Underground Tank Vitrification: Engineering-Scale Test Results

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June 1990

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UNDERGROUND TANK VITRIFICATION:
ENGINEERING-SCALE TEST RESULTS

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June 1990

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SUMMARY

Contamination associated with underground tanks at U.S. Department of Energy sites and other sites may be effectively remediated by application of in situ vitrification (ISV) technology. In situ vitrification converts contaminated soil and buried wastes such as underground tanks into a glass and crystalline block, similar to obsidian with crystalline phases. A radioactive engineering-scale test performed at Pacific Northwest Laboratory in September 1989 demonstrated the feasibility of using ISV for this application. A 30-cm-diameter (12-in.-diameter) buried steel and concrete tank containing simulated tank sludge was vitrified, producing a solid block. The tank sludge used in the test simulated materials in tanks at Oak Ridge National Laboratory. Hazardous components of the tank sludge were immobilized or removed and captured in the off-gas treatment system. The steel tank was converted to ingots near the bottom of the block and the concrete walls were dissolved into the resulting glass and crystalline block. Although one of the four moving electrodes "froze" in place about halfway into the test, operations were able to continue. The test was successfully completed and all the tank sludge was vitrified.

ACKNOWLEDGMENTS

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INTRODUCTION

Underground storage tanks containing sludges and salt cakes of radio-
active and/or hazardous chemicals are present at many U.S. Department of
Energy (DOE) sites. Recent enactment of stringent environmental regulations
requires timely remediation of certain inactive tanks. Studies evaluating
tank remediation alternatives show that many of the tanks can be stabilized in
place. This option not only represents significantly less cost, but the risks
of personnel exposure and environmental release are greatly reduced by elimin-
ating the need to exhume and handle the contaminated materials. Tanks contain-
ing material that cannot be economically removed and tanks with outlying soil
contamination are likely candidates for in-place treatment by in situ vitri-
fication (ISV). Funded by the Hazardous Waste Remedial Action Program, this
project provides a technique for cost-effectively remediating contaminated
underground tanks.

In situ vitrification is a process that converts contaminated soils and
sludges into a durable glass and crystalline product that is similar to obsi-
dian commingled with crystalline phases. The system is based on the joule-
heating principle of glass melter technology developed at Pacific Northwest
Laboratory (PNL)[a] for immobilizing high-level nuclear waste. In situ vitri-
fication was originally tested by researchers at PNL in August 1980 (U.S
Patent 4,376,598 - Brouns, Buelt, and Bonner 1983). Since then, this tech-
nology has been developed through a series of bench-, engineering-, pilot-,
and large-scale tests. Vitrification of contaminated soil has been evaluated
in 74 separate tests under a variety of waste and soil conditions. These
include 17 pilot-scale tests, each processing 10-50 metric tonnes (t) of con-
taminated soil, and 5 large-scale tests, each processing 400-800 t of con-
taminated soil. In situ vitrification has emerged in recent years as a tech-
nology that is ready for field demonstration and application for many waste
types and soil conditions.

One of the most promising applications for ISV is remediation of under-
ground storage tanks. By filling the tanks with clean or contaminated soil
and vitrifying the tank, tank contents, and surrounding soil, not only are the
tank contents immobilized, but soil contaminated from possible leakage outside
the tank is also stabilized. Although only a conceptual analysis has been

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performed for underground storage tanks, the cost of the vitrification operation itself may not be greatly more than for contaminated soil sites. Using conservative assumptions, the estimated tank vitrification costs represent the possibility of more than an order-of-magnitude savings in costs over present projections for cleanup of tanks containing mixed waste. Consequently, ISV capabilities are being demonstrated on underground tanks to provide a useful tool to DOE for remediation actions.

The Underground Tank Vitrification (UTV) project is underway at PNL to assess the application of ISV in remediating underground storage tanks. Since most DOE sites contain contaminated underground storage tanks, personnel from each of the major DOE sites were contacted for information regarding the characteristics of tanks at each site. Based upon site needs, this project is proceeding in two phases: 1) vitrification of tanks up to 8 m (20 ft) in diameter containing sludges, and 2) vitrification of large tanks containing mainly salts. An engineering-scale test was performed as part of phase 1 testing based on data obtained from 33 recently sampled tanks at Oak Ridge National Laboratory (ORNL)(Autrey et al. 1989). A scaled tank containing a hazardous and radioactive simulated sludge was used for this engineering-scale test. The primary purpose of the test was to determine the applicability of ISV in treating underground tanks containing residual radioactive and hazardous sludges, and to study the immobilization of an underground tank, connecting piping, tank contents, and surrounding soil. Other objectives for the test are listed below:

- demonstrate ISV operations on an underground tank

- evaluate hazardous material retention, immobilization, destruction, volatilization, and thermal transport effects

- assess the use of electrode feeding on an underground tank

- evaluate tank pressure effects during ISV operations.

This report presents the results of the engineering-scale ISV treatability test conducted on a simulated underground storage tank containing a simulated residual sludge. The report provides conclusions based on test results, a brief description of the ISV technology and how it operates, a description of the specific engineering-scale treatability test, and a summary and analysis of the test results.

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CONCLUSIONS

A radioactive engineering-scale test conducted by PNL in September 1989 has demonstrated the feasibility of using ISV to remediate contaminated underground storage tanks at DOE sites. In this test, a 30-cm-diameter steel and concrete tank was converted to a solid vitrified block. The tank, which contained simulated tank sludge and soil, was buried 15 cm (6 in.) below surface. The contents of the tank were representative of material within the buried tanks and surrounding soil at ORNL. Conclusions based on the test results are listed below:

- Metal and/or concrete tanks can be vitrified by filling the tank with soil and applying ISV.

- The electrode feeding system used for this application is adequate for UTV. Electrical shorting through a continuous metallic layer is prevented by raising one or more of the electrodes in the event of electrical shorting. In addition, use of coated graphite electrodes, rather than the more expensive and complex molybdenum/graphite composite electrodes, is feasible.

- Sludge components are destroyed during processing and/or immobilized in the ISV block. Volatile species are collected in the off-gas treatment system. High retention (>99.9%) was demonstrated for nonvolatile metals (Cr, U, Cs, Sr, and Tc). Lower retention (15-50%) was shown for Pb and Hg; however, volatilized species are collected in the off-gas treatment system by scrubbing and filtration.

- The vitrified product shows a homogeneous distribution of hazardous constituents.

- No detectable transport of hazardous constituents to surrounding soil was observed.

- Samples of the ISV-generated glass and metal phases subjected to Extraction Procedure Toxicity (EP Tox) testing each produced leach concentrations significantly below the U.S. Environmental Protection Agency (EPA) limits.

DESCRIPTION OF UNDERGROUND TANK VITRIFICATION

The UTV process converts underground tanks and associated hazardous materials to a solid block, thereby immobilizing the contaminated tank, sludge, and surrounding soil. Figure 1 depicts the UTV process. Prior to treatment by ISV, contaminated underground tanks are filled with soil and all attendant piping is blocked off. A hood for containment of volatilized materials and support of the electrodes is placed over the area to be vitrified. A square array of four silicon carbide-coated graphite electrodes is inserted a few centimeters into the ground. Because soil is not electrically conductive when moisture has been driven off, a graphite and glass frit starter material is spread between the electrodes to form a conductive starter path. An electric potential applied to the electrodes establishes an electric current in the starter path. The resultant power heats the starter path, creating temperatures high enough to melt the soil (typically about 1700°C). The starter path is consumed by oxidation, and the current is transferred to the molten soil, which is electrically conductive.

As the molten zone grows downward, the electrodes are allowed to move at the same rate. As the molten soil encounters a metal object such as a steel tank, the high temperatures melt the metal and the metal flows to the bottom of the molten pool. Other materials encountered, such as concrete, decompose and dissolve in the molten mass. The enlarging molten mass encompasses the soil, tank wall, and sludge in the bottom of the tank. Melting may also
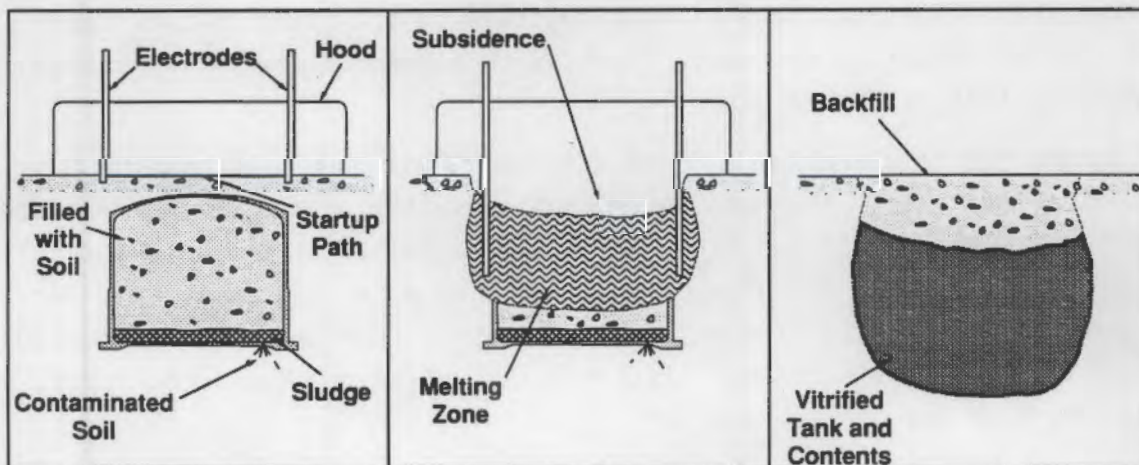
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FIGURE 1. Operating Sequence for Underground Tank Vitrification

continue downward, if desired, to immobilize contaminated soil below the tank. The melt incorporates radionuclides and nonvolatile hazardous elements such as heavy metals, and destroys organic components by pyrolysis. The pyrolyzed byproducts migrate to the surface of the vitrified zone, where they burn in the presence of air. The metal tank melts and forms ingots near the bottom of the melted mass.

As the vitrified zone grows, the resistance of the melt decreases, thus requiring periodic adjustments of the ratio between the voltage and the current to maintain operation at a constant power. Operations for each pair of electrodes follow the power equation

$$P = I^2 \times R$$

where P = power, I = current, and R = resistance. The PNL large-scale ISV system primarily consists of five major subsystems: 1) electrical power supply, 2) off-gas hood, 3) off-gas treatment, and 4) process control.

The PNL large-scale system contains a 3750-kW power system. Operating typically at an energy-to-mass ratio of 0.8 kW/kg of product, the process is capable of melting soil at 3 to 5 t/h.

The product resulting from ISV is a glass and crystalline mass resembling natural obsidian and a metal ingot. For typical earthen materials, final ISV block density varies from 2.3 to 2.5 g/cm^3 (144-156 lb/ft^3). Though the ISV block is only 3% to 11% heavier than concrete, it possesses about 5 to 10 times the strength of unreinforced concrete in both tension and compression. The ISV block is extremely inert, with a chemical leach resistance approaching that of Pyrex® glass.

Except for the hood, all of the ISV components are contained in three transportable trailers that can be moved to any site over a compacted surface. The off-gas hood and off-gas line, which are installed at the site for collecting gaseous effluents, are dismantled and placed on a flatbed trailer for transport between tanks. The effluents exhausted from the hood are cooled and treated in the off-gas treatment system. The entire process is monitored and controlled from the process trailer.

®Pyrex is a registered tradename of E.I. duPont de Nemours and Company, Wilmington, Delaware.

The off-gas treatment system is the most complex and expensive of the components. It cools, scrubs, and filters the gaseous effluents exhausted from the hood. Its primary components include a wet-scrubber system, two heat exchangers, two process scrub tanks, two scrub solution pumps, mist eliminators, a heater, a charcoal/filter assembly, and a blower system.

For routine operations on a site, all three trailers are coupled and may be moved from one tank to another by pulling them as a unit. The off-gas hood, electrode feed system, and off-gaslines are moved by crane for use on nearby tanks or dismantled and placed on a flatbed trailer for transport between distant tanks.

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ors, a heater, a charcoal filter assembly, and a blower system.

For routine operations on a site, all three chillers are coupled and may
be moved from one team to another or built into them as a unit. The off-gas
hood, off-gas feed system, and off-positions are moved whenever the hood or
hood, are dismantled and closed on a flatbed trailer for the transport
between systems is ....

TEST DESCRIPTION

This section describes the pre-test soil characterization, the engineering-scale test equipment and setup, and the off-gas system used for the test. The test was conducted using the engineering-scale test equipment located in the Engineering Development Laboratory 101 of the 324 Building at Hanford.

SLUDGE AND SOIL CHARACTERIZATION

This section outlines the compositions of the chemically simulated sludge and the uncontaminated ORNL soil used as tank filler and surrounding material. Of interest in this test was the ability of the ISV process to treat tanks with residual sludges containing radionuclides and hazardous materials. To maximize the applicability of the data produced from this test, analyses of the contents of inactive ORNL tanks were reviewed (Autrey et al. 1989). Typical maximum concentrations of hazardous and radioactive species were identified. These concentrations were compared with projected minimum detectable concentrations in the ISV block, soil, and off gas, and the highest value was selected. The objective was to select the sludge composition that would present the most challenge to ISV. Table 1 lists the components and

TABLE 1. Concentrations of Radionuclide and Hazardous Components in the Simulated Sludge

Component	Concentration, wt%
Oil	1.0
Cr_2O_3	0.04
HgO	0.005
Pb	0.005
UO_3	0.9
$CsNO_3$	0.4
$SrCO_3$	4.6
CoO	0.35
Tc-99	0.003
H_2O	12.9
Soil	79.8
Total	100.0

their concentrations in the simulated sludge. Radioactive species used in this test were depleted uranium and technetium. Hazardous species such as chromium, mercury, and lead were typically found to be present in the waste sludges and were therefore used in the simulant. Although the ORNL test results did not indicate the presence of technetium, it is expected to be present in the sludge. Performance analyses performed by PNL (Sewart et al. 1987) in support of the Hanford Grout Facility show that long-term dose to maximally exposed individuals is a strong function of the technetium concentration in the waste. Therefore, knowledge of technetium behavior during ISV is important. A light machine oil was used in the test to simulate a mixture of organic materials found in several of the tanks.

Pre-test sampling of the uncontaminated ORNL soil was performed to identify the presence of any hazardous sludge components. No significant concentrations of contaminants were found. This sampling also determined the presence and quantity of glass-forming materials (i.e., SiO_2 and Al_2O_3) and fluxes (i.e., Na_2O, K_2O and CaO) that would contribute to proper melting at the ISV process temperature range of 1200°C to 2000°C (Table 2).

TEST EQUIPMENT AND SETUP

The PNL engineering-scale unit consists of a 1.8-m- (6-ft-) diameter by 2.4-m- (8-ft-) tall sealed chamber containing the tank and soil to be vitrified (Figure 2). Four graphite cylindrical electrodes are placed 30 cm (12 in.) apart in a square array and fed vertically into the soil that surrounds the tank. Figure 3 diagrams the setup for the engineering-scale test. For this test, uncontaminated ORNL soil was used to surround the tank and fill the void space within the tank. The containment module is capable of operation at a slightly negative pressure to contain and sample off gases generated during the process. The off gases from the vitrified area can be continuously sampled throughout the test. The test was conducted using four 5.1-cm- (2.0-in.-) diameter, silicon carbide-coated graphite electrodes (Figure 2). The electrodes were coated to prevent excessive oxidation that could otherwise occur at the interface of the oxygen-containing hood environment and the molten soil. The electrode feed system is shown in Figure 4. Gravity feeding was used in this test, as opposed to buried, fixed electrodes, to allow recovery from shorting conditions that could occur due to the metal contained within the test zone. A shorting condition occurs when a continuous molten

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TABLE 2. Composition of Uncontaminated ORNL Soil

Component	Uncontaminated Soil	
	Total Soil, wt%	Dry Basis, wt%
Al_2O_3	16.1	18.7
B_2O_3	0.04	0.05
BaO	0.05	0.06
CaO	9.28	10.8
Cr_2O_3	0.02	0.02
Cs_2O	0.0002	0.0002
Fe_2O_3	5.51	6.41
K_2O	3.94	4.58
MgO	2.03	2.36
MnO_2	0.09	0.10
Na_2O	0.73	0.85
P_2O_5	0.19	0.22
SiO_2	47.2	54.9
SrO	0.03	0.03
TiO_2	0.74	0.86
V_2O_3	0.01	0.01
ZrO_2	0.034	0.039
H_2O	14.0	0.0
Weight % Oxide	100.0	100.0

metal pool spreads between two or more of the electrodes. In this situation very little heating occurs, and the electrodes must be withdrawn from the metal pool to continue vitrification.

The tank, constructed of 0.32-cm- (1/8-in.-) thick mild steel, was covered with a nominal 2.5-cm (1.0-in.) layer of concrete. The tank as it appeared before adding the outer concrete layer is shown in Figure 5. Exit piping and airlift circulators were added to the tank to more completely simulate an actual DOE underground tank. The exit piping also permitted monitoring of pressure fluctuations during processing. A 2.5-cm (1-in.) layer of simulated sludge was added to the tank, with clean ORNL soil used to fill the remaining void space in the tank.
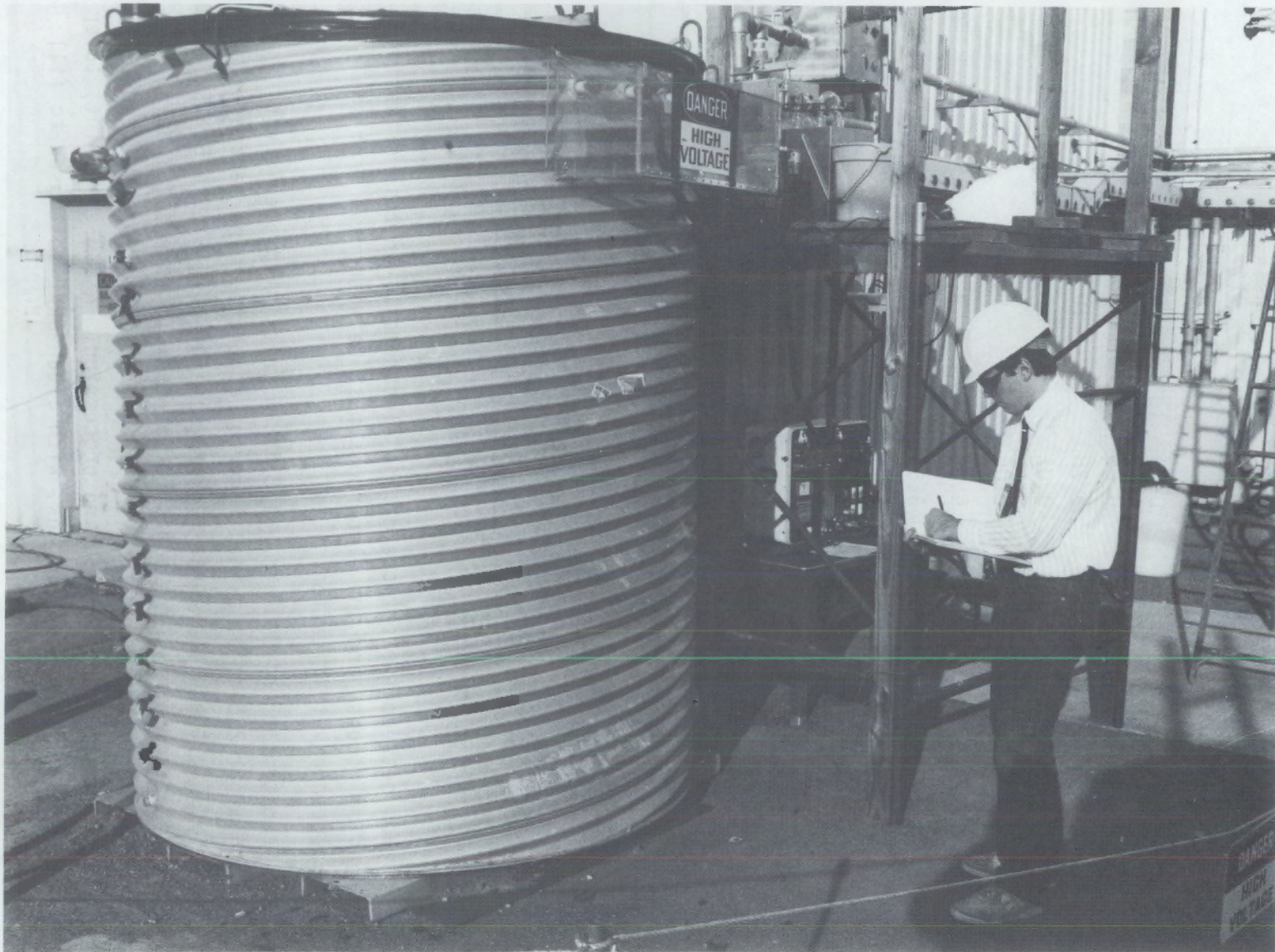
FIGURE 2. Engineering-Scale Test Containment

Gravity/Mechanically Fed Electrodes

30 cm

Air Lift Circulator

Piping (pressure measurements)

Surrounding Soil

Fill Soil

33 cm

Sludge

30 cm

Steel Tank

Cement Outer Liner
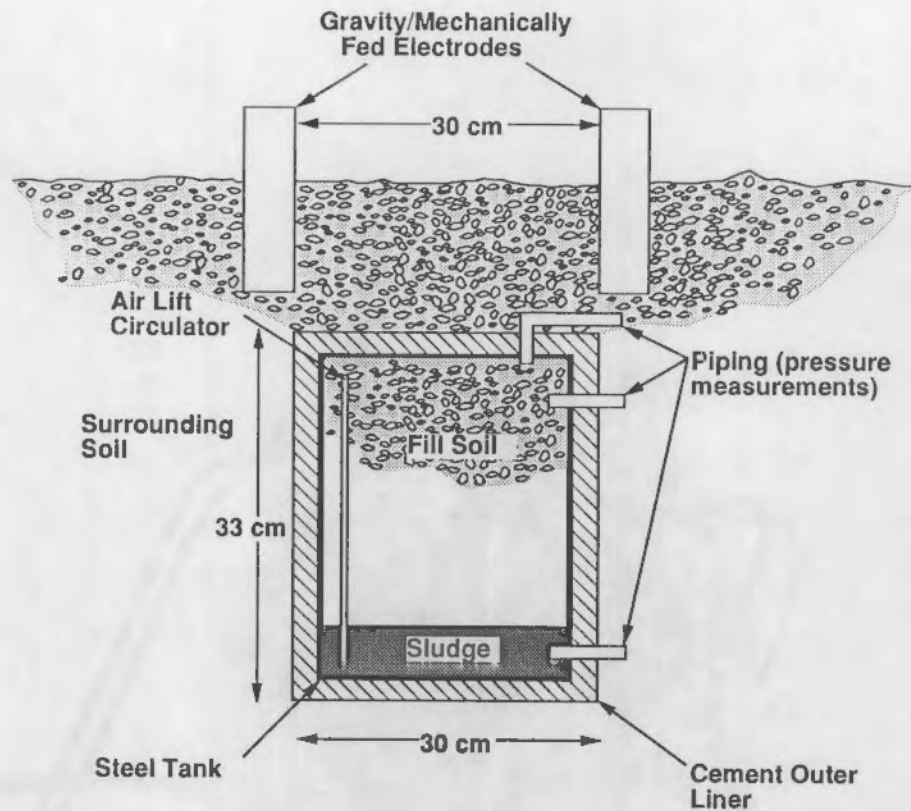
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FIGURE 3. Schematic of Engineering-Scale ISV Test Configuration

Thermocouples were installed vertically in the center of the test drum and horizontally at the tank midpoint to monitor the melt shape. The upper vertical Type K thermocouple was placed 5-cm (2-in.) below the soil surface and then at 5-cm (2-in.) intervals to a depth of 104 cm (41 in.). A Type K thermocouple possesses a maximum temperature limit of 1400°C. In addition, nine Type K thermocouples were placed at the 31-cm (12-in.) depth to monitor the horizontal growth of the melt and various isotherms in the surrounding uncontaminated soil. The isotherm information was used to determine locations for samples in the surrounding soil. These thermocouples were spaced at 5-cm (2-in.) intervals, starting at the plane of the electrode array and moving out to the edge of the test drum.

The actual temperature of the vitrified melt was monitored using a Type C thermocouple. A Type C thermocouple is a more expensive junction of tungsten-5% rhenium and tungsten-26% rhenium in a molybdenum sheath. It is capable of reading molten glass temperatures up to 2300°C, but because of rapid oxidation of the molybdenum sheath at high temperatures, it has a

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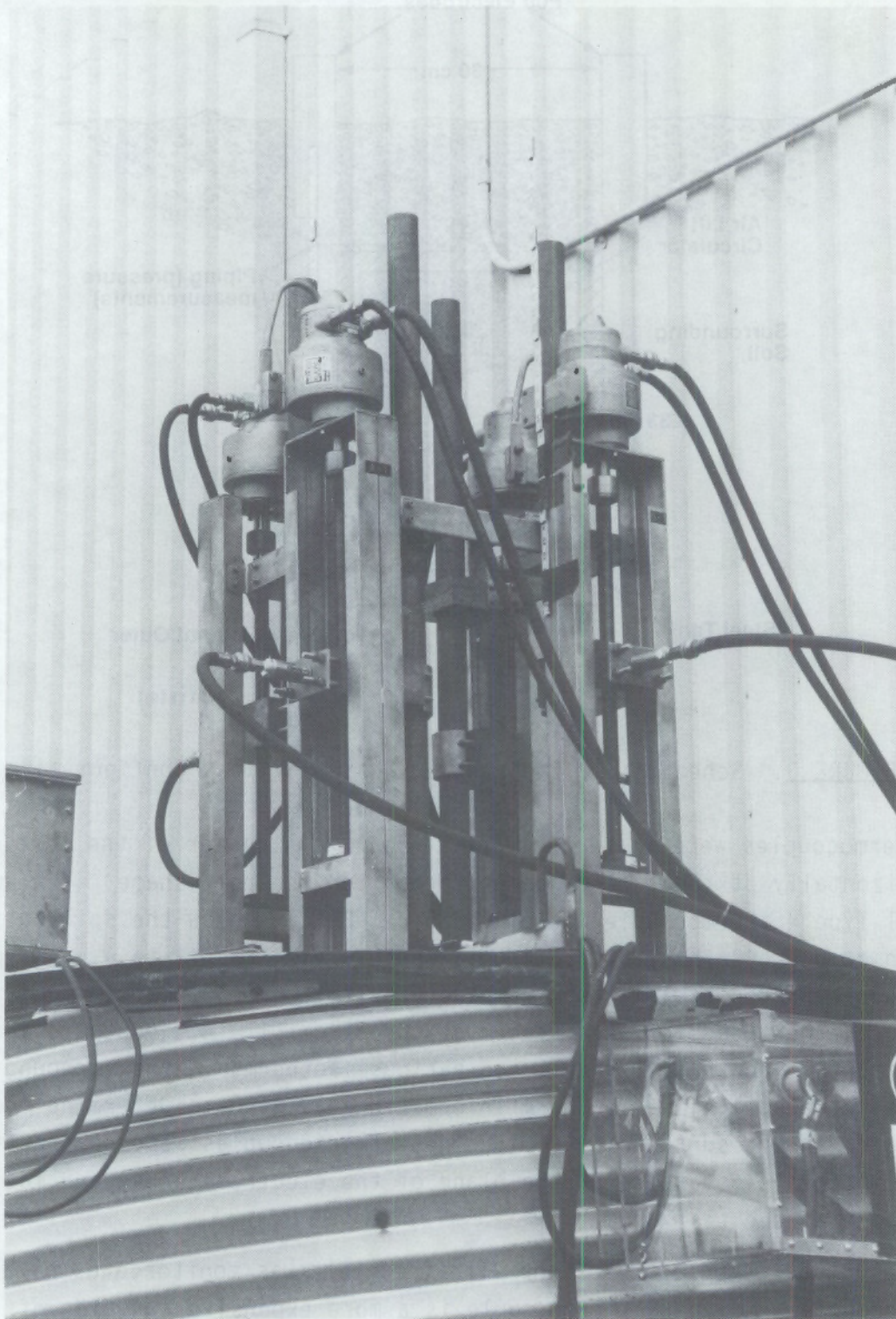
FIGURE 4. Electrode Feeding System
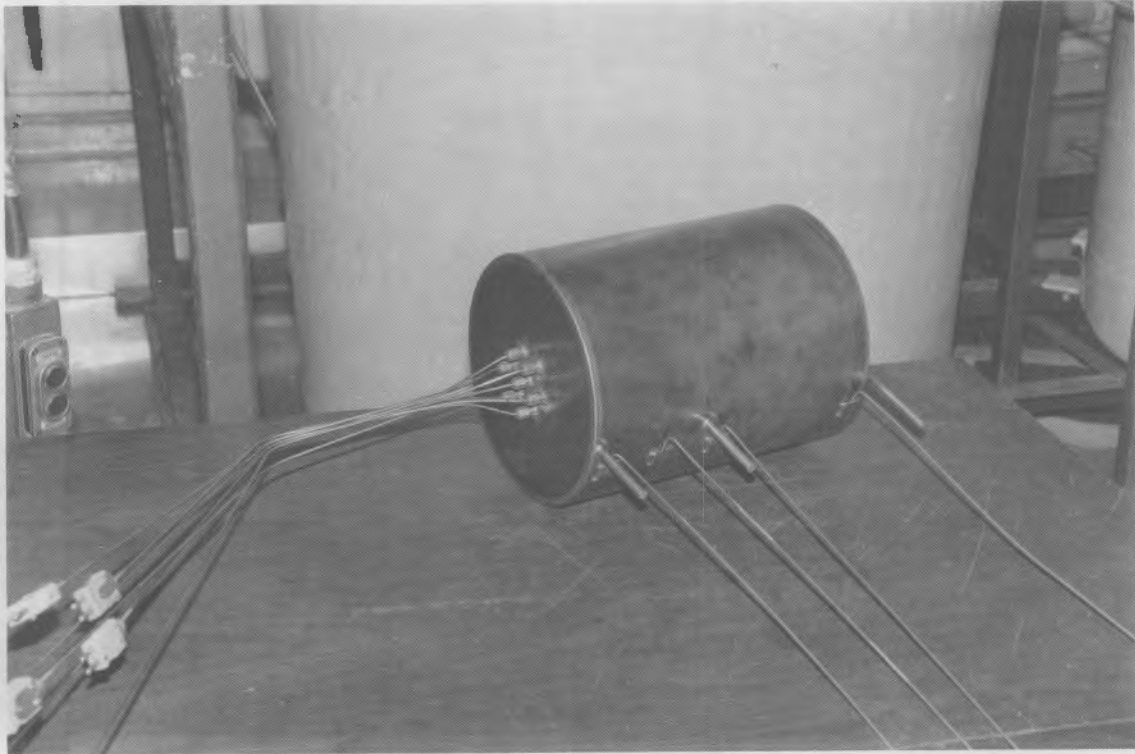
FIGURE 5. Metal Tank Prior to Addition of Concrete Coating

limited service life above 1700°C. An alumina sheath was placed over the Type C thermocouple to prevent excessive oxidation from occurring. The Type C thermocouple was located in the center of the melt area, directly beneath the tank. The Type C thermocouple was also used as a secondary indication to verify that the process had vitrified down past the bottom of the tank. Figure 6 shows the tank as it was being installed in the test container.

A starter path consisting of graphite flake and glass frit was laid in a square and "X" pattern so that a direct conductive path was provided among the four electrodes.

The power system used in this engineering-scale test consisted of a two-phase 30-kW capacity Scott-Tee transformer. The transformer contained 16 voltage taps and was wired for secondary control with each phase having a saturable reactor. The test was set to run at a target control power of 15 kW to more closely match power densities anticipated for the large-scale system.

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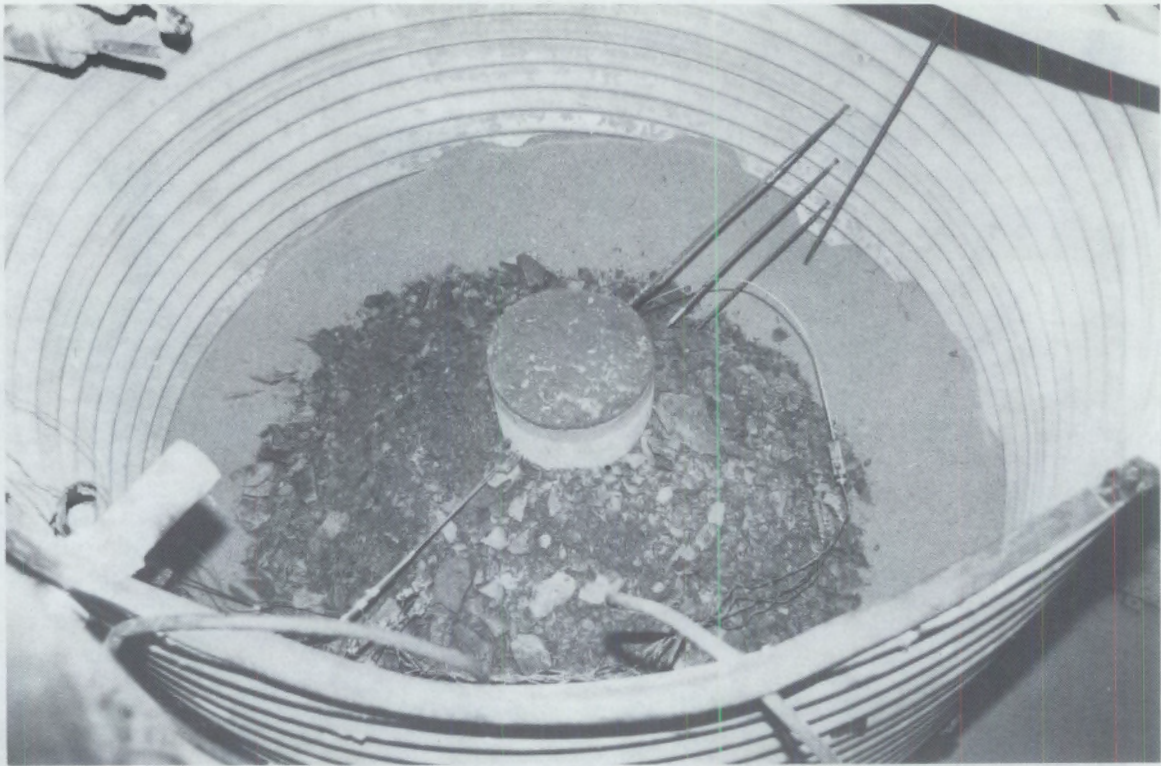
FIGURE 6. Simulated Tank in Vitrification Test Chamber

OFF-GAS SYSTEM

The off-gas sampling system was designed to collect particulates and volatile compounds present in the simulated sludge and the uncontaminated ORNL soil. The sampling train used in this test was an approved modification of EPA method 5 consisting of a heated glass fiber filter, two 500-mL gas impingers, a silica gel bed, a vacuum pump, a flow meter, and a wet test meter (Figure 7). A portion of the total off-gas stream was isokinetically drawn through the sampling system and then piped back to the ISV system off gas.

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Off-Gas Line

Heated Zone

Glass Filter

0.1 N HNO3

5% KMnO4, 10% H2SO4

Silica Gel

Ice Bath

Return to Off-gas Stream

Vacuum Pump

Flow Totalizer

FIGURE 7. Engineering-Scale Sampling System
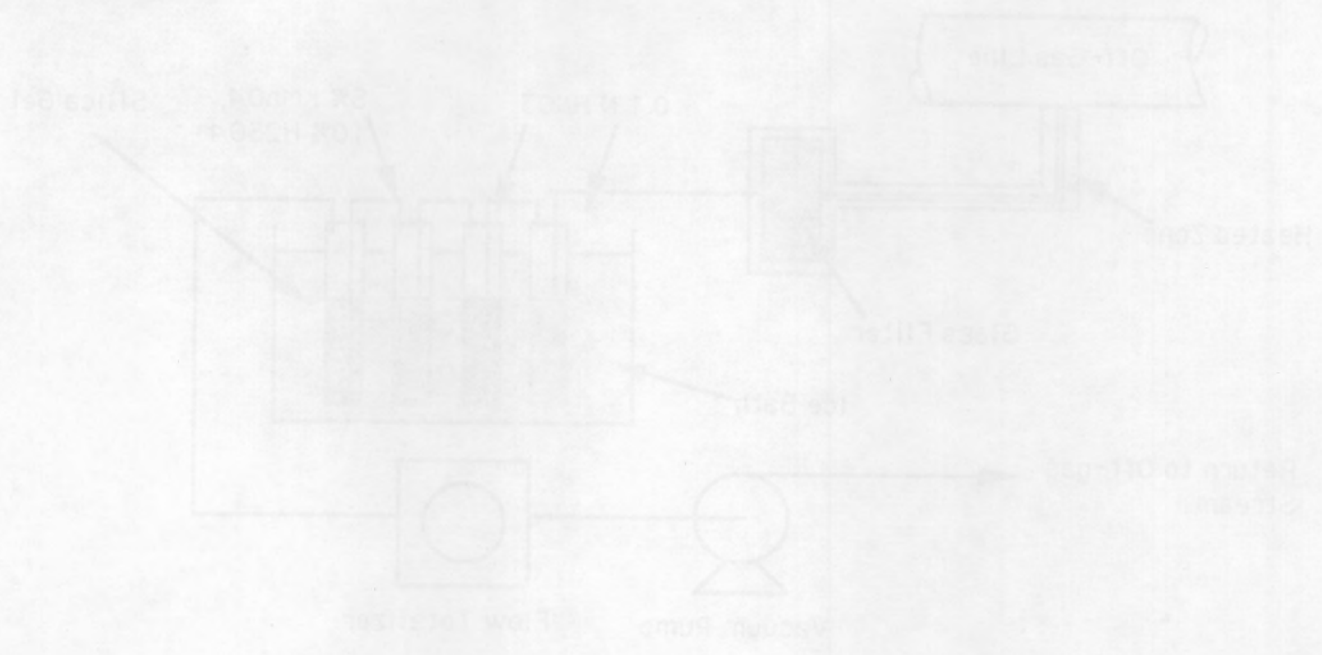
FIGURE 1. Condensate/Vapor-Phase Sampling System

The UTV engineering-scale test was completed on September 14, 1989 after a run time of 23.5 hours. Because void fractions in the soil prevented a continuous starter path from developing during startup, a 5-cm (2-in.) layer of sand was placed over the soil to provide a more consistent matrix for the formation of a starter path. The layer of sand allowed the test to be successfully restarted.

Voltage and current fluctuations, which are common during engineering-scale test startup when buried, fixed electrodes are used, were evident throughout the test. Early in the test, these fluctuations were attributed to occasional arcing among the graphite particles as the starter path was consumed by oxidation. Later in the test, the fluctuations appeared to be due to int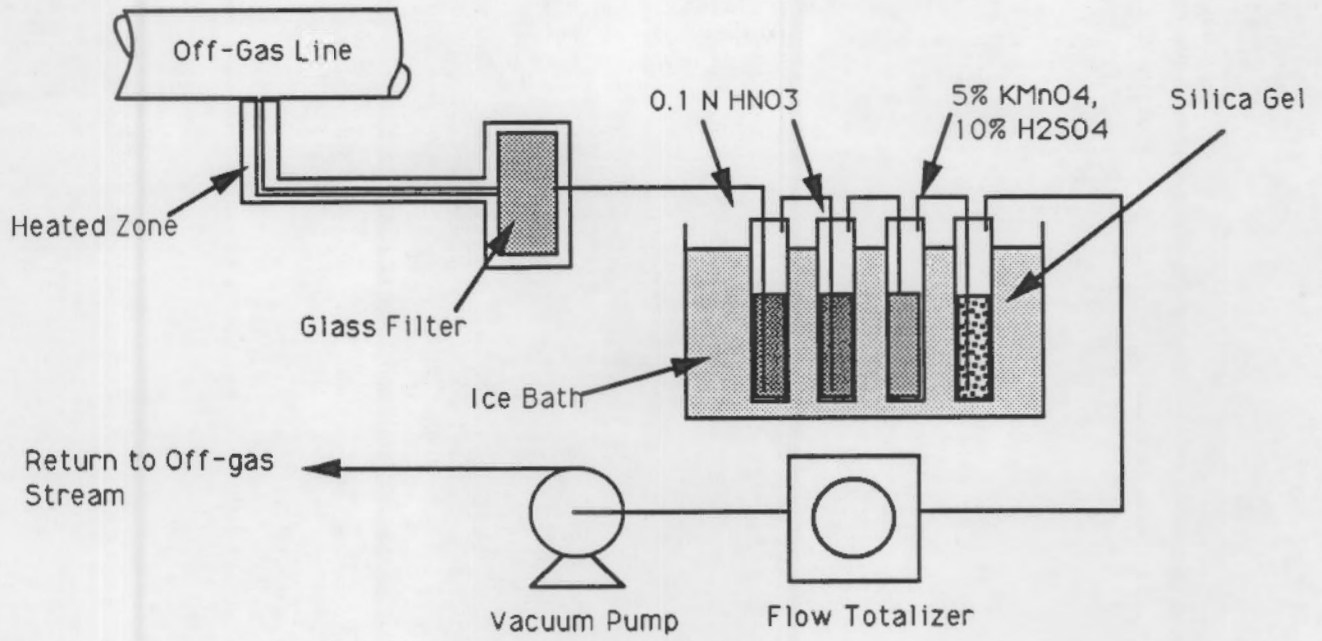ermittent difficulty in feeding the electrodes downward. Operating experience has demonstrated that arcing during startup occurs more frequently in the smaller-scale tests than with the large-scale system.

After the successful startup of the test, 338 kWh of electrical energy were consumed in the melt area over the 23.5-hour test period. As observed in previous tests, a slow decrease in the electrical resistivity between the electrodes occurred as the test proceeded. This decrease in resistivity occurs because melting of more soil provides additional charge-carrying ions. The resistivity of the melt continues to decrease until the molten glass reaches an equilibrium operating temperature. This equilibrium occurred 17 hours into the test, at a resistivity of 0.6 ohms. Figure 8 shows the total power input to the soil as a function of time. As the resistivity decreases, current to the electrodes is controlled to maintain a relatively constant power input of 15 kW to the melt.

The average off-gas flow rate exiting the process containment during the test was 672 L/min (23.7 cfm). From this flow, a representative sample was drawn isokinetically through a stainless steel sample tube and through the off-gas sampling train at 24 L/min (0.86 cfm).

The vitrification process produced a block weighing 201 kg (442 lb). The maximum melt temperature recorded during the test was 1610°C. Vitrification proceeded to a nominal depth of 60 cm (24 in.), with a maximum depth of 66 cm (26.0 in.) observed on one side of the block (Figure 9). The block was
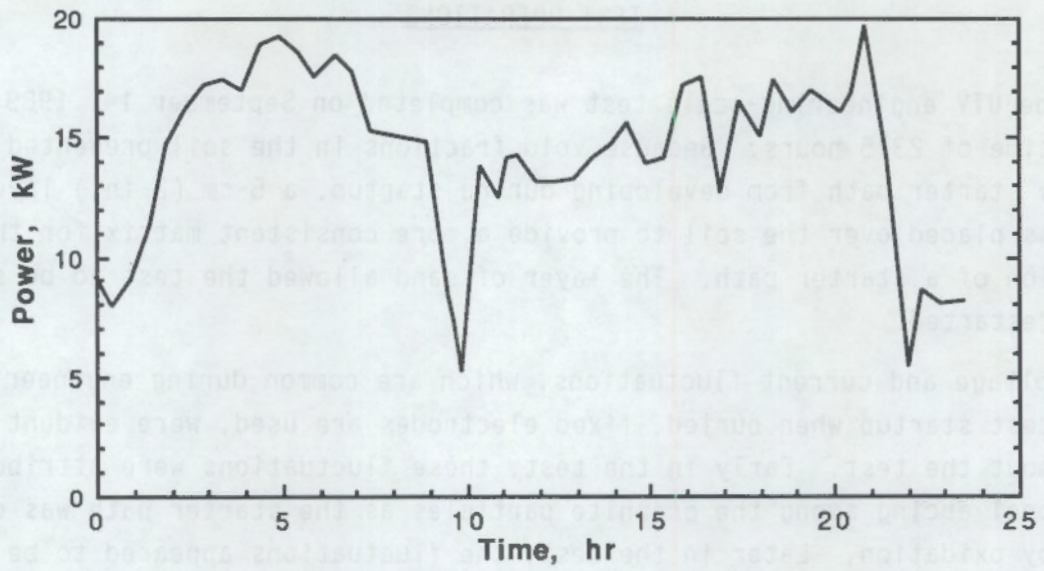
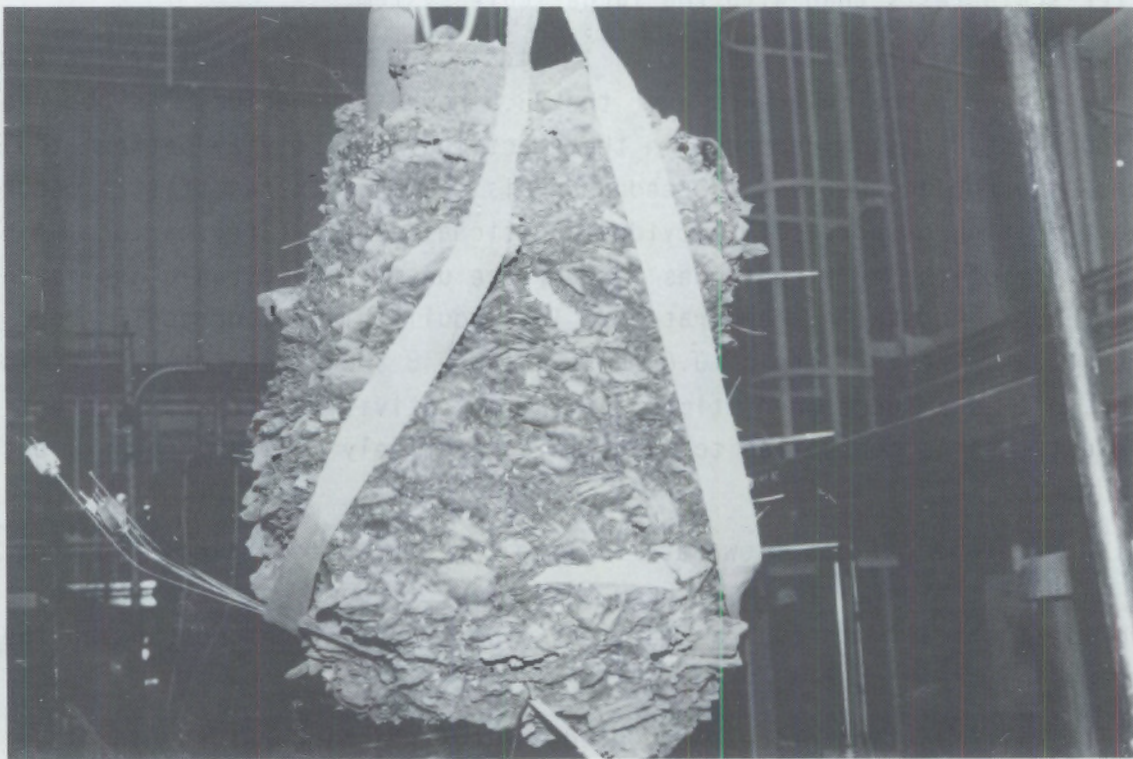FIGURE 8. Electrical Power Input to UTV Test

FIGURE 9. UTV Engineering-Scale Vitrified Block

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relatively square, with approximately 40-cm (16-in.) sides and rounded edges. The sides of the block were vertical (rather than the tear drop shape frequently observed) presumably due to the effects from the electrode feed system and the metal present in the vitrified zone. It appears that the metal in the tank served as a passive electrode, concentrating the power density between the electrodes and directing the melt downward instead of laterally.

No subsidence was evident at the surface of the melt, although a void space approximately 10 L (700 in.^{3}) was found at the top of the block in between the electrodes. The void space was caused by cooling of the surface glass and the subsequent formation of a cold cap over the melt area. The high viscosity of the glass and the silicon-carbide coating on the electrodes contributed to the formation of the cold cap, which caused the glass to adhere to the electrodes and bridge across the surface instead of slumping into a subsidence. Observations made after completion of the test showed that the insulation placed over the melt area had been incorporated into the vitrified block, thus eliminating its ability to promote subsidence by preventing a cold cap from forming.

The glass and crystalline block exhibited physical characteristics similar to those produced in previous ISV tests (Figure 10). The interior of the vitrified block was relatively homogeneous, indicating that the contents of the sludge and the fill material as well as some surrounding soil were mixed during melting. Further investigation indicated that, as predicted, the metal had melted and migrated downward to just above the interface of molten glass and soil.

As predicted, electrical shorting conditions developed when the steel tank walls melted forming a semi-continuous molten metal pool between the electrodes at the bottom of the melt. Recovery from shorting conditions was accomplished by raising the electrodes 1 cm for about an hour then resuming the vitrification downward. Intermittent difficulty was encountered during the test in feeding the electrodes downward, resulting in the eventual binding of one electrode 6 hours into the test (Figure 11). Binding is believed to have resulted from molten soil adhering to the silicon-carbide coating used on the electrodes. The depth of the other electrodes was not ultimately affected by the adhesion of glass. It is expected that electrode binding will not

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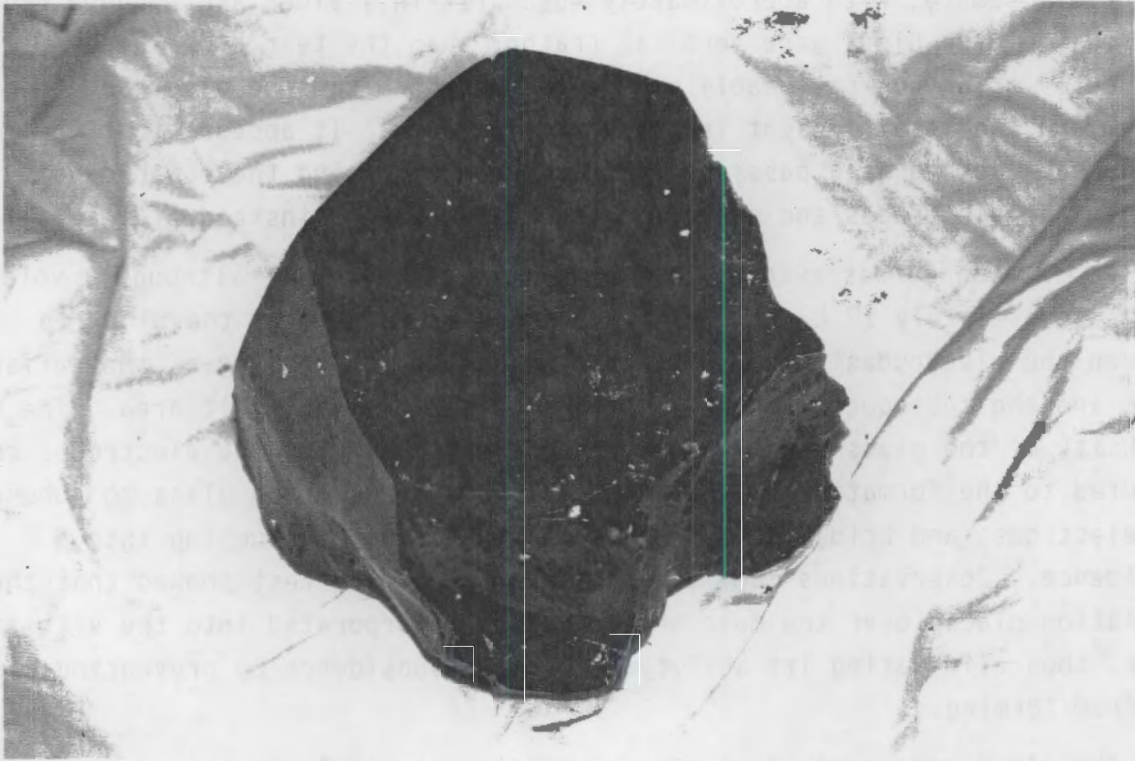
FIGURE 10. Glass Produced from Underground Tank Vitrification
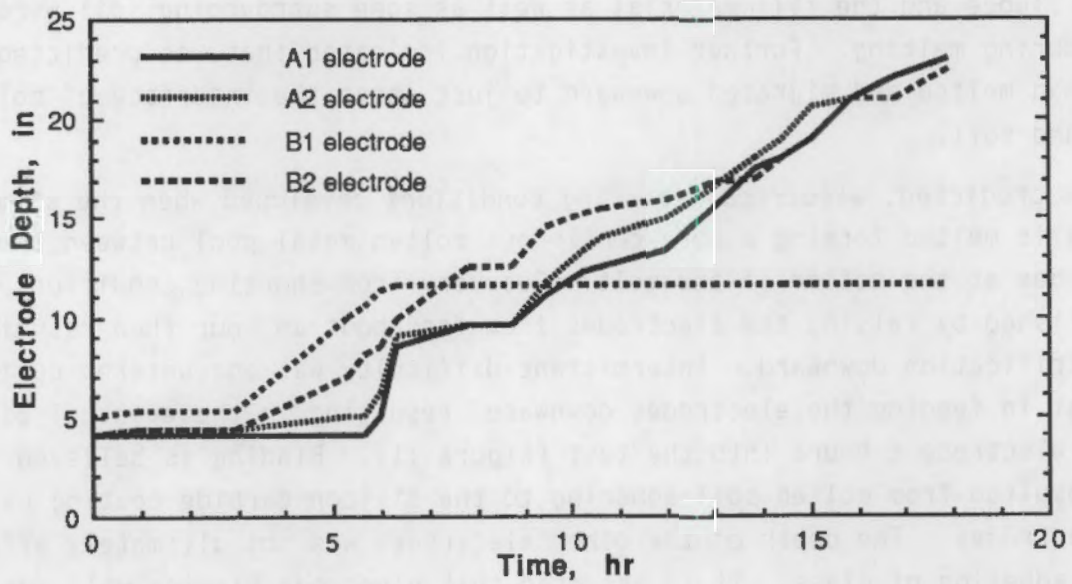
FIGURE 11. Electrode Feed Rates

occur with the larger scale systems because of increased surface heat transfer around the electrodes for larger scale tests and the use of stronger electrode gripping and moving devices.

Throughout the test, the depth of vitrification was determined by monitoring both the depth of the gravity-fed electrodes' and the buried thermocouple temperatures. Except during startup, when the electrodes' tips were buried 10 cm (4 in.) deep, and during shorting periods when they were slightly withdrawn, the electrodes gravity fed to the bottom of the melt area. Figure 12 compares the average electrode depth with the 1200°C isotherm depth. Once a 15-kW power level was achieved, the electrodes fed downward at nominally the same rate as the movement of the 1200°C isotherm. The electrode depth was consistently slightly deeper than the 1200°C isotherm. The greater depth for the electrodes is attributed to the preferential melting caused by higher power densities around each electrode and a fusion temperature of 1400°C for the ORNL soil (Carter, Bates, and Maupin 1987).

Three of the silicon-carbide coated electrodes were withdrawn from the melt following the test to observe the condition of oxidation resistant coating. No electrode oxidation was evident. Minor amounts of the coating
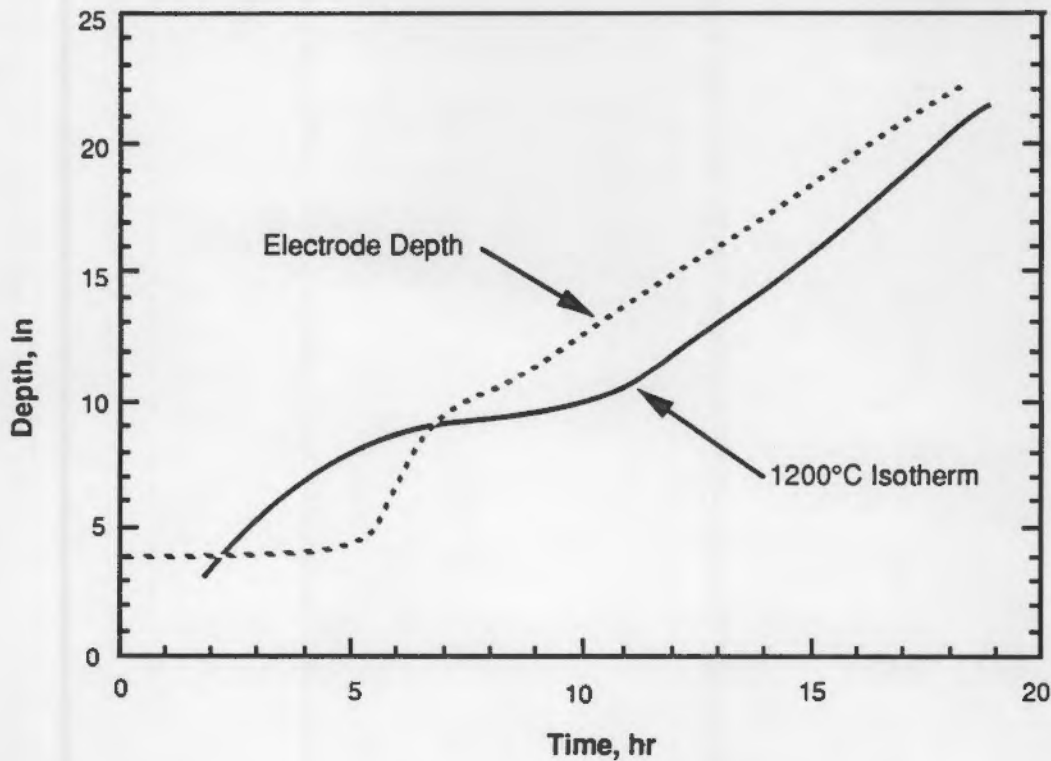
FIGURE 12. Comparison of Electrode Depth to Vitrification Depth

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flaked; however, it appeared that the coating was successful in protecting the graphite electrodes. Dissection of the block showed similar behavior for the bound electrode.

Observations from the test show that the ORNL soil was easily vitrified by the ISV process, despite the presence of 300 cm^3 (18 in.^{3}) of metal in the vitrification zone. Analysis of the thermocouple data indicates that a maximum tank wall temperature rise of 120°C up to 13 cm (5 in.) below the melt was present. This indicates that the metal tank wall does not provide a significant heat fin effect to the lower portion of the tank and its contents. The conductive heat transfer to the surrounding media limits any heat fin effect of the metal tank.
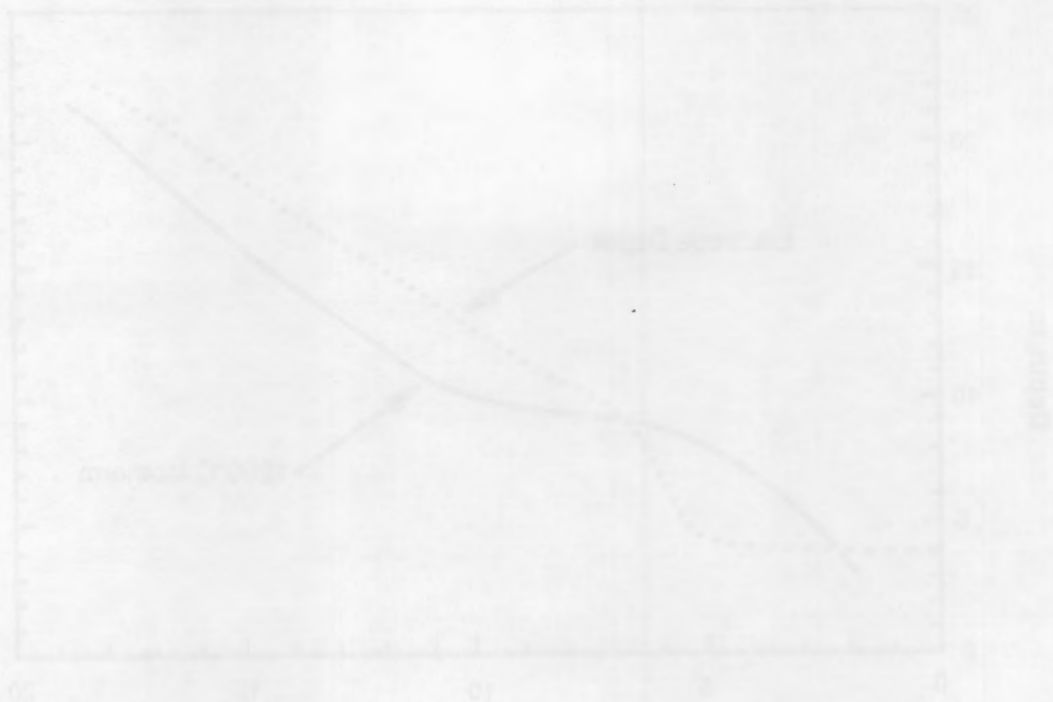
TEST RESULTS

Following completion of the test, analyses were conducted on the vitrified block to determine specific material retention within the block, on the surrounding soil to determine thermal transport effects, and on the off-gas emissions to obtain release information on the volatile components added to the sludge. The analytical data indicates that an underground tank containing residual sludges can be treated using the ISV process in conjunction with an off-gas treatment system.

CHARACTERIZATION OF GLASS PRODUCT AND SURROUNDING SOIL

Of primary interest in this test was the ability of the ISV process to remediate hazardous and radionuclide-bearing sludges contained within a buried tank. Determination of contaminant concentrations contained within the vitrified product and the presence of any thermal transport effects were of importance in assessing treatability by ISV. Three samples (top, middle, and bottom) of vitrified product were analyzed for the presence of the contaminants contained in the sludge. The data indicate that a fairly homogeneous block was formed. However, the volatile compounds, specifically mercury and lead, slightly decreased in concentration as melt depth increased. This is due to partial volatilizing and movement upwards through the molten area, where they eventually either evolved to the off-gas system or were concentrated and contained in the cooler upper regions of the melt. Some heavy metals (Cr_2O_3, UO_3, and Cs_2O) present in the sludge exhibited slightly greater concentrations as the depth of the block increased. This may be due to the sludge being initially located in the bottom of the tank and the ISV process characteristics of the engineering-scale system. It has been shown that the larger scale ISV systems provide enhanced melt mixing characteristics, thus providing a more homogeneous product (Buelt et al. 1987).

Because of the low concentrations of some sludge components and the inherent efficiency of the ISV process, determining accurate mass balances was difficult because some materials were present at or below the detection limits of the instrumentation[a].

Surrounding soil samples were taken to determine if any species had migrated outside the vitrified zone. Sampling locations were determined by the presence of thermal gradients originating from the heat generated in the molten material. Soil samples at the 400°C and 100°C isotherms (zones where the maximum temperature reached during or after operation was 400°C and 100°C respectively) were analyzed for the components added to the sludge. No migration of heavy metal contaminants into the surrounding soil occurred. Small amounts of technetium were found in the 400°C soil sample; however, the concentration amounted to 10^{-6} percent of the total amount of Tc-99 added to the sludge. Additional samples of soil from the area next to the block, of the 400°C and 100°C isotherms, and of ambient soil have been submitted for analyses to verify the presence of technetium.

OFF-GAS CHARACTERIZATION

Off-gas sampling and analyses were conducted to quantify the contaminants evolved during processing of the simulated tank. The amount was determined by analyses of a hood smear, insulation placed over the melt area, off-gas fiber filters, impinger solutions, and a rinse solution of the off-gas sample line.

During testing, the off-gas fiber filter was changed to prevent loading of the filter. It appeared that most of the Hg and Pb volatilization occurred prior to the sludge in the tank being vitrified. This indicates that heating

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(a) Some analyses of the vitrified product were complicated by interferences caused by the matrices of the samples. The normal procedure for analyzing the vitrified product and the surrounding soil involves performing a potassium-nickel fusion, which can then be analyzed by ion-coupled plasma (ICP) techniques. This technique works well for heavy metals; however, any volatile compounds present in the product are driven off during the heating process. This proved evident in analyzing for the lead, mercury, and technetium present in this test. Thus, a best available technique was used to determine the presence of the volatile compounds. A microwave chemical fusion was performed in a sealed container, which traps any compounds that volatilize. Upon cooling, the volatile species recondense into the solution and are then analyzed by ICP techniques.

from the melt and possibly from the tank walls may have contributed to increasing the release of these volatile components early in the test operations prior to actual melting of the sludge region.

As expected, up to 50% of the volatile Hg and Pb compounds added to the sludge were released to the off-gas stream. However, particulate releases in these ranges will be effectively removed by the off-gas treatment system, which consists of wet scrubbing and filtration. Small amounts of contaminants were caught in the insulation placed over the melt area, with lead present at 2.5% of the total amount of lead added to the sludge. The sample of insulation that was analyzed was taken from the edge of the melt area since the insulation over the center of the melt was incorporated into the vitrified product. During large-scale application, insulation will be placed directly over the melt area so that all contamination caught in the insulation will be incorporated in the vitrified product or entrained in the off gas and removed by scrubbing and filtration.

Plateout of a contaminant was observed only in the case of mercury. A maximum 1.5% of the mercury in the off gas plated onto the test containment. A hood smear sample was taken directly above the melt area where previous testing (Timmerman and Oma, 1984) has demonstrated that maximum plating occurs. Thus, the actual mercury content is expected to be far less than reported, since the calculation assumes this concentration for all surfaces available for plateout.

PRODUCT EVALUATION

Samples of the vitrified product taken from the top, middle, and bottom of the vitrified block, as well as a sample of the metal ingot, were subjected to the Extraction Procedure Toxicity (EP Tox) test. The EP Tox test measures the concentration of specific metals in leachate generated from immersing powdered vitrified product in deionized water at room temperature for 24 hours. In general, the EP Tox test is used to determine the regulatory requirements for final disposal of a waste form. Results of the testing are listed in Table 3. The results obtained from the leach testing fell considerably below those limits prescribed by the EPA.

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TABLE 3. EP Toxicity Concentrations for the UTV Engineering-Scale Product

Contaminant	Glass mg/L	Metal Ingot mg/L	Max. Allowed EP Tox Conc. mg/L
Arsenic	<0.01	<0.1	5.0
Barium	0.006	0.002	100.0
Cadmium	<0.004	0.004	1.0
Chromium	<0.02	<0.02	5.0
Lead	<1.0	<0.1	5.0
Mercury	<0.0001	<0.0001	0.2
Selenium	<0.01	<0.01	1.9
Silver	<0.1	<0.1	5.0

These results, in combination with previous testing of ORNL soil (Carter, Koegler, and Bates 1988), indicate that the vitrified product would be an excellent waste form and would provide a long-term isolation of the radioactive and hazardous components present in residual sludges contained in underground tanks.

RETENTION OF RADIONUCLIDES AND HAZARDOUS CHEMICALS

The efficiency of retaining or destroying hazardous chemicals and radionuclides by the ISV process can be expressed as a percent retention in the vitrified product. It is defined as follows:

$$\% \text{ Retention} = (1 - M_e/M_i) \times 100$$

where M_e = mass of species released to the off gas

M_i = mass of the species present in the soil to be vitrified.

Species released during processing include those amounts present in the off-gas stream, any plateout that occurred in the head space of the system container or off-gas piping, and contamination caught in the insulation used to minimize cold cap formation.

Table 4 lists the measured and expected percent retention in the vitrified soil for the hazardous and radioactive components added to the sludge. The expected retention reflects data obtained from previous ISV testing at PNL (Buelt et al. 1987).

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TABLE 4. Contaminant Retention in the Vitrified Soil

Constituent	Measured Percent Retention	Expected Percent Retention
Cr	99.95	-
Hg	46	-
Pb	18.7	97
U	99.994	99.9
Cs	99.992	99.3
Sr	99.98	99.99
Co	99.85	99
Tc	99.996	-

The burial depth of the contaminants has a direct effect on retention (Buelt, Timmerman, and Westsik 1989). Data from pilot-scale and large-scale testing (Buelt et al. 1987) routinely exhibit improved retention of species in the ISV block for larger scale applications.

The effective retention of metals added to the sludge can be seen in Table 4. The small quantity of radionuclide and hazardous constituents not retained in the melt is completely removed from the gaseous effluents before being exhausted to the atmosphere. The efficiency of the off-gas system is measured by a decontamination factor (DF), which is defined as:

$$DF = M_i / M_e$$

where M_e = mass of species released to the off gas

   M_i = mass of the species present in the soil to be vitrified.

The DF is another way of expressing retention where $R = 1-1/DF$. The system DF, which includes contaminant retention in the melt and removal by the off-gas system, is an overall measure of the ISV system efficiency. Typical DFs for the off-gas system, the overall system DFs and percent retention of the overall system are listed in Table 5. This test and previous testing has demonstrated effective retention of all contaminant species present in the sludge. It appears that vitrification of underground tanks will provide an effective and permanent treatment for contaminated underground tanks.

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TABLE 5. Decontamination Factors of Metals (Buelt, Timmerman and Westsik, 1989)

Type of Metal	Off-Gas Treatment DF	Overall DF	Overall Percent Retention
Particulates			
Sr, Pu, U, Cr	10^5	10^{10}	99.99999999
Semivolatiles			
Co, Cs, Tc	10^4	10^6	99.9999
Volatiles			
Cd, Pb, Hg	10^4	10^5	99.999

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