

# UNDERGROUND STORAGE TANK REMEDIATION BY USE OF IN SITU VITRIFICATION

Leo E. Thompson  
Pacific Northwest Laboratory  
Richland, Washington

## ABSTRACT

Pacific Northwest Laboratory (PNL) is developing a remedial action technology for underground storage tanks through the adaptation of the in situ vitrification (ISV) process. The ISV process is a thermal treatment process that was originally developed for the stabilization of contaminated soil contaminated with transuranic waste at the Hanford Site in southeastern Washington for the Department of Energy (DOE). The application of ISV to underground storage tanks represents an entirely new application of the ISV technology and is being performed in support of the DOE primarily for the Hanford site and the Oak Ridge National Laboratory (ORNL).

A field scale test was conducted in September 1990 at Hanford on a small cement and stainless steel tank (1-m dia.) that contained a simulated refractory sludge representing a worst-case sludge composition. The tank design and sludge composition was based on conditions present at the ORNL. The sludge contained high concentrations of heavy metals including Lead, Mercury, and Cadmium, and also contained high levels of stable Cesium and Strontium to represent the predominant radionuclide species present in the surrounding soil was transformed into a highly leach resistant glass and crystalline block with a mass of approximately 30 tons. During the process, the metal shell of the tank forms a metal pool at the base of the molten soil. Upon cooling, the glass and metal phases were subjected to TCLP testing and passed the TCLP criteria. Additional sampling and analyses are ongoing to determine the bulk composition of the waste forms, the fraction of volatile or semi-volatile species released to the off-gas treatment system, and to determine whether any soil surrounding the monolith was contaminated as a result of the ISV process.

## INTRODUCTION

Underground storage tanks containing sludges and salt cakes of radioactive and/or hazardous wastes represent a significant environmental concern and a major technological clean-up challenge facing many Department of Energy (DOE) sites. Numerous inactive tanks at the Oak Ridge National Laboratory (ORNL), Hanford and other sites require timely remediation to comply with state or federal environmental regulations. Several single-shell tanks at Hanford and tanks at ORNL have been placed out of service due to leaking or other operational difficulties.(1,2) Highly contaminated tanks, tanks that contain materials that cannot be economically or safely removed, and leaking tanks that have resulted in outlying contaminated soil are likely candidates for permanent remediation using the in situ vitrification (ISV) technology.

Application of ISV to underground tanks appears to be a cost-effective, safe, and environmentally sound remedial technology for a majority of tanks at DOE facilities. Using conservative assumptions, the estimated tank vitrification costs indicate the possibility of a cost savings of greater than one order of magnitude over alternative remedial technologies. By filling tanks with clean or contaminated soil and vitrifying the tank, the tank contents, and any contaminated surrounding soil, the tank is destroyed and essentially all radioactive and nonvolatile hazardous constituents are removed or immobilized in the glass for geologic periods.

This paper details the results of the first pilot-scale ISV test on a simulated underground tank and builds upon a much smaller engineering-scale test conducted by Pacific Northwest Laboratory (PNL) in 1989. The primary objectives of this test were to verify the applicability of the ISV process for tank remediation and to determine near full-scale process behavior when vitrifying tanks. Results of operational data and posttest sampling and analyses reveal that the test succeeded in completely destroying the tank and its supporting structures and immobilized nonradioactive simulants uniformly throughout the resulting monolith. Significant operational data relative to understanding the behavior of the ISV process during tank processing were obtained from this test.

## SUMMARY AND CONCLUSIONS

The first pilot-scale ISV test of a simulated underground tank buried in ORNL soil and containing a simulated refractory sludge was successfully completed by researchers at PNL in September 1990. Analyses of posttest samples and operation data indicate that the ISV process is a viable treatment technology for a majority of radioactively contaminated underground tanks.

Key observations and conclusions regarding the performance of the ISV process for this test are summarized below. The ISV process completely destroyed the tank and the tank's supporting structures and vitrified the tank contents and the soil below the tank to the target depth of 2.4 m (8 ft). A uniform glass and crystalline monolith was

produced with a mass estimated to be approximately 30 tons.

Overall, it is expected that the ISV process effectively immobilized, destroyed, or captured greater than 99.99% of all chemical species originally present in the tank sludge. For example, greater than 90% of the lead was effectively incorporated into the waste. Analyses are not yet complete on other species; however, consistent with past studies, the ISV process can be expected to effectively immobilize greater than 99.999% of the nonradioactive strontium and greater than 99.9% of the nonradioactive cesium in the resulting monolith.<sup>(3)</sup> Similar retentions can be expected for other nonvolatile or semivolatile hazardous metals. Less than 90% of the volatile hazardous species such as mercury and cadmium are expected to be retained in the melt but would be effectively removed by the off-gas treatment system.

The resulting glass and crystalline waste form easily passed Toxic Characteristic Leach Procedure (TCLP) criteria for all regulated metals.

Tanks constructed of steel create a metal waste form that sinks to the bottom of the molten pool of soil as the steel is melted. Most hazardous metal contaminants remain in an oxide form dissolved in the glass. However, some hazardous metals are reduced by the ISV process and mix or alloy with the metal phase. The resulting metal waste form passed TCLP criteria for all regulated metals (mercury data are not yet available).

A previously unknown phenomenon affecting containment was identified and characterized during the test. Due to transient gas releases from the tank up through the molten glass, the top layer of frozen glass covering the melt was rapidly disrupted causing the molten glass to almost instantaneously radiate heat to the dust and smoke particulate in the containment hood resulting in a brief period of positive pressure inside the containment hood. An engineered solution involving a radiant heat shield and a vent pipe in the melt was installed and the test continued without further incident.

Electrode feeding technology (moveable electrodes that can be inserted or retracted) proved to be invaluable in recovering from electrical short circuits when the electrodes approached or contacted molten pools of metal in the bottom of the melt. By simply raising one or more electrodes a few centimeters off the bottom of the molten glass pool, recovery from electrical short circuits was achieved.

A barrier wall made of castable refractory designed to deflect the melt shape directly contacted the molten soil for the duration of the test and survived the test with essentially no degradation. For actual remedial operations, it may be necessary to protect nearby tanks and active pipelines from the destructive forces of the vitrification process. The wall

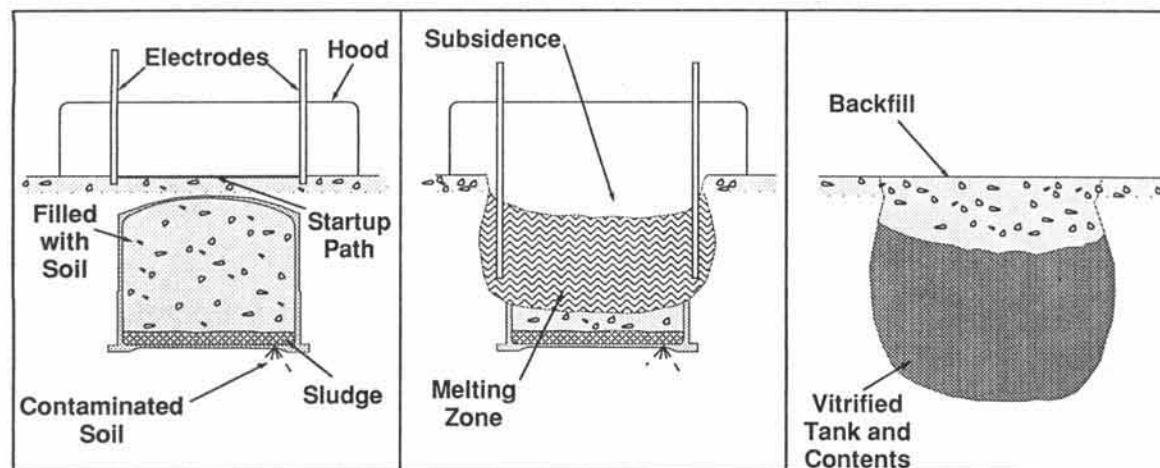
was designed to test a candidate material under actual conditions. Active cooling by the use of an air blower in the area immediately behind such a wall should result in acceptably cool temperatures to protect nearby tanks and pipelines.

Additional testing currently scheduled will be necessary to support scale-up efforts to increase the capacity of the process for application to larger tanks such as the 1-million-gallon single-shell tanks at Hanford and the 500,000-gallon tanks at ORNL. In addition to testing the process on refractory sludges, additional work will be required to evaluate the processing behavior and resulting waste form associated with tanks containing high concentrations of salts. The salt cake contained in many tanks poses unique concerns such as the influence salt has on the electrical conductivity of the melt as well as the resulting waste form.

### PROCESS DESCRIPTION AND STATUS OF DEVELOPMENT

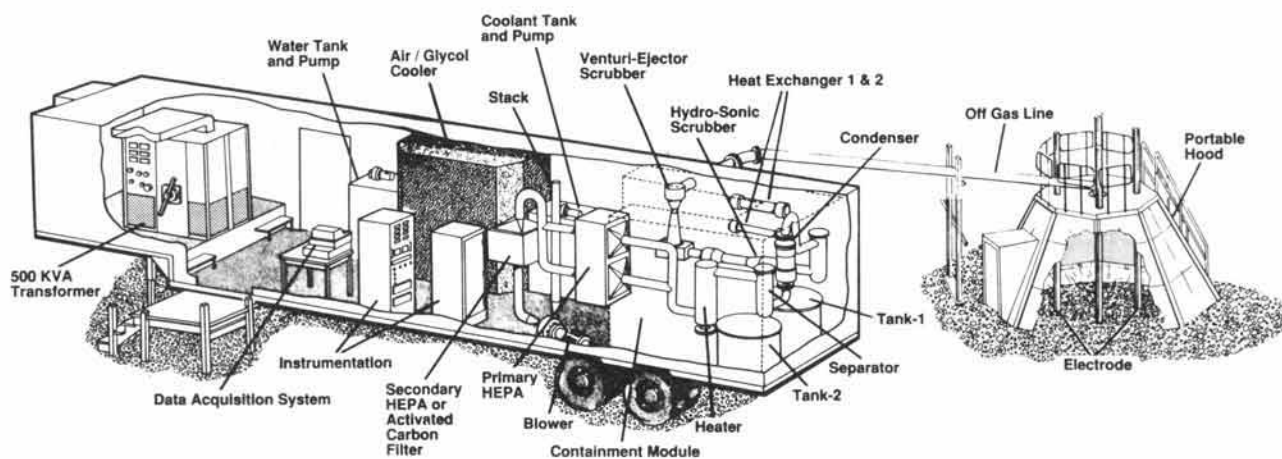
In situ vitrification has been developed as a remedial action process for soils contaminated with hazardous chemical wastes and/or radionuclides. Fig. 1 illustrates the operation of the ISV process. A square array of four graphite electrodes is inserted into the ground a few inches. Because soil is not electrically conductive when its moisture has been driven off, a conductive mixture of flaked graphite and glass frit is placed among the electrodes to serve as a starter path. An electrical potential is applied to the electrodes to establish an electrical current in the starter path. The flow of current heats the starter path and surrounding soil to well above the initial soil-melting temperatures of 1100°C to 1400°C. The graphite starter path is eventually consumed by oxidation and the current is transferred to the molten soil, which is processed at temperatures between 1450°C and 2000°C. As the molten or vitrified zone grows, it incorporates or encapsulates any radionuclides and nonvolatile hazardous elements such as heavy metals into the glass structure. The resulting glass and crystalline monolith is stable for geologic periods and is highly resistant to leaching. The high temperature of the process destroys organic components by pyrolysis. The pyrolyzed byproducts migrate to the surface of the vitrified zone, where they combust in the presence of air. A hood placed over the area being vitrified directs the gaseous effluents to an off-gas treatment system. A cutaway view of the pilot-scale ISV system is shown as Fig. 2.

In situ vitrification was originally tested by PNL researchers in August 1980.<sup>(4)</sup> Since then, numerous developmental tests and demonstrations ranging from small bench- and engineering-scale tests to larger field-sized pilot- and large-scale tests have been conducted with resulting monoliths as large as 900 tons and 12 m in diameter. In



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Fig. 1. Operating sequence for underground tank vitrification.



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Fig. 2. Cutaway view of the pilot-scale ISV process trailer and off-gas hood.



situ vitrification has emerged in recent years as an effective and efficient technology for the remediation of contaminated soil sites, and the technology has recently been transferred to the Geosafe Corporation for commercial application to soils contaminated with hazardous wastes.

## TEST CONFIGURATION

### Tank Configuration

The tank used for this test consisted of a stainless steel shell (0.9 m in diameter x 1.1 m in height) encased in a 10-cm layer of reinforced concrete. The tank design was based on a study of the 33 inactive ORNL tanks and represented a majority of tank construction styles. Rather than using just stainless steel or just concrete to represent the predominant tank styles at ORNL, the combination of concrete and steel was used to provide process-related behavior when vitrifying both materials. Other features that represent tank construction typical of other DOE sites were added to produce the most useful information possible from a single test. Instrumentation used to monitor conditions inside the tank during processing included six Type K thermocouples and three pressure taps.

### Site Layout

The tank was buried in a 2.1-m x 3-m rectangular zone of ORNL soil that extended to a depth of 3.4 m. The tank was installed in the zone of ORNL soil to provide representative soil for vitrification and posttest sampling. The tank was surrounded by a cocoon of limestone gravel that is representative of ORNL tank construction techniques. A simplified view of the site layout is shown in Fig. 3.

Instrumentation in the surrounding soil included two arrays of Type K thermocouples directly below the tank and to one side of the tank at a 1.5-m depth. The thermocouples were used to monitor the progression of melt growth as well as to track the movement of the thermal gradients following the test. A single Type C thermocouple was located in the center of the cement pad directly below the tank to provide a positive indicator of melt depth as well as to provide an indication of the melt temperature.

A wall of castable refractory with a melting temperature of greater than 1800°C and measuring 2.4 m x 1.8 m x 15 cm thick was located adjacent to the tank. The purpose of the wall was to demonstrate that the shape and growth of the melt could be controlled in order to protect nearby pipes or tanks. A rock zone was located behind the wall and two arrays of Type K thermocouples were located behind the wall.

### Tank Sludge Composition

The chemicals used to simulate the sludge were selected based on an ORNL inactive tank characterization

effort.(2) The simulated sludge was designed to represent a refractory-type sludge as opposed to a salt cake. The simulated sludge composition, which is shown in Table I, was established by selecting the maximum actual concentrations of the various tank sludge components measured in any single tank.(2) The chemicals were mixed with approximately 220 L of soil to provide a simulated sludge equaling 30% of the tank's volume, and the balance of the tank was backfilled with soil. Soil was used as a base material for the sludge and represented an alumina-silica base. Alternate materials that may have more closely represented the bulk sludge composition were not able to be defined since actual data for the bulk composition of the sludge were not yet available from ongoing tank characterization studies. The alumina-silica base material is considered to be a suitably conservative surrogate since the sludge layer in most tanks represents only a few percent by volume and the tank would be backfilled with soil prior to processing.

## OPERATIONS

The underground tank vitrification pilot-scale test was initiated on September 11, 1990. The test proceeded smoothly through the early hours of the test with relatively balanced electrode power and smooth performance of the off-gas treatment system. The overall rate of downward melt growth averaged 5.6 cm/h. The melt depth was approximately 1.1 m when the off-gas containment hood pressurized for approximately 10 s. The pressurization, caused by an unexpected transient gas release from the melt, occurred at 19 h resulting in the temporary suspension of the test.

Following an evaluation of the pressurization event, it was determined that the pressurization was caused by a relatively small volume of steam and soil being released from the melt to the hood. The steam and particulate erupted up through the molten glass and rapidly disrupted the layer of frozen glass (cold cap) covering the top of the molten pool. Once disrupted, the molten pool of glass radiantly transferred heat to the dirty gas in the hood causing the gas to dramatically expand more rapidly than gas was being withdrawn from the off-gas containment hood. To prevent the recurrence of this type of event during the remainder of the test, a radiant heat shield was installed inside the off-gas containment hood. The shield was made of a carbon steel frame covered with a high-temperature cloth fabric and spanned the area being vitrified to block the radiant heat from the melt. In addition to the heat shield, a graphite pipe was installed to the bottom of the tank to act as a passive vent to release gases from the tank as they were produced.

The test was restarted from grade level on September 25, 1990. The test proceeded rapidly through the glass that had been formed during the initial phase of the test at a rate of greater than 7 cm/h and then slowed to 5.6 cm/h once the

## Pilot - Scale Test Site Configuration

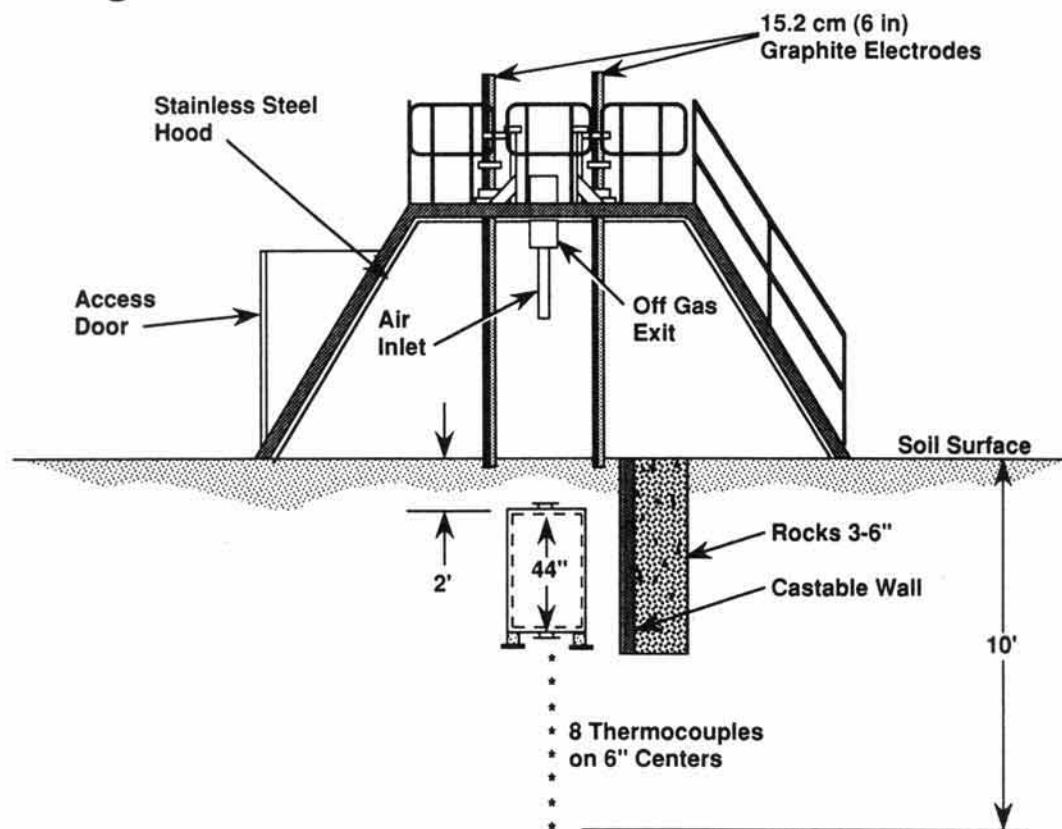


Fig. 3. Pilot-scale test site configuration.

TABLE I

Chemicals Used for Simulated Sludge

Species	Total Quantity Used (g)	Wt% in Sludge
Chromium III Oxide (Cr <sub>2</sub> O <sub>3</sub> )	2315	0.62
Cobalt Oxide (CoO)	420	0.11
Tributyl Phosphate (TBP)	990	0.26
Mercury II Oxide (HgO)	270	0.072
Cesium Nitrate (CsNO <sub>3</sub> )	270	0.072
Strontium Nitrate [Sr(NO <sub>3</sub> ) <sub>2</sub> ]	675	0.18
Lead (Pb) (granular, 30 mesh)	4620	1.23
Nickel (Ni) (powder)	1000	0.29
Barium Oxide (BaO)	3012	0.80
Cadmium Oxide (CdO)	62	0.0082
Hydraulic Oil (source of TOC)	9900	2.6
Total	25,534	~6.0
Balance ORNL soil	375 kg	

melt front proceeded into previously unmelted regions of the tank. The test proceeded smoothly with no transient gas releases from the melt, and the remainder of the test was relatively uneventful.

Power levels generally averaged around 350 kW for the duration of the test. A total of 4,750 kWh was used during the initial 19-h period, and a total of 21,000 kWh were used for the second phase of the test for a total of approximately 26,000 kWh. However, the total kWh is high since this included remelting the initial 1.1 m of glass.

Overall, the off-gas treatment system performed well during the test. The primary wet scrubber, the Hydro-Sonic scrubber, maintained a differential pressure well above 50-in. water column throughout the test. By design, this would have resulted in a particulate removal efficiency of greater than 90% for particles sized  $0.5\ \mu\text{m}$  and larger. The differential pressure for the Hydro-Sonic scrubber and for the primary high-efficiency particulate air (HEPA) filter in the off-gas treatment system are shown in Fig. 4. The differential pressure on the HEPA filter remained relatively constant throughout the test, indicating that the scrubbers effectively removed the vast majority of particulate and the filters were not becoming loaded.

## POSTTEST CHEMICAL ANALYTICAL RESULTS

### Waste Form Characteristics

The resulting glass and crystalline monolith was characteristically homogenous and had a mass of approximately 30 tons. The 2.4-m-deep monolith had a diameter of approximately 3.0 m (see Fig. 5). Samples of the waste form were submitted for chemical analyses and TCLP testing; the results, which are provided in Table II, show that both the glass and metal waste forms pass the TCLP tests. The waste form is highly resistant to leaching even though the concentration of toxic metals originally present in the waste represented extremely high concentrations that were not characteristic of most underground storage tanks. Limited compositional data for glass available at this time are presented in Table III.

### Surrounding Soil Analyses

Soil samples were collected adjacent to the monolith on the side and below the block. Composite samples were collected from soil zones defined by thermal isotherms. Sample locations were selected based on the temperature profiles measured during and after processing. The intent of this isothermal sampling approach was to ensure the collection of any contaminants transported by water vapor

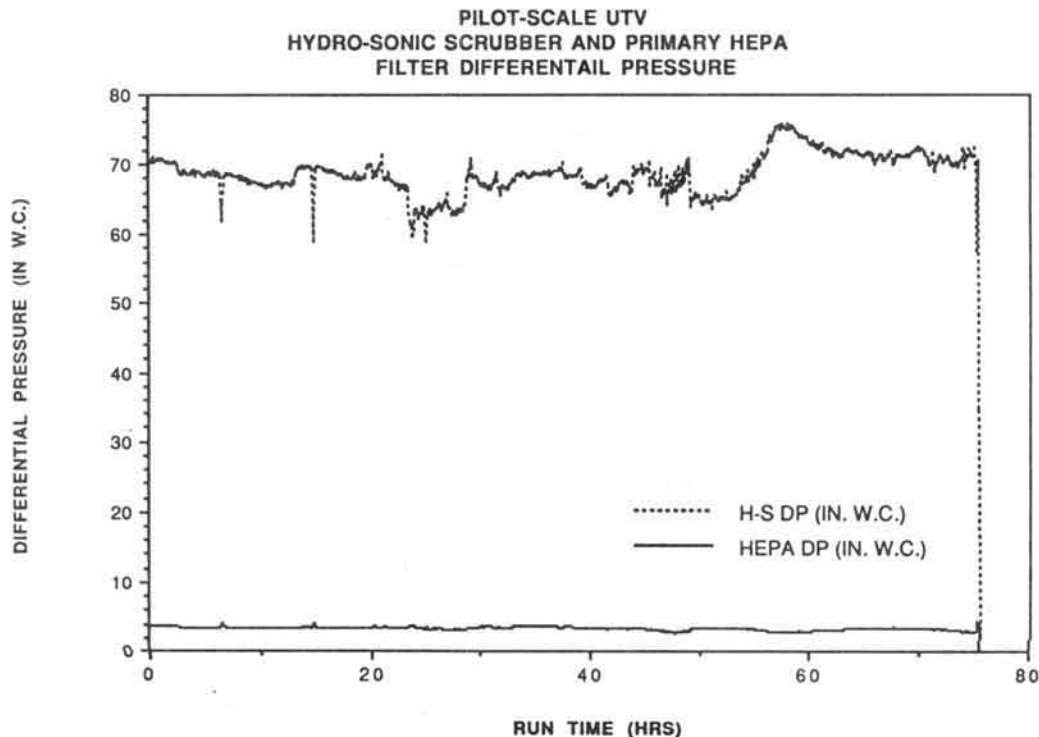


Fig. 4. Hydro-sonic scrubber and primary HEPA filter differential pressure.



Fig. 5. Vitrified block resulting from pilot-scale test of underground tank vitrification.

TABLE II

TCLP Leach Test Results of Glass and Metal

Species	Glass (ppm)	Metal (ppm)	Allowable Limit (ppm)
Arsenic	0.012	0.01	5.0
Barium	< 0.05	0.08	100.0
Cadmium	0.27	0.72	1.0
Chromium	0.28	0.40	5.0
Lead	0.07	0.14	5.0
Mercury	< 0.0004	(a)	0.2
Selenium	< 0.01	0.01	1.0
Silver	< 0.05	0.05	5.0

(a) Not available at the time of this writing.

or the contaminants own vapor pressure. Sample results are not yet available, but are expected by the presentation date.

#### Off-Gas Sampling

Off-gas samples were collected on the off-gas line, prior to treatment by the off-gas treatment system, and at the stack, after off-gas treatment via EPA Method 5 off-gas samplers. An isokinetic sample was continuously drawn through the samplers to collect particulates and heavy metals. Results indicate that greater than 90% of the lead was effectively incorporated into the waste. Analyses are not yet complete on other species. Based on previous studies,(3) it is anticipated that the vast majority of radionuclide simulants will be immobilized in the glass, and semivolatile species will be partially incorporated into the glass and the remainder will be effectively removed by the off-gas treatment system.

#### Metal Waste Form

The layer of metal slag resulting from the steel of the tank pooled near the bottom of the vitrified monolith. The higher density molten metal flowed to the bottom of the pool of molten soil and solidified once the vitrification process was terminated. The metal, which constitutes less than 1% of the overall waste form, was highly crystallized as a result of a very slow cooling process. Several samples were col-

lected for chemical analyses and TCLP testing with the results provided in Table II. The results indicate that the metal waste form passed TCLP criteria for the data obtained to date. Mercury analyses have not yet been completed; however, due to the durability of the metallic phase and the volatile nature of mercury, the leachability from the waste form is expected to pass TCLP criteria. Limited compositional data for metal are presented in Table III.

#### ACKNOWLEDGMENTS

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**TABLE III**  
Limited Compositional Data for Glass and Metal

<u>Species</u>	<u>Glass (<math>\mu\text{g/g}</math>)</u>	<u>Metal (<math>\mu\text{g/g}</math>)</u>
Barium	939	8
Cadmium	376	889
Chromium	2704	16,794
Cobalt	209	1329
Copper	125	1542
Iron	46,557	785,437
Lead	954	198
Manganese	1056	1969
Nickel	197	42,422
Silver	89	22
Vanadium	526	644
Zinc	91	557