitrification (Open or Closed System)

A. Complete Test System Readiness

i. The following items should be present before starting the test.

Date Initials

- |       |       |  |
|-------|-------|--|
| _____ | _____ | Crucible (labeled with ceramic high temp. marker)  |
| _____ | _____ | Gas Sample Bags (22 and 65 L) - closed system only   |
| _____ | _____ | Condensate Sample Bottles (1000 ml)  |
| _____ | _____ | Glass Former Chemicals and Waste Composite Samples   |
| _____ | _____ | Miscellaneous Supplies: sample labeling tags, Sharpie marking pens, work place copy of the test plan, wrenches, face shields, leather gloves, high temperature gloves, normal working gloves, clean-up supplies, waste drums |

ii. The following items should be given an operability check prior to starting the test.

Date Initials

- |       |       |  |
|-------|-------|--|
| _____ | _____ | Control panel and Instrumentation  |
|       |       | - verify that all instruments have power   |
|       |       | - verify chart recorder settings   |
|       |       | - verify over temperature limit setting (max of 1550 °C)   |
|       |       | - verify that thermocouples are closed and reading close to ambient  |
|       |       | - verify that furnace temp. controller is getting a signal from the thermocouples and it is close to ambient   |
| _____ | _____ | Furnace  |
|       |       | - check condition of the insulation  |
|       |       | - visually check the power cables and heaters  |
| _____ | _____ | Off-gas Cooling System   |
|       |       | - check water level in cooler (the cooler must be on or water from the tubing will overflow) and the condition of the water (i.e., if there is algal growth) |
|       |       | - check that power turns on and it pumps water   |
|       |       | - make sure there are no leaks   |
| _____ | _____ | Off-gas Pump   |

Test Number \_\_\_\_\_

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\_\_\_\_\_

**Radon Gas Monitor**

- check the functionality of the monitors according to the instructions in the operating manual
- verify that there is paper in the printer

\_\_\_\_\_

**Flow meters**

- verify that the valves are fully open

\_\_\_\_\_

**Electronic Balances (Mettler BB240 and Mettler PJ6000)**

- verify that balance functions
- verify that calibration is up to date

**B. Formulate Glass for Sequence Tests**

Date Initials

\_\_\_\_\_

Record and/or measure the moisture content of various components of the glass formulation. For chemical additives, this will be measured once at the beginning of the bench-scale testing and recorded in the LRB, while for the waste materials, it will be measured for the material actually used in the mix.

<u>Material</u>	<u>Moisture Content (%)</u>
K-65 Mix	_____
Bento-grout	_____
Silo 3 Mix	_____
Na <sub>2</sub> CO <sub>3</sub>	_____
SiO <sub>2</sub>	_____
Al <sub>2</sub> O <sub>3</sub>	_____
H <sub>3</sub> BO <sub>3</sub>	_____
C	_____

\_\_\_\_\_

Calculate the actual formulation based upon the moisture contents measured above and desired make-up determined from the 100 g tests. Add the actual quantity below to a stainless steel beaker and mix thoroughly.

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Chemical	A	B	Actual Quantity [g]
	Desired Dry Quantity [g]	1 - %moisture/100	A / B
K-65 Mix	_____	_____	_____
Bento-grout	_____	_____	_____
Silo 3 Mix	_____	_____	_____
Na <sub>2</sub> CO <sub>3</sub>	_____	_____	_____
SiO <sub>2</sub>	_____	_____	_____
Al <sub>2</sub> O <sub>3</sub>	_____	_____	_____
H <sub>3</sub> BO <sub>3</sub>	_____	_____	_____
C	_____	_____	_____

\_\_\_\_\_ Label a crucible with the test number using a high temperature ceramic marker, number = \_\_\_\_\_

\_\_\_\_\_ Record the weight of the empty crucible \_\_\_\_\_ g

\_\_\_\_\_ Weigh the beaker with the mix test material \_\_\_\_\_ g

\_\_\_\_\_ Transfer the material to the crucible and weigh the stainless beaker \_\_\_\_\_ g

\_\_\_\_\_ Load the crucible into the furnace. Replace the door and front plate of the furnace and secure them with clamps.

C. Perform Vitrification

1. Open System

a. Pre-Vitrification Preparation

\_\_\_\_\_ Start with valves V1, V3, V4, V11, and V12 open and all others closed. Refer to Fig. 2 for these valve positions. Turn on the off-gas pump and adjust the flow through F1 to 20 scfh using the valve on the pump inlet. Allow to pump several hours or overnight.

\_\_\_\_\_ Verify the seal on the furnace door. Close V11 while pumping at 20 scfh. The vacuum at the furnace outlet should be greater than 0.1" H<sub>2</sub>O

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\_\_\_\_\_

Set the parameters on the Pylon AB-5 as follows:

- Continuous mode, one minute counting interval

\_\_\_\_\_

Turn on the Pylon AB-5 pump. Adjust the flow through the Pylon to 5 scfh (F2) using the flow adjustment screw on the back panel of the monitor.

\_\_\_\_\_

Check the printer to make sure it is recording the radon emanation data

\_\_\_\_\_

Program the temperature controller for the appropriate ramp and soak profile.

- Heat from room temp to sample melting temp at a \_\_\_\_\_ °C/hr (max of 300)
- Record sample melting temperature \_\_\_\_\_ °C
- Hold at melting temperature for \_\_\_\_\_ hours

b. Vitrification Test

\_\_\_\_\_

Turn on the Pylon and monitor the radon concentration in the off-gas using the following procedure:

- With ambient air being flushed through the cell (V4 open and V5 closed) monitor the counts for 2 intervals to obtain the cell background.
- At the end of the second interval, close V4 and open V5.
- Continue counting for two more intervals. At the end of the fourth interval, close V5 and open V4. Stop the counting, but leave the pump on to flush the cell.

\_\_\_\_\_

Turn on cooling water for the heat exchanger

\_\_\_\_\_

Label a 1 L bottle with the test number, \_\_\_\_\_ and place it in the condensate collection trap

\_\_\_\_\_

Open valves V9 and V10

\_\_\_\_\_

Start the chart recorder. Check all data acquisition equipment (temperature profile and radon concentrations) to make sure they are being recorded. Start the recorder  
Power up the furnace

\_\_\_\_\_

- Turn on the breakers
- Run the ramp and soak profile on the temperature controller

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- \_\_\_\_ Verify that the temperature profile is being followed as programmed
- \_\_\_\_ Every 30 minutes, perform the radon monitoring procedure described above. Ensure that a hard copy of the data is printed as the monitoring procedure is carried out.
- \_\_\_\_ Periodically check the off-gas flowrate. Adjust as needed to maintain a flow of 20 scfh in F1
- \_\_\_\_ Periodically check all instrumentation to verify that it is functioning. Report any out of the ordinary occurrences and other observations in the laboratory notebook

c. Post-Vitrification

- \_\_\_\_ Verify that output from the controller is 0%; then *disengage* breakers
- \_\_\_\_ With V4 open and V5 closed, leave the Pylon pump on for at least 20 minutes after the last measurement; then close V4 and turn off the monitor.
- \_\_\_\_ Turn off the off-gas pump and close valve V3
- \_\_\_\_ Turn off cooling water when the inlet temperature to the HX has fallen below 50 °C
- \_\_\_\_ Close V9 and V10 and remove the 1 L bottle from the condensate collection, screw the lid on, and verify that it is labelled with the test number. Prepare the sample for shipping as required.
- \_\_\_\_ Verify that the breakers are turned off and that the furnace has cooled sufficiently to remove the crucible. Remove the crucible from the furnace to the hood.
- \_\_\_\_ Record the mass of the crucible and glass \_\_\_\_\_ g
- \_\_\_\_ Remove all charts (furnace temperatures, off-gas temperatures, and radon concentrations) and label them with the test number. Insert into the lab record book

2. Closed System

a. Pre-Vitrification Preparation

- \_\_\_\_ Program the temperature controller for the appropriate ramp

0111

Test Number \_\_\_\_\_

and soak profile.

- Heat from room temp to sample melting temp at a \_\_\_\_\_ °C/hr (maximum of 300)
- Record sample melting temperature \_\_\_\_\_ °C
- Hold at melting temperature for \_\_\_\_\_ hours

\_\_\_\_\_  
\_\_\_\_\_

Verify that the chart recorder is functioning

\_\_\_\_\_  
\_\_\_\_\_

Check the seal on the furnace by closing valve V11 and drawing a vacuum on the furnace (a flow of 20 Scfh). Record the vacuum at the furnace outlet. If it is less than 0.1" then adjust the seal.

b. Vitrification Test

\_\_\_\_\_  
\_\_\_\_\_

Turn on cooling water for the heat exchanger

\_\_\_\_\_  
\_\_\_\_\_

Label a 1 L bottle with the test number, \_\_\_\_\_ and place it in the condensate collection trap

\_\_\_\_\_  
\_\_\_\_\_

Open valves V9 and V10

\_\_\_\_\_  
\_\_\_\_\_

Adjust valves for the closed system. Valves V1 and V11 shall be closed and valve V12 shall be opened. Refer to Fig. 3

\_\_\_\_\_  
\_\_\_\_\_

Label a gas sample bag with the test number, \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

Place the gas sample bag on the gas sample manifold at position V13 and open the valve

\_\_\_\_\_  
\_\_\_\_\_

Power up the furnace

- Turn on the breakers
- Start the temperature controller

\_\_\_\_\_  
\_\_\_\_\_

Verify that the temperature profile is being followed as programmed and proper operation of instrumentation

\_\_\_\_\_  
\_\_\_\_\_

Report observation and any out of the ordinary occurrences in the laboratory notebook

\_\_\_\_\_  
\_\_\_\_\_

Observe that the gas sample bag is filling. If the bag becomes full, place another bag (labeled with the test number - 2 ) at position V14. Open valve V14 and close valve V13. If this bag becomes full, place another bag (labelled with the test number - 3 ) at position V15. Open valve V15 and then close valve V14.

Test Number \_\_\_\_\_

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\_\_\_\_\_ When the ramp and soak profile is complete (after holding at melting temperature for specified time), close the gas sample bags and close the gas sample valves (V13, V14, and V15)

\_\_\_\_\_ Open valve V11 to allow air in as the furnace cools

c. Post-Vitrification

\_\_\_\_\_ Disengage the breakers

\_\_\_\_\_ Turn off cooling water when the inlet temperature to the heat exchanger has fallen to less than 50°C

\_\_\_\_\_ Close V9 and V10 and remove the 1 L bottle from the condensate collection, screw the lid on, and verify that it is labelled with the test number. Prepare the sample for shipping as required.

\_\_\_\_\_ Verify that the breakers are turned off and that the furnace has cooled sufficiently to remove the crucible. Remove the crucible from the furnace to the hood.

\_\_\_\_\_ Remove all charts (temperatures and radon monitoring) and label them with the test number and enter in the laboratory notebook

III. PHASE II - Physical Property Determination

A. Complete Test System Readiness

i. The following items should be present before starting the test.

Date

Initials

\_\_\_\_\_ Fracture Chamber (for breaking up crucible and glass)

\_\_\_\_\_ Stainless steel mesh basket for apparent density determination

\_\_\_\_\_ Miscellaneous Supplies: sample labeling tags, Sharpie marking pens, sample cans, fishing line, work place copy of the test plan, wrenches, face shields, leather gloves, high temperature gloves, normal working gloves, clean-up supplies, waste drums

0113

ii. The following items should be given an operability check prior to starting the test.

Date	Initials	
_____	_____	Electronic Balances (Mettler BB240 and Mettler PJ6000) - verify that power is on - verify that calibration is up to date
_____	_____	Hanford Cutie Pie (CP) - verify that power is on - verify that calibration is up to date
_____	_____	Radon Gas Monitor - check that power is on - check the functionality of the monitors according to the instructions in the operating manual

B. Gamma Dose Rate of Vitrified Waste

_____	_____	Place the cooled crucible in a plastic bag and remove it from the hood
_____	_____	Measure the background dose rate using the CP at the measurement location. This location should be away from the hood, sample storage, and other sources of radiation. The background reading should be taken just before each measurement on the vitrified waste. Record the background dose rate _____ mR/hr
_____	_____	Take the crucible to the measurement location.
_____	_____	Place the window of the CP in contact with the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr
_____	_____	Place the window of the CP at a distance of 6" from the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr
_____	_____	Place the window of the CP at a distance of 12" from the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr
_____	_____	Place the window of the CP at a distance of 24" from the

bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate \_\_\_\_\_ mR/hr

C. Break up the Vitrified Glass

- \_\_\_\_\_ \_\_\_\_\_ Return the crucible to the hood and place it in the fracture chamber
- \_\_\_\_\_ \_\_\_\_\_ Break up the crucible
- \_\_\_\_\_ \_\_\_\_\_ Place ~ 100 g of the broken glass into a labelled sample can for the modified TCLP test. Record the mass of glass put in the can. \_\_\_\_\_ g
- \_\_\_\_\_ \_\_\_\_\_ Place ~ 300 g of the broken glass into a labelled sample can for the full TCLP test. Record the mass of glass put in the can. \_\_\_\_\_ g
- \_\_\_\_\_ \_\_\_\_\_ Place ~ 300 g of the broken glass into a labelled sample can for PCT testing and conductivity and viscosity analysis. Record the mass of glass put in the can. \_\_\_\_\_ g
- \_\_\_\_\_ \_\_\_\_\_ Place the remainder of the broken glass into a labelled sample can. This glass will be used for the apparent density measurement and the radon emanation measurement at 7 and 30 days. Record the mass of glass put in the can \_\_\_\_\_ g
- \_\_\_\_\_ \_\_\_\_\_ Place the remainder of the broken crucible in a labelled sample can

D. Transfer of Samples

- \_\_\_\_\_ \_\_\_\_\_ Send sample can containing ~ 100 g glass (# \_\_\_\_\_) to CEP for the modified TCLP test
- \_\_\_\_\_ \_\_\_\_\_ Send sample can containing ~ 500 g ( \_\_\_\_\_ ) to the off-site laboratory for the full TCLP test
- \_\_\_\_\_ \_\_\_\_\_ Send the condensate to CEP for analysis following the required shipping procedures (temperature, etc.)
- \_\_\_\_\_ \_\_\_\_\_ Send the gas sample to the 325 building for analysis
- \_\_\_\_\_ \_\_\_\_\_ Send sample to the 3720 building for the PCT analysis. When results from the modified TCLP are positive, have them also perform the conductivity and viscosity analysis

E. Apparent Density of the Vitrified Waste

\_\_\_\_\_ \_\_\_\_\_ Fill a 2000 ml beaker about three-fourths full with de-ionized water, place it on the electronic balance, and tare the scale

\_\_\_\_\_ \_\_\_\_\_ Suspend a stainless steel mesh basket from a fine wire (or fishing line) with a well defined mark to which the basket can be consistently submerged. Submerge the basket to this mark in the beaker and tare the scale.

\_\_\_\_\_ \_\_\_\_\_ Lift the basket out of the water being sure to keep it over the beaker so any water that drips off the basket falls into the beaker. Place a known mass of vitrified sample (about 50-100 g) in the basket. The pieces must be large enough to stay in the basket. Record the mass of glass placed in the basket,  $m_s =$  \_\_\_\_\_ g

\_\_\_\_\_ \_\_\_\_\_ Submerge the basket to the mark. Record the mass from the electronic scale,  $F_b =$  \_\_\_\_\_ g. This is the buoyant force.

\_\_\_\_\_ \_\_\_\_\_ Measure and record the temperature of the water in the beaker. \_\_\_\_\_ °C

\_\_\_\_\_ \_\_\_\_\_ Look up the density of water at the above temperature,  $\rho =$  \_\_\_\_\_ g/cm<sup>3</sup>

\_\_\_\_\_ \_\_\_\_\_ Calculate the apparent density of the vitrified waste as follows: apparent density =  $m_s / (F_b / \rho)$

where:

$m_s$  = mass of the vitrified sample submerged

$F_b$  = buoyant force

$\rho$  = density of water at measured temperature

Apparent density = \_\_\_\_\_ g/cm<sup>3</sup>

F. Radon Emanation from Vitrified K-65 Waste at 7 and 30 Days

Radon emanation data at 7 and 30 days is only required for K-65 waste (Sequence A, B, and D). This will be measured with a Pylon AB-5 monitor operating with a flow of about 0.2 scfh. Figure 4 shows the valve positions for performing this measurement.

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\_\_\_\_\_

Set the Pylon in the radon mode and enter the required data. Adjust the flow to 0.2 scfh

\_\_\_\_\_

Open valves V6 and V8 and close V7. Flush the radon monitor with clean air and measure the background. Record the background measurement \_\_\_\_\_ pCi/L

\_\_\_\_\_

Place the lid on the empty sample container and clamp it. Close V6 and open V7 and repeat the background count. Record the background measurement \_\_\_\_\_ pCi/L. Stop the monitor and enter this new value as the background.

\_\_\_\_\_

Place a known mass of the vitrified sample (~ 100-200 g) into a sample can of 4" diameter. Label the can with the test number and an explanation of the contents. Distribute the material evenly in the can. Record the actual mass of vitrified sample \_\_\_\_\_ g. Estimate the surface area of the sample being measured.

\_\_\_\_\_

Place the can in the monitoring chamber and clamp the lid

\_\_\_\_\_

Start the monitor and record the flowrate at F3 \_\_\_\_\_ scfh

\_\_\_\_\_

Monitor the radon levels until the concentration reaches steady state. Record the steady state concentration,

\_\_\_\_\_

\_\_\_\_\_ pCi/L

\_\_\_\_\_

Repeat the above steps at 30 days and fill in the following table

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Test Number \_\_\_\_\_

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	Sample Mass (g)	Estimated Surface Area (m <sup>2</sup> )	Background (pCi/L)	Flow at F3 (scfh)	Steady-state Conc. (pCi/L)
7 days					
30 days					



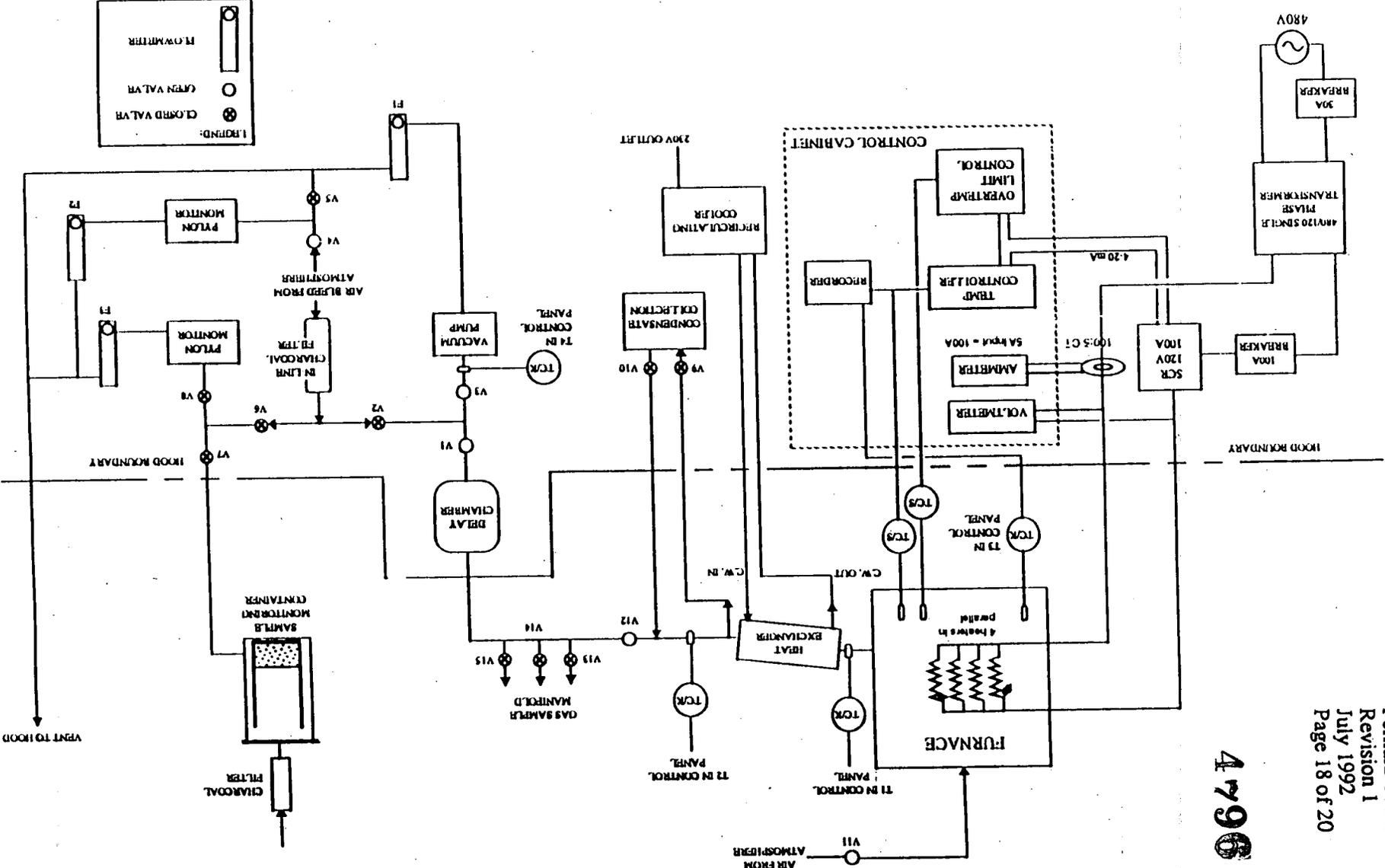
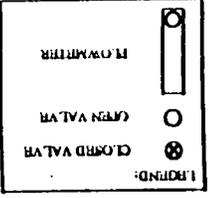


Figure 2. Valve Positions for Open System Vitrification



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0120

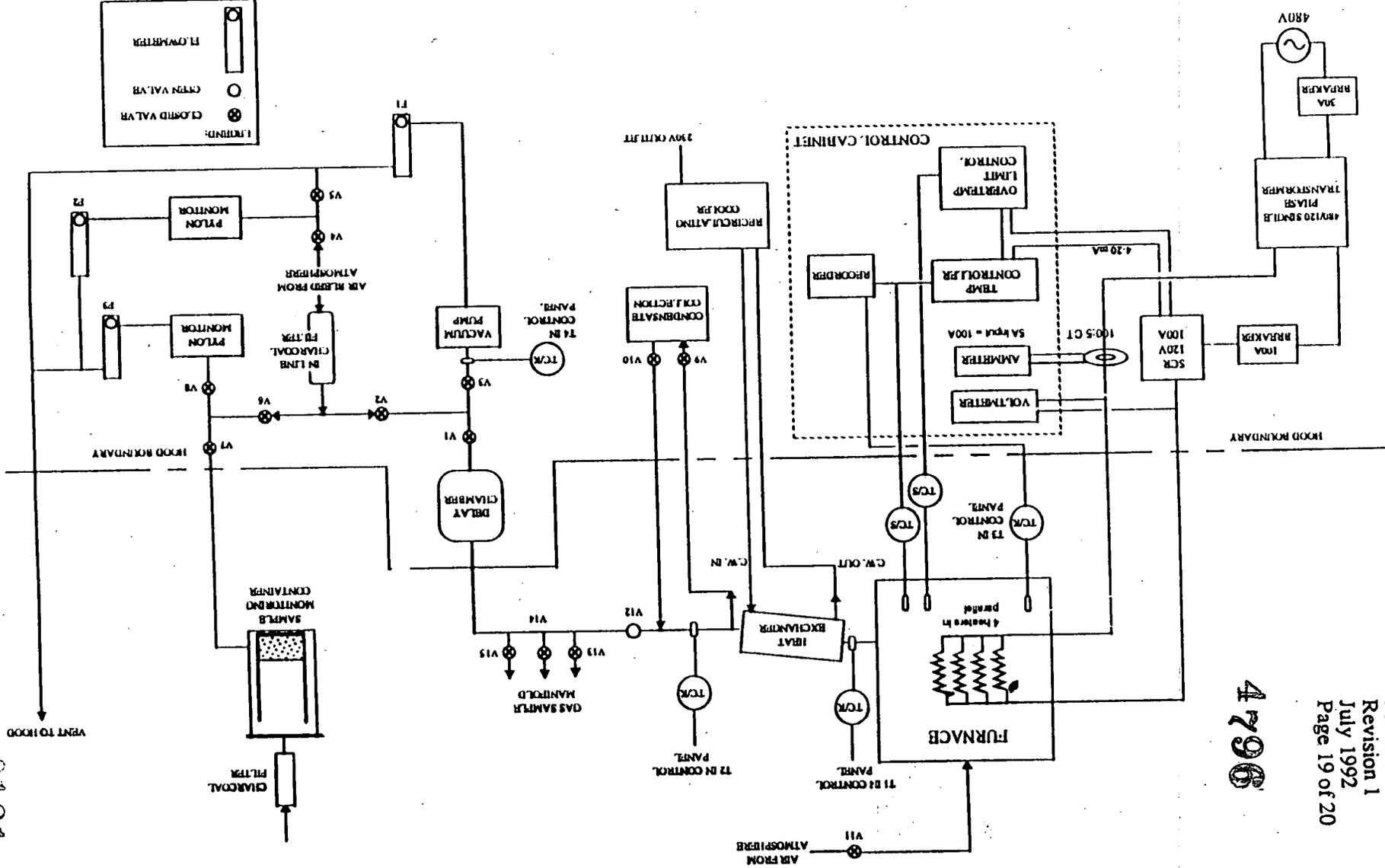


Figure 3. Valve Positions for Closed System Purification

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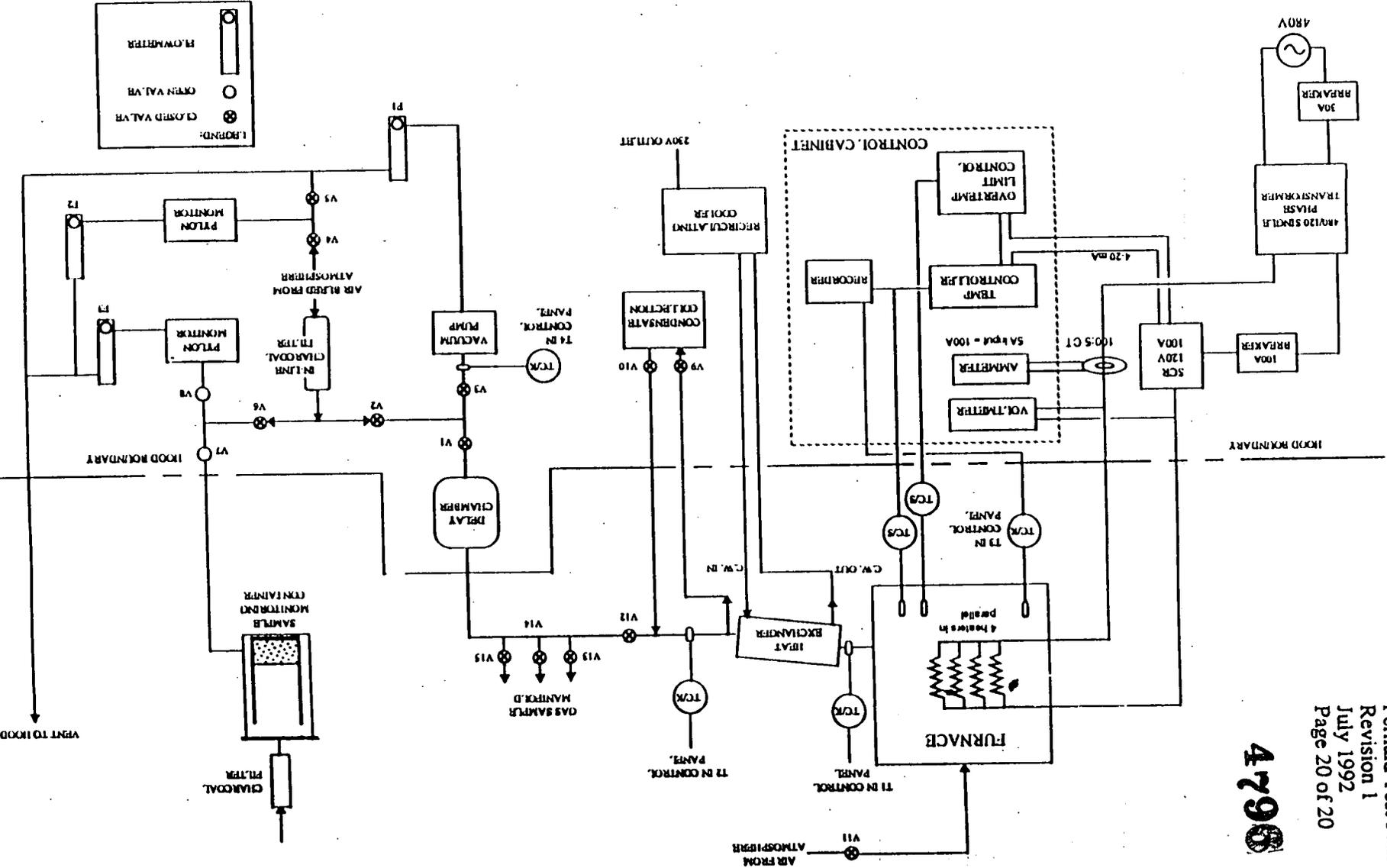


Figure 4. Valve Positions for Radon Monitoring on the Verified Product

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APPENDIX C  
TREATABILITY LABORATORY QA PLAN

C-1

0123

QA PLAN

QA Plan No. WTC-060 Rev. 1  
Effective Date May 11, 1992  
Page 1 of 4

PROJECT IMPACT LEVEL: II

TITLE: QA Plan for Fernald Support Project

- SCOPE: The overall objectives of this scope of work are as follows:
- Determine chemical and physical properties of the K-65 residue and the Silo-3 metal oxides.
  - Develop formulations for vitrifying these materials including blends of the K-65 with the Silo-3 materials and blends of the K-65 residue with Bento-Grout.
  - Determine the amount of radon emanation from the K-65 material during vitrification.
  - Determine the amount of radon emanation from the vitrified K-65 residue and K-65 blends.
  - Determine the composition of both the process off gas and the condensates.

CLIENT: Westinghouse Environmental Management Company of Ohio (WEMCO),  
Fernald Environmental Management Project (FEMP)

AUTHORIZING DOCUMENT: WEMCO Purchase Order 625151, Project No. 16611

CONCURRENCES AND APPROVAL:

<u><i>Sam Jank</i></u>	<u>5/8/92</u>
Project Manager (Concurrence)	Date
<u><i>J.E. McDaniel</i></u> <i>KEM 5/8/92</i>	<u>5/11/92</u>
Process Quality (Concurrence)	Date
<u><i>Chris Chapman</i></u>	<u>5/12/92</u>
Line Manager (Approval)	Date

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QA REQUIREMENT SPECIFICATION(S):

- [x] ASME NQA-1 as delineated in PNL-MA-70
- [x] Operable Unit 4 Treatability Study Work Plan For Vitrification of Residues From Silos 1,2, and 3. (Work Plan), March 1992

Impact Level II WBS element activities shall comply with the applicable requirements, as appropriate for the work being performed, in Parts 1 and 3 of PNL-MA-70. Impact Level III activities shall comply with the GPS Standards located in Part 2 of PNL-MA-70. If other quality-related activities are later performed, the appropriate PNL-MA-70 requirements and procedures shall be applied, unless specifically excluded in one of the above listed management documents.

QA PROGRAM/ORGANIZATION: See Exhibit 2 for Internal Organization Structure

Project Manager: DS Janke

Task 1	DS Janke
Task 2	SM Cote
Task 3	JT Jeffs
Task 4	RA Merrill
Task 5	DS Janke

Material Custodian:	Each task leader or designee
Records Custodian:	" "
M&TE Custodian:	" "
Training Custodian:	ED Golding
Quality Engineer:	KR Martin
WEMCO Tech. Rep.:	RA Vogel

IMPACT LEVEL: The project impact level has been determined to be Impact Level II. See Exhibit 1, Impact Level Matrices, for project element impact levels.

SPECIAL CLIENT REQUIREMENTS:

A. Covered by Part(s) 1 and/or 3 of PNL-MA-70.

1. Client Requirement

As described in "Operable Unit Treatability Study Work Plan", reference section 7.0, third paragraph: "TCLP analyses performed on vitrified materials will follow standard QA/QC protocol in the QAPP and Volume 4 on the RI/FS Work Plan".

0125

Disposition Schedule/File Index (RIDS). Task records shall be provided to the task records custodian within 30 days of its origination. All records for completed tasks will be transferred to WEMCO and Building 712 within 90 days after project completion.

B. Material Control

All work performed within PNL shall have material control procedures per PAP-70-801. In this QA Plan, section B, #1, describes when Chain of Custody Forms are required. Also see this QA Plan, section C, #2 and #3 for other material control requirements.

C. Test plans for this project shall be in accordance with PAP-70-1101. Approval authority for each test plan shall be the following applicable PNL staff members:

- Test Plan Preparer
- Project Manager
- Quality Engineer
- Building Manager

D. Laboratory Record Books shall be reviewed at least quarterly or sooner if deemed necessary by the Project Manager. Reviews and other LRB documentation shall be recorded per instructions in PNL-MA-68, Section 6.4.

E. All contracted analytical work shall be in accordance with PAP-70-401, and PAP-70-404, as appropriate.

F. Prior to PNL releasing the Final Report, an Independent Technical Review (ITR) per PAP-70-604 shall be performed. WEMCO shall also be given the opportunity to provide a review at that time. The Project Manager shall keep all documents resulting from the review as project records.

Program: Fernald Support Project  
 Date: 5/8/92 Rev.No.: 1

Battelle							WBS Impact Level			Remarks		
Index No.	WBS Element Level						WBS Element Title	WBS Element Code	Impact Level			
	1	2	3	4	5	6			I		II	III
1	X						Project Administration	1.0		X		
2	X						Project Control	1.1		X		
3	X						Project Support	1.2		X		
4		X					Test Documentation	2.0		X		
5			X				Laboratory Screening Work	3.0		X		As specified in WEMCO Work Plan
6				X			Bench Scale Test	4.0		X		
7				X			Task Management	4.1		X		
8				X			Equipment Modification	4.2			X	
9				X			Equipment Preparation	4.3		X		
10				X			Shakedown	4.4			X	
11				X			Test	4.5		X		
12				X			Equipment Standby	4.6			X	
13				X			Waste Management	4.7			X	
14				X			Analytical Work	4.8		X		As specified in WEMCO Work Plan
15					X		Technical Reports	5.0		X		

0127

Exhibit 1

1796

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Where Covered

The EPA standard TCLP Method 1311 with Data Quality Objective (DQO) levels II and V, was appended to the Work Plan. Since PNL and its subcontractors are only required to perform modified TCLP, WEMCO has specified NQA-1 as the primary protocol for QA requirements, and will take precedence over all other QA sources. NQA-1 is interpreted by PNL through PNL-MA-70 and this QA Plan. However, PNL will expect the selected subcontractor to meet the minimum requirements of EPA's SW-846, Method 1311, section 8.1; and SW-846, Chapter 1, QA/QC requirements. These requirements shall be specified in a PNL Statement of Work to the subcontractor as delineated in PAP-70-404, Exhibit 1. This QA Plan will satisfy the QA requirements for all other work performed by PNL. (Ref. WEMCO meeting minutes, dated March 2, 1992, or PNL RIDS, Project 16611, File C.5.1, - Subject: Operable Unit 4 Vitriification Treatability Studies Meeting - February 18, 1992, Page 1 of 4, Question 1.).

- B. Not covered by Part(s) 1 and/or 3 of PNL-MA-70.
1. WEMCO Chain of Custody Forms and Procedures will be furnished by WEMCO. These forms and procedures will be used on TCLP samples submitted to International Technology Analytical Services (IT).
  2. Deviations to the Work Plan are to be verbally discussed with WEMCO and EPA, when they are identified. A Document Change Request (DCR) furnished by WEMCO shall be used to document any changes to the EPA approved Work Plan.
- C. Client required exclusions or limitations of procedure applicability.
1. Radon emanation tests for sequences A, B, and D are called out in the Work Plan and project specific test procedures/plans at intervals of 7 day and 30 day durations. These intervals are intended to be only approximations. (Ref. Meeting Minutes of March 2, 1992, minor issues, #2)
  2. WEMCO shall provide to PNL a procedure and point of contact for the shipment of waste to FEMP. (Ref. meeting minutes, March 2, 1992, minor issue, #4)

**OTHER REQUIREMENTS, LIMITATIONS, DIRECTIONS, OR PLANNING:**

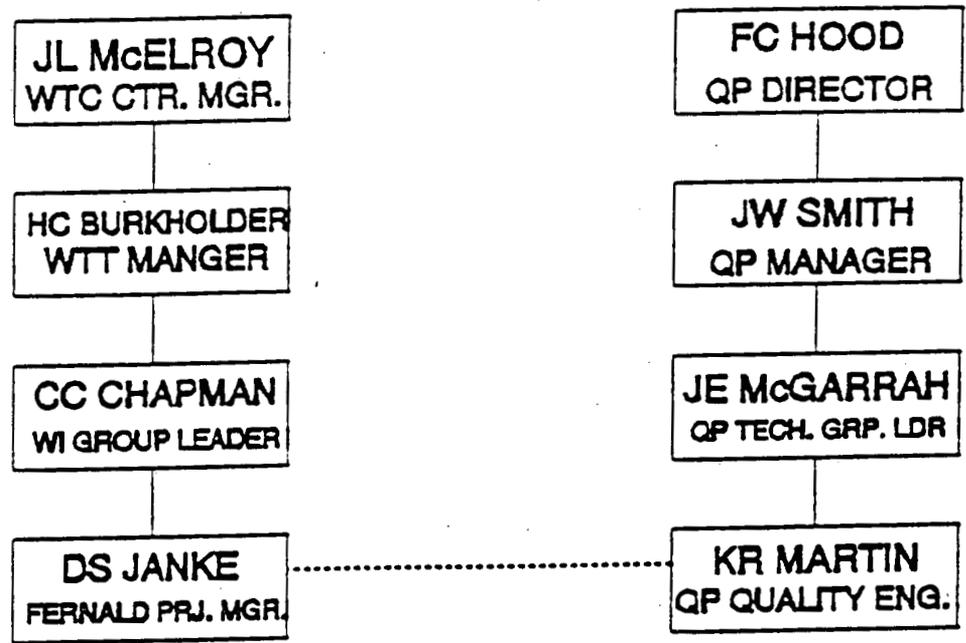
A. Disposition of Records

Records shall be indexed and maintained in accordance with PNL-MA-70 Administrative Procedures PAP-70-1701, Records System. The retention period shall be specified as nonpermanent. The cognizant Quality Engineer shall review and concur with the Records Inventory and

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### ORGANIZATION CHART EXHIBIT 2



4796

APPENDIX D  
VALIDATED ANALYTICAL DATA

D-1

0130

**SAMPLE INDEX FOR OPERABLE UNIT 4  
TREATABILITY STUDY VITRIFICATION TESTING**

**4796**

<u>Sample No.</u>	<u>Description</u>
75551	Glass from Sequence A Open System
75552	Glass from Sequence B Open System
75553	Glass from Sequence C Open System
75554	Glass from Sequence D Open System
75555	Glass from Sequence A Closed System
75556	Glass from Sequence B Closed System
75557	Glass from Sequence C Closed System
75558	Glass from Sequence D Closed System

Suffix Codes

001 - TCLP Leachate, Radiological and Inorganic Analysis  
012 - PCT Leachate, Replicate 1, Inorganic Analysis  
022 - PCT Leachate, Replicate 2, Inorganic Analysis  
032 - PCT Leachate, Replicate 3, Inorganic Analysis  
132 - PCT Leachate, Replicate 3, Radiological Analysis

Sequence Description

Sequence A - 100% K-65 Material  
Sequence B - 50% K-65 Material, 50% BentoGrout  
Sequence C - 100% Silo 3 Material  
Sequence D - 70% K-65 Material, 30% Silo 3 Material

0131

LABORATORY QUALIFIERS

4796

Inorganic Qualifiers

Concentration Qualifiers (C)

- "B" Reported value was obtained from a reading that was less than Contract Required Detection Limit (CRQL) but greater than or equal to the Instrument Detection Limit (IDL).
- "U" Analyte was analyzed for but not detected.

Quality Qualifiers (Q)

- "E" The reported value is estimated because of the presence of interference.
- "N" Spiked sample recovery not within control limits.
- "S" The reported value was determined by the Method of Standard Additions.
- "W" Post-digestion spike for Furnace AA analysis is not out of control limits (85-115%), while sample absorbance is less than 50% of spike absorbance.
- "•" Duplicate analysis not within control limits.
- "M" Duplicate injection precision not met.
- "G" Native analyte > 4 times spike added, therefore acceptance criteria do not apply.
- "X" Detection limit is higher than normal due to sample matrix interferences.
- "+" Correlation coefficient for the MSA is less than 0.955.

0132

CHEMICAL VALIDATION QUALIFIERS

4796

- "N" Tentative identification. Consider present. Special methods may be needed to confirm its presence or absence in future sampling efforts.
- "K" Analyte present. Reported value may be biased high. Actual value is expected to be lower.
- "L" Analyte present. Reported value may be biased low. Actual value is expected to be higher.
- "UJ" Not detected, quantitation limit may be inaccurate or imprecise.
- "UB" Not detected, quantitation limit is probably higher.
- "JB" Approximate data due to blank contamination.
- "J" Analyte present. Reported value may not be accurate or precise.
- "R" Results unusable. Analyte may or may not be present in the sample. Supporting data necessary to confirm result. Resampling and reanalysis would be necessary.
- "-" Validated, but not qualified.

## RADIOLOGICAL DATA VALIDATION QUALIFIERS

4796

- "C" The total uranium analytical result (mass) does not agree within +/- 20% of the calculated uranium mass as determined by isotope specific analyses. This qualifier is not applied to analytical results which are less than ten (10) times the contract required quantitation limit (CRQL).
- "D" The radionuclide was analyzed for but not detected. The reported SQL exceeds the CRQL and professional judgement must be exercised in the use of this data depending on the media that was sampled and the end use of the data (ie. risk assessment, nature and extent, etc.).
- "E" The calculated U-235/U-238 mass ratio is outside of 0.2 - 1.3% enrichment and may indicate man's involvement in isotope depletion or enrichment. Professional judgement should be exercised in evaluating the likelihood of this occurrence. The U-235/U-238 ratio for soil in nature is 0.0072. This qualifier is not applied to analytical results which are less than ten (10) times the contract required CRQL.
- "F" The calculated U-234/U-238 activity ratio is less than 0.4 or greater than 1.3 and may indicate man's involvement in isotope separation. Professional judgement should be exercised in evaluating the likelihood of this occurrence. The U-234 and U-238 isotopes are generally in equilibrium (or slightly depleted in U-234) in soil impacted groundwater. This qualifier is not applied to analytical results which are less than ten (10) times the contract required CRQL.
- "M" The matrix spike per cent recovery is not within the control limits of 70-130%.
- "J" The reported value should be considered an estimate based on laboratory quality control results or lack of QC documentation.
- "R" Laboratory quality control results indicates that the data are unusable (analyte may or may not be present). Re-sampling and/or re-analysis is necessary for verification.
- "-" The analysis meets all requirements of the indicated analytical support level (ASL).

0134

**TABLE D-1**  
**SUMMARY OF TCLP RADIOLOGICAL ANALYSIS FOR SILO 3 RAW MATERIAL**  
 (Results reported in pCi/l)

Analyte	100074	a	b
Protactinium-231	< 647		D
Actinium-227	5.54	1.94	-
Lead-210	87.1	9.2	J
Polonium-210	245	110	J
Radium-226	2455	558	-
Radium-228	< 110		D
Thorium-228	3.17	1.42	J
Thorium-230	10.4	2.8	J
Thorium-232	< 1.0		-
Uranium-234	92.2	13.8	-
Uranium-235/236	5.09	1.59	-
Uranium-238	86.0	13.0	-
Gross Alpha	3150	830	J
Gross Beta	670	340	J

a-two sigma error  
 b-validation qualifier

**TABLE D-2**  
**SUMMARY OF TCLP METALS ANALYSES FOR SILO 3 RAW MATERIAL**  
 (Results reported in ug/l)

**4798**

Analyte	100074	a	b
Aluminum	3230	-	J
Antimony	6.4	B	J
Arsenic	6420	-	J
Barium	123	B	UJ
Beryllium	10	U	UJ
Cadmium	109	-	J
Calcium	739000	-	J
Chromium	6020	-	J
Cobalt	21200	-	J
Copper	1040	-	J
Iron	101	B	UJ
Lead	26.1	-	J
Magnesium	2010000	-	J
Manganese	4160	-	J
Mercury	0.27	-	J
Nickel	39200	-	J
Potassium	370000	B	J
Selenium	982	-	J
Silver	50	U	UJ
Sodium	1670000	-	J
Thallium	67	-	R
Vanadium	2720	-	J
Zinc	271	-	UJ
Molybendum	NA		
Silicon	96800	-	J
Boron	17600	-	J
Lithium	72500	-	J

a-laboratory qualifier  
 b-validation qualifier

0136

**TABLE D-3**  
**SUMMARY OF TCLP RADIOLOGICAL ANALYSIS FOR VITRIFIED WASTE**  
 (Results in pCi/l)

~~4796~~ 4796

**SEQUENCE A**

Analyte	75551-001		75555-001			
	(open)	a	b	(closed)	a	b
Protactinium-231	< 546		D	< 474		D
Actinium-227	1.32	0.42	J	1.73	0.55	-
Lead-210	4140	410	-	2800	280	-
Polonium-210	735	179	-	302	66	-
Radium-226	4630	670	-	4200	610	-
Radium-228	13.1	5.4	R	13.2	4.8	R
Thorium-228	4.94	0.92	-	5.44	1.12	-
Thorium-230	468	56	-	515	62	-
Thorium-232	< 1.0		-	8.13	1.44	-
Uranium-234	14.3	2.9	-	10.1	1.8	-
Uranium-235/236	< 1.0		-	< 1.0		-
Uranium-238	14.7	2.9	-	10.4	1.9	-
Total Uranium <sup>c</sup>	44.1	9	-	31.5	5.7	-
Total Thorium <sup>c</sup>	6.17	2.47	-	73.4	13.0	-

a-two sigma error  
 b-validation qualifier  
 c-results reported in ug/l

0137

**TABLE D-4**  
**SUMMARY OF TCLP RADIOLOGICAL ANALYSIS FOR VITRIFIED WASTE**  
 (Results in pCi/l)

**4796**

**SEQUENCE B**

Analyte	75552-001			75556-001		
	(open)	a	b	(closed)	a	b
Protactinium-231	< 350		-	< 350		-
Actinium-227	< 1.0		-	< 1.0		-
Lead-210	1620	160	-	1760	180	-
Polonium-210	358	128	-	244	52	-
Radium-226	3446	550	-	1660	250	-
Radium-228	15.0	5.20	R	11.3	4.2	R
Thorium-228	1.16	0.42	J	2.19	0.75	J
Thorium-230	142	17	-	103	13	-
Thorium-232	< 1.0		-	< 1.0		-
Uranium-234	8.97	2.31	-	11.8	3	-
Uranium-235/236	2.76	1.22	-	< 1.1		-
Uranium-238	5.29	1.71	-	11.5	2.9	-
Total Uranium <sup>c</sup>	17.0	5.60	-	34.7	9.1	-
Total Thorium <sup>c</sup>	5.83	2.70	-	< 3.4		-

a-two sigma error

b-validation qualifier

c-results reported in ug/l

**TABLE D-5**  
**SUMMARY OF TCLP RADIOLOGICAL ANALYSIS FOR VITRIFIED WASTE**  
 (Results in pCi/l)

**4796**

**SEQUENCE C**

Analyte	75553-001 (open)			75557-001 (closed)		
		a	b		a	b
Protactinium-231	< 350		-	< 350		-
Actinium-227	2.62	2.62	-	< 1.0		-
Lead-210	48.5	5.5	-	61.4	6.9	-
Polonium-210	7.22	2.68	-	8.29	1.73	-
Radium-226	38.6	5.8	-	51.7	7.7	-
Radium-228	< 6.4		D,R	< 7.5		D,R
Thorium-228	1.13	0.72	-	< 1.0		-
Thorium-230	6.07	1.51	-	27.4	3.9	-
Thorium-232	< 1.0		-	< 1.0		-
Uranium-234	94.3	12	-	90.2	11.5	-
Uranium-235/236	4.31	1.34	-	4.00	1.26	-
Uranium-238	95.9	12.2	-	94.5	12	-
Total Uranium <sup>c</sup>	287	37.0	-	283	36	-
Total Thorium <sup>c</sup>	2.15	2.17	-	< 3.9		-

a-two sigma error

b-validation qualifier

c-results reported in ug/l

0139

**TABLE D-6**  
**SUMMARY OF TCLP RADIOLOGICAL ANALYSIS FOR VITRIFIED WASTE**  
 (Results in pCi/l)

**4798**

**SEQUENCE D**

Analyte	75554-001			75558-001		
	(open)	a	b	(closed)	a	b
Protactinium-231	<434		D	<447		D
Actinium-227	2.21	0.62	J	1.94	0.55	J
Lead-210	2150	220	-	2190	220	-
Polonium-210	259	70	-	256	56	-
Radium-226	2360	350	-	1930	290	-
Radium-228	41.7	7.5	R	28.9	5.4	R
Thorium-228	2.90	0.72	J	2.35	0.64	J
Thorium-230	140	17	-	109	13	-
Thorium-232	1.0		-	<1.0		-
Uranium-234	12.1	2.2	-	10.7	1.9	-
Uranium-235/236	1.14	0.58	J	<1.0		-
Uranium-238	11.6	2.1	-	11.0	2.0	-
Total Uranium <sup>c</sup>	34.9	6.6	-	33.0	6.0	-
Total Thorium <sup>c</sup>	7.04	3.03	-	3.45	2.35	-

a-two sigma error

b-validation qualifier

c-results reported in ug/l

0140

**TABLE D-7**  
**SUMMARY OF TCLP METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

4796

**SEQUENCE A**

Analyte	75551-001			75555-001		
	(open)	a	b	(closed)	a	b
Aluminum	172	B	-	137	B	-
Antimony	ND	U	-	5.0	U	-
Arsenic	3.8	B	-	4.7	B	-
Barium	866	-	-	691	-	-
Beryllium	2.0	U	-	2.0	U	-
Cadmium	5.0	U	-	5.0	U	-
Calcium	345	B	-	245	B	-
Chromium	10.0	U	-	10.0	U	-
Cobalt	26	B	-	21.2	B	-
Copper	29.7	-	-	27.6	-	-
Lead	1200	-	-	806	-	-
Magnesium	156	B	-	131	B	-
Manganese	10.0	U	-	11.4	B	-
Mercury	0.20	U	-	0.20	U	-
Nickel	58.6	-	-	44.8	-	-
Potassium	261	B	-	234	B	-
Selenium	2.0	U	-	2.0	U	-
Silver	10.0	U	-	10.0	U	-
Sodium	100	U	-	100	U	-
Thallium	N2.0	U	-	2.0	U	-
Vanadium	10.0	U	-	10.0	U	-
Zinc	32.3	-	-	74.8	-	-
Molybendum	44.4	-	-	29.2	-	-
Silicon	1860	-	-	1640	-	-
Boron	20.7	-	-	12.6	-	-
Lithium	50.0	U	-	50.0	U	-

a-laboratory qualifier  
 b-validation qualifier

0141

4796

**TABLE D-8**  
**SUMMARY OF TCLP METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

**SEQUENCE B**

Analyte	75552-001		75556-001			
	(open)	a	b	(closed)	a	b
Aluminum	318	-	-	253	-	-
Antimony	5.0	U	-	5.0	U	-
Arsenic	2.6	B	-	29	-	-
Barium	429	-	-	561	-	-
Beryllium	2.0	U	-	2.0	U	-
Cadmium	5.0	U	-	5.0	U	-
Calcium	595	B	-	770	B	-
Chromium	10.0	U	-	10.0	U	-
Cobalt	11.6	B	-	10.9	B	-
Copper	25.1	-	-	34.7	-	-
Lead	473	-	-	377	-	-
Magnesium	176	B	-	543	B	-
Manganese	14.6	B	-	54.6	-	-
Mercury	0.20	U	-	0.20	U	-
Nickel	30.0	B	-	126	-	-
Potassium	244	B	-	254	B	-
Selenium	2.0	U	-	2.0	U	-
Silver	10.0	U	-	10.0	U	-
Sodium	100	U	-	100	U	-
Thallium	2.0	U	-	2.0	U	-
Vanadium	10.0	U	-	18	B	-
Zinc	23.2	-	-	121	-	-
Molybendum	23.9	-	-	39.7	-	-
Silicon	1460	-	-	1130	-	-
Boron	10.0	U	-	57.1	-	-
Lithium	50.0	U	-	50.0	U	-

a-laboratory qualifier  
 b-validation qualifier

1796

**TABLE D-9**  
**SUMMARY OF TCLP METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

**SEQUENCE C**

Analyte	75553-001		75557-001			
	(open)	a	b	(closed)	a	b
Aluminum	410	-	-	383	-	-
Antimony	5.0	U	-	5.0	U	-
Arsenic	786	-	-	470	-	-
Barium	27.5	B	-	73.8	B	-
Beryllium	3.1	B	-	2.4	B	-
Cadmium	11.5	-	-	7.0	-	-
Calcium	10400	-	-	6780	-	-
Chromium	10.0	U	-	10.0	U	-
Cobalt	172	-	-	51.6	-	-
Copper	472	-	-	289	-	-
Lead	1606	-	-	18.5	-	-
Magnesium	15400	-	-	8420	-	-
Manganese	1220	-	-	761	-	-
Mercury	0.20	U	-	0.20	U	-
Nickel	20.0	U	-	20.0	U	-
Potassium	777	B	-	593	B	-
Selenium	2.0	U	-	2.0	U	-
Silver	10.0	U	-	10.0	U	-
Sodium	100	U	-	100	U	-
Thallium	2.0	U	-	2.0	U	-
Vanadium	488	-	-	271	-	-
Zinc	60.7	-	-	36.7	-	-
Molybendum	345	-	-	177	-	-
Silicon	3570	-	-	1720	-	-
Boron	1730	-	-	832	-	-
Lithium	487	-	-	276	-	-

a-laboratory qualifier  
 b-validation qualifier

**TABLE D-10**  
**SUMMARY OF TCLP METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

**SEQUENCE D**

Analyte	75554-001		75558-001			
	(open)	a	b	(closed)	a	b
Aluminum	106	B	-	146	B	-
Antimony	5.0	U	-	5.0	U	-
Arsenic	66.9	-	-	37.8	-	-
Barium	1990	-	-	1570	-	-
Beryllium	2.0	U	-	2.0	U	-
Cadmium	5.0	U	-	5.0	U	-
Calcium	1540	B	-	895	B	-
Chromium	10.0	U	-	10.0	U	-
Cobalt	30.3	B	-	25.4	B	-
Copper	110	-	-	59.1	-	-
Lead	499	-	-	577	-	-
Magnesium	646	B	-	527	B	-
Manganese	46.7	-	-	30.3	-	-
Mercury	0.20	U	-	0.20	U	-
Nickel	66.6	-	-	54.1	-	-
Potassium	299	B	-	245	B	-
Selenium	2.0	U	-	2.0	U	-
Silver	10.0	U	-	10.0	U	-
Sodium	100	U	-	100	U	-
Thallium	2.0	U	-	2.0	U	-
Vanadium	33.6	B	-	23.3	B	-
Zinc	61.2	-	-	34.5	-	-
Molybendum	50.2	-	-	21.5	-	-
Silicon	1480	-	-	1690	-	-
Boron	1805	-	-	10.0	U	-
Lithium	50.0	U	-	50.0	U	-

a-laboratory qualifier

b-validation qualifier

**TABLE D-11**  
**SUMMARY OF PCT RADIOLOGICAL ANALYSIS FOR VITRIFIED WASTE**  
 (Results in pCi/l)

**4796**

**SEQUENCE A**

Analyte	75551-132			75555-132		
	(open)	a	b	(closed)	a	b
Radium-226	8390	1380	-	7230	1210	-
Radium-228	<115		-	<105		-
Total thorium <sup>c</sup>	<8.6		J	<10.1		J
Total uranium <sup>c</sup>	<1.0		-	1.79	0.19	J

**SEQUENCE B**

Analyte	75552-132			75556-132		
	(open)	a	b	(closed)	a	b
Radium-226	1480	390	-	1410	390	-
Radium-228	<74.5		-	<71.3		-
Total Thorium <sup>c</sup>	<6.2		J	<4.7		J
Total Uranium <sup>c</sup>	9.18	1.8	-	13.2	1.9	-

**SEQUENCE C**

Analyte	75553-132			75557-132		
	(open)	a	b	(closed)	a	b
Radium-226	<1420		D	<1225		D
Radium-228	<289		-	<375		-
Total Thorium <sup>c</sup>	<6.1		D	14.2	6.8	J
Total Uranium <sup>c</sup>	43.0	6.2	-	29.4	4.3	-

**SEQUENCE D**

Analyte	75554-132			75558-132		
	(open)	a	b	(closed)	a	b
Radium-226	2560	570	-	2480	550	-
Radium-228	<105		-	<72.3		-
Total Thorium <sup>c</sup>	<10.1	1.75	J	5.45	2.68	J
Total Uranium <sup>c</sup>	1.79	0.3	J	1.36	0.14	J

a-two sigma error

b-two sigma error

c-results reported in ug/l

0145

**TABLE D-12**  
**SUMMARY OF PCT METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

4796

**SEQUENCE A REPLICATE 1**

Analyte	75551-012			75555-012		
	(open)	a	b	(closed)	a	b
Potassium	1490	B	-	1730	B	-
Sodium	124000	-	-	153000	-	-
Silicon	70500	-	-	84500	-	-
Boron	182	-	-	208	-	-
Lithium	50	U	-	50	U	-

**SEQUENCE A REPLICATE 2**

Analyte	75551-022			75555-022		
	(open)	a	b	(closed)	a	b
Potassium	1620	B	-	2000	B	-
Sodium	125000	-	-	150000	-	-
Silicon	71900	-	-	85100	-	-
Boron	143	-	-	186	-	-
Lithium	50	U	-	50	U	-

**SEQUENCE A REPLICATE 3**

Analyte	75551-032			75555-032		
	(open)	a	b	(closed)	a	b
Potassium	1400	B	-	1480	B	-
Sodium	96900	-	J	101000	-	J
Silicon	52700	-	J	54500	-	J
Boron	102	U	UJ	97	U	UJ
Lithium	50	U	J	50	U	J

a-laboratory qualifier

b-validation qualifier

0146

**TABLE D-13**  
**SUMMARY OF PCT METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

4796

**SEQUENCE B REPLICATE 1**

Analyte	75552-012			75556-012		
	(open)	a	b	(closed)	a	b
Potassium	518	B	-	522	B	-
Sodium	42900	-	-	43700	-	-
Silicon	37100	-	-	37300	-	-
Boron	89.3	-	-	67.8	-	-
Lithium	50	U	-	50	U	-

**SEQUENCE B REPLICATE 2**

Analyte	75552-022			75556-022		
	(open)	a	b	(closed)	a	b
Potassium	610	B	-	617	B	-
Sodium	44200	-	-	46700	-	-
Silicon	38700	-	-	39900	-	-
Boron	73.0	-	-	79.3	-	-
Lithium	50	U	-	50	U	-

**SEQUENCE B REPLICATE 3**

Analyte	75552-032			75556-032		
	(open)	a	b	(closed)	a	b
Potassium	552	B	-	546	B	-
Sodium	33200	-	J	33200	-	J
Silicon	27300	-	J	27500	-	J
Boron	50	U	UJ	62.2	U	UJ
Lithium	50	U	UJ	50	U	UJ

a-laboratory qualifier  
 b-validation qualifier

0147

**TABLE D-14**  
**SUMMARY OF PCT METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

**4796**

**SEQUENCE C REPLICATE 1**

Analyte	75553-012			75557-012		
	(open)	a	b	(closed)	a	b
Potassium	1420	B	-	1140	B	-
Sodium	8070	-	-	6750	-	-
Silicon	15000	-	-	15000	-	-
Boron	2250	-	-	2270	-	-
Lithium	728	-	-	711	-	-

**SEQUENCE C REPLICATE 2**

Analyte	75553-022			75557-022		
	(open)	a	b	(closed)	a	b
Potassium	1640	B	-	1280	B	-
Sodium	8360	-	-	6890	-	-
Silicon	15500	-	-	15100	-	-
Boron	2170	-	-	2060	-	-
Lithium	753	-	-	733	-	-

**SEQUENCE C REPLICATE 3**

Analyte	75553-032			75557-032		
	(open)	a	b	(closed)	a	b
Potassium	1540	B	-	1280	B	-
Sodium	7100	-	J	5620	-	J
Silicon	14700	-	J	13800	-	J
Boron	1860	-	J	1700	-	J
Lithium	630	-	J	580	-	J

a-laboratory qualifier

b-validation qualifier

0148

**TABLE D-15**  
**SUMMARY OF PCT METALS ANALYSES FOR VITRIFIED WASTE**  
 (Results reported in ug/l)

**SEQUENCE D REPLICATE 1**

Analyte	75554-012		75558-012		a	b
	(open)	a	b	(closed)		
Potassium	1520	B	-	1580	B	-
Sodium	61000	-	-	69700	-	-
Silicon	62200	-	-	65400	-	-
Boron	146	-	-	173	-	-
Lithium	249	-	-	298	-	-

**SEQUENCE D REPLICATE 2**

Analyte	75554-022		75558-022		a	b
	(open)	a	b	(closed)		
Potassium	1810	B	-	1870	B	-
Sodium	62100	-	-	69100	-	-
Silicon	64400	-	-	67200	-	-
Boron	141	-	-	145	-	-
Lithium	254	-	-	293	-	-

**SEQUENCE D REPLICATE 3**

Analyte	75554-032		75558-032		a	b
	(open)	a	b	(closed)		
Potassium	1400	B	-	1450	B	-
Sodium	48000	-	J	48900	-	J
Silicon	45500	-	J	46100	-	J
Boron	78.6	U	UJ	103	U	UJ
Lithium	173	-	J	183	-	J

a-laboratory qualifier

b-validation qualifier