INNOVATIVE VITRIFICATION METHOD DEMONSTRATED FOR THE TREATMENT OF PYROPHORIC URANIUM CHIPS AND OIL

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ABSTRACT

In August of 1999, Geosafe completed a treatability test using its GeoMelt™ vitrification process to treat a canister of wastes containing depleted uranium (DU) chips mixed with PCB-contaminated oil. The test was performed using engineering-scale equipment at the 618-4 Burial Ground located in Hanford's 300 Area North. During the 8-hr test, 0.9-kg of DU chips and 1.4 liters of oil intermixed with soil was processed without difficulty. Upon cooling, the resulting vitrified monolith had a β/γ contact dose reading of 72,000-dpm. An electron microprobe analysis determined the vitrified product contained approximately 9,000-ppm U_3O_8, which correlated well with the projected theoretical concentration. The DU concentration in the target treatment zone was calculated to be 3.2-wt%. A TCLP analysis of the vitrified product found the concentration of all RCRA metals in the TCLP leachate to be below detection limits with the exception of barium, which was present at slightly above its detection limit. The TCLP results were found to meet the more stringent EPA Universal Treatment standards, attesting to the durability of the vitrified product. As expected, no organic material was detected in the vitrified product. Several off-gas grab samples were collected upstream of a thermal oxidizer which was used as a polishing step. Analysis of the grab samples determined the highest concentrations of organics occurred during the initial processing of the oil-laden soil. These results indicated the concentration of all organics to be at or below 52-ppm, and most averaged less than 5-ppm. Subsequent downstream processing of the off-gas by a thermal oxidizer insured the complete destruction of any residual organics present in the off-gas.

Based upon these favorable results, Geosafe believes that GeoMelt vitrification is a viable treatment alternative for these DU wastes. It provides a convenient method for directly converting pyrophoric uranium, which may be contaminated with a suite of organics and RCRA metals, into a safe and durable waste form that can easily be handled for offsite disposal purposes.

INTRODUCTION

Thousands of tons of waste DU chips and fines were generated throughout the DOE complex as the result of uranium milling operations. In its pure form, uranium metal is pyrophoric and will rapidly oxidize when exposed to air as shown in equations 1 and 2. The rate at which oxidation will occur is greatly effected by the particle size of the uranium. Smaller particles, having a large surface area, will rapidly oxidize at ambient room temperatures; larger chunk-size pieces may require preheating before oxidation can be initiated.

$$U + 0_2 \rightarrow UO_2 + \Delta h \ \ (1085 \text{ kJ/mole } UO_2) \qquad \text{(Eq. 1)}$$

$$3U + 40_2 \rightarrow U_30_8 + \Delta h \text{ (3575 kJ/mole } U_3O_8) \quad \text{(Eq. 2)}$$

Uranium can also react in the absences of air by hydrolyzing water, as shown in equation 3, forming explosive hydrogen gas. To prevent oxidation from occurring, uranium chips were commonly stored in drums submerged in oil. For disposal purposes, these drums were often buried intact.

$$U + 2H_20 \rightarrow UO_2 + 2H_2 + \Delta h \text{ (601 kJ/mole } UO_2) \quad \text{(Eq. 3)}$$

The practice of burying DU has led to contamination problems at Hanford, Oak Ridge, Paducah, and Rocky Flats which require remediation to prevent the further spread of contamination into the environment. Two widely used disposal practices for DU involved dumping the waste into pits and promoting its oxidization, or direct disposal of drummed material in a land disposal facility. Both disposal methods present significant groundwater contamination threats, as well as a safety hazard if significant quantities of explosive hydrogen gas are being generated.

DOE has identified the need for a safe and regulatory-acceptable treatment technologies for this waste. One factor complicating treatment is that much of the DU is contaminated with PCBs, thus making it a "tri-regulated" (hazardous, LLW, and TSCA) waste. Currently no onsite or off-site treatment facilities are permitted to receive "tri-regulated" waste of this nature. Given the difficulties of obtaining the necessary operating permits, the cost for DOE to bring a facility online are likely to be prohibitive.

Geosafe Corporation, in cooperation with Bechtel Hanford Inc. (BHI) and DOE's Mixed Waste Focus Area, performed a test using GeoMelt^{TM} vitrification to address this need. The test was performed at the 618-4 Burial Ground located in the Hanford 300 Area North Site.

Remediation activities at this burial ground were halted in 1998 after 330 drums of DU-contaminated wastes were excavated. Of these drums, 260 were found to contain DU chips packaged in oil; the remaining drums contained a dry uranium oxide. Characterization of the DU chips found them to contain hazardous levels of arsenic, lead, chromium, and selenium. The packing oil was found to contain uranium and PCBs, as well as hazardous levels of TCE and heavy metals. Characterization of the oil-filled drums found that they contained an average of 28-kg DU, and 56-kg (60-L) oil. An additional 1200 drums are expected to be excavated from the 618-4 Burial Ground when remediation activities are completed.

In the past, GeoMelt vitrification has been successfully applied to uranium oxides, but it has never been tested on pyrophoric uranium. Therefore, the treatability test performed for this study was specifically designed to address this issue. Descriptions of the test, configuration, sample preparation, and results are provided below.

TECHNOLOGY DESCRIPTION

The traditional GeoMelt process (also known as In Situ Vitrification or ISV) involves using joule heat to melt the earthen materials in a top-down fashion. Beginning in 1980, DOE, through Battelle – Pacific Northwest National Laboratory (PNNL), developed ISV for the treatment of soils contaminated with radionuclides. In 1986, Battelle acquired worldwide rights for the commercialization the ISV technology. Battelle then formed Geosafe Corporation to pursue this business opportunity. After its formation, Geosafe spent several additional years developing the ISV technology before commercially offering it in 1993. Geosafe has since developed the technology far beyond the DOE-funded state. In order to differentiate these new developments from the traditional ISV technology, Geosafe initiated the term "GeoMelt" technologies to encompass the original (traditional) ISV technology and subsequent developments.

The GeoMelt process differs from other types of vitrification in that it is performed at a much larger scale and uses soil as a replacement for the refractory lining typically found in ex-situ melters. This feature allows the GeoMelt process to operate at a much higher temperature, and eliminates many of the operating problems associated with conventional melter vitrification (e.g., liner deterioration). Other advantages include: 1) the ability to process large amounts of waste and debris materials without difficulty, 2) essentially no operating temperature limitations, 3) eliminates the need for chemical additives to reduce melt temperature, 4) insures a superior vitrified product relative to that generated by melters operating at a lower temperature, and 5) significantly lower capital and operating costs.

GeoMelt vitrification uses electrical energy applied to the treatment zone by means of graphite electrodes to joule-heat earthen type materials. The high temperature generated during the GeoMelting (1500 to 2000ºC for most soils) destroys even the most recalcitrant organic contaminants. GeoMelt vitrification is usually performed in a large-batch mode configuration. Upon cooling, the melt solidifies into a vitrified product that can be left in place or recovered (at a very nominal cost) for offsite disposal. The resulting vitrified product is free of organic material, typically exhibits no hazardous characteristics, and is extremely leach resistant.

As illustrated in Figure 1, the GeoMelt vitrification process can be applied in two different modes of operation: conventional or "top-down", and planar or "sideways". In the conventional mode, the melt is initiated at the ground surface and grows downward and outward through the treatment zone. After the melt has gained a thickness of several feet, a cold-cap forms on its surface significantly reducing the amount of radiant heat loss to the plenum. Generally, the nominal operating temperature of the off-gas plenum is 250ºC, but higher temperatures can be experienced if the concentration of organic material exceeds 10 wt %.

The Planar melting mode of operation is a recent development of the ISV technology. It offers several advantages for processing containerized waste, such as would be expected with DU. Planar melting differs from conventional ISV in that two separate vertical melts are established on opposite sides of the target treatment zone (Figure 1). The planar melts grow downward and sideways and, after a period of time, will join to form one contiguous melt. Prior to the planar melts joining, the area between them is thoroughly dried of all liquids. This eliminates the potential for vapors to be trapped and potentially cause a melt upset. Planar melting is more energy efficient than conventional melting because the melt surface is always covered with an insulating blanket of soil. The off-gas plenum temperature for a planar melt is typically in the range of 50ºC. Planar-ISV can also be used to obtain deeper processing depths and narrower melts.

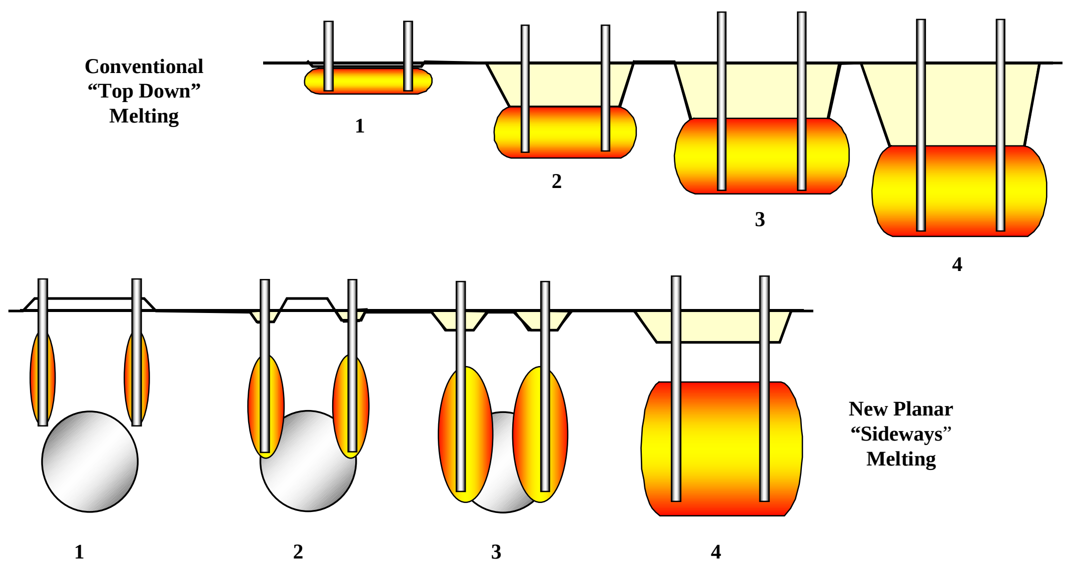

Figure 1: Comparison of Conventional Top-down and Planar GeoMelt Vitrification

TEST OBJECTIVES

The primary objectives of this treatability test were:

- Demonstrate Planar-ISV processing of DU chips mixed with oil
- Demonstrate that the vitrified product is TCLP compliant
- Determine if oxidation of uranium detrimentally effects the ISV process
- Provide data to evaluate full-scale treatment of the Hanford 618-4 drummed wastes

DESCRIPTION OF TREATABILITY SYSTEM

The Geosafe Engineering-Scale ISV System consists of a 30-kW power supply, off-gas container, test drum, and off-gas treatment system. The system is capable of producing melts in the 200 to 300-kg range. A schematic of the engineering-scale off-gas treatment system used in this test is shown in Figure 2. It consisted of HEPA filtration, knockout box (moisture trap), and thermal oxidizer. The nuclear grade HEPA filtration system is designed to provide better than 99.97% removal of particulate greater than 0.3 micron in size. This was more than adequate to ensure that no soot or uranium contaminated particulate could be released during the test. The engineering-scale test equipment is designed to provide up to a six-9's DRE (destruction/removal efficiency) for organics.

It should be emphasized that Geosafe's engineering-scale off-gas treatment system, while sufficient to meet the requirements of this test, it is not an exact scaled-down version of it's large-scale system. The large-scale system also includes a wet scrubber and an acid gas neutralization system. The increased melt size and additional off-gas treatment system components, increase the DREs attainable at large scale. A DRE of greater than 6-9s for organics is readily achieved with the large-scale system.

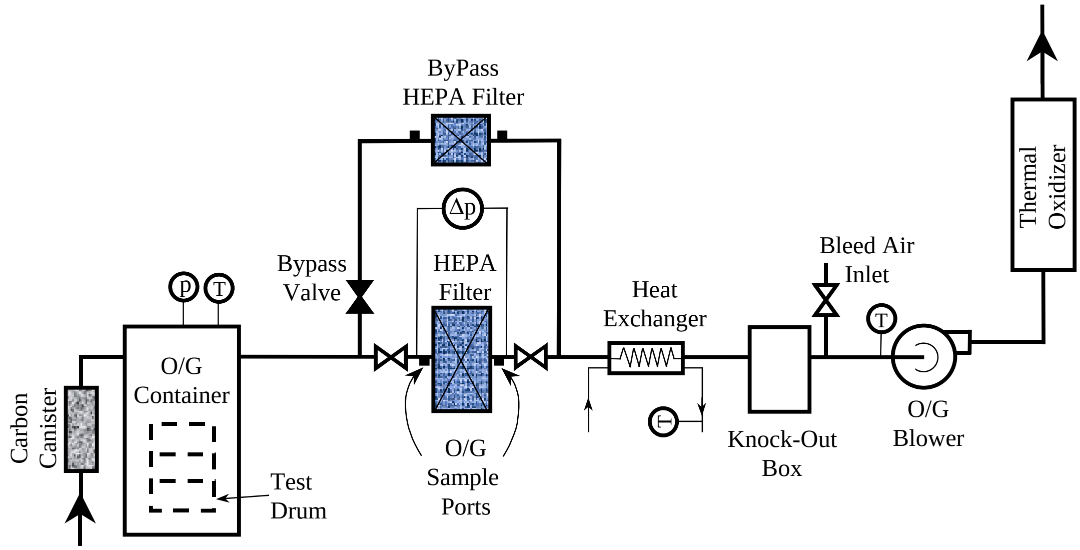

Figure 2: Process Schematic of the Engineering-Scale Off-Gas Treatment System

TEST SETUP AND CONFIGURATION

Geosafe elected to use Planar-ISV melting for the treatability test to avoid any potential of vapor entrapment during processing. Planar melting has been demonstrated at large-scale, and has been shown to have a competitive advantage over conventional top-down melting.

The treatability test was conducted using Geosafe's engineering-scale test system mobilized to the 618-4 Burial Ground located in Hanford's 300 Area North Site. All support equipment (which included a power generator, power transformer control system, and data logging system) was located outside of the exclusion zone. The containment vessel and off-gas treatment systems were located within the exclusion zone. The test was conducted in an 85-gal steel drum that was placed in a rectangular-shaped containment vessel. A negative air pressure was maintained in the containment vessel to prevent the release of vapors. Off-gas extracted from the containment vessel was processed through an off-gas treatment system (Figure 2) before being vented to the atmosphere.

Prior to conducting the test, the 85-gal drum was prepared to receive the 1-gal sample canister. The graphite electrodes were inserted into the test drum and two vertical starter planes were installed between electrode the pairs. A number of thermocouples were positioned around the treatment zone to facilitate monitoring the melt's progress. A sketch showing the test configuration is provided in Figure 3.

SAMPLE PREPARATION

On August 24,1999 BHI personnel collected a DU sample from a drum that had been previously characterized and found to contain a mixture of organics (including PCBs) and heavy metals in oil, as well as a high concentration of depleted uranium. This drum is thought to be representative of the highest concentration of DUexpected to be encountered in the 618-4 Burial Ground. The DU chips or turnings were extracted from the drum using a fork attached to a rod. The DU sample was placed in a 1-gal metal canister along with 1.4 liters of oil that was also extracted from the drum. The oil was contaminated with depleted uranium, heavy metals (e.g. – cadmium, chromium, lead, and mercury), solvents, and PCBs. Waste characterization results for this drum are presented in Tables I and II.

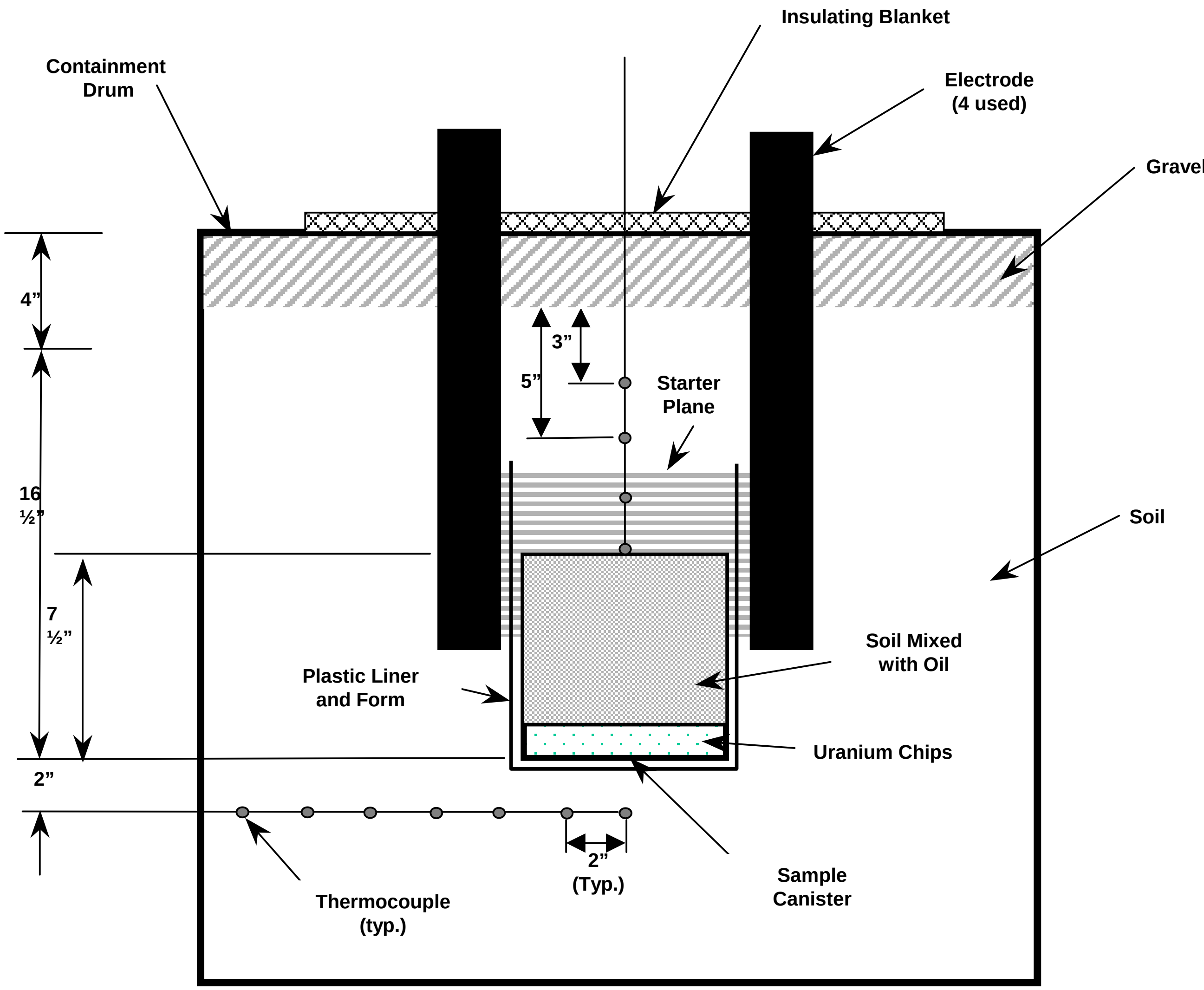

Figure 3: Configuration of the Sample Canister in Test Drum

The sample canister was then positioned in the 85-gal drum as shown in Figure 4. To contain the oil within the treatment zone, a plastic liner was placed around the outside of the sample canister. The canister and then filled with Hanford soil. The region above the canister was filled with soil and gravel. An insulating blanket was then placed on the gravel surface to provide additional insulation and filtration of off-gases emanating from the treatment zone during processing. It was calculated that the soil within the treatment zone absorbed 4.4-wt% oil. The DU loading in the treatment zone was calculated to be 3.2-wt%.

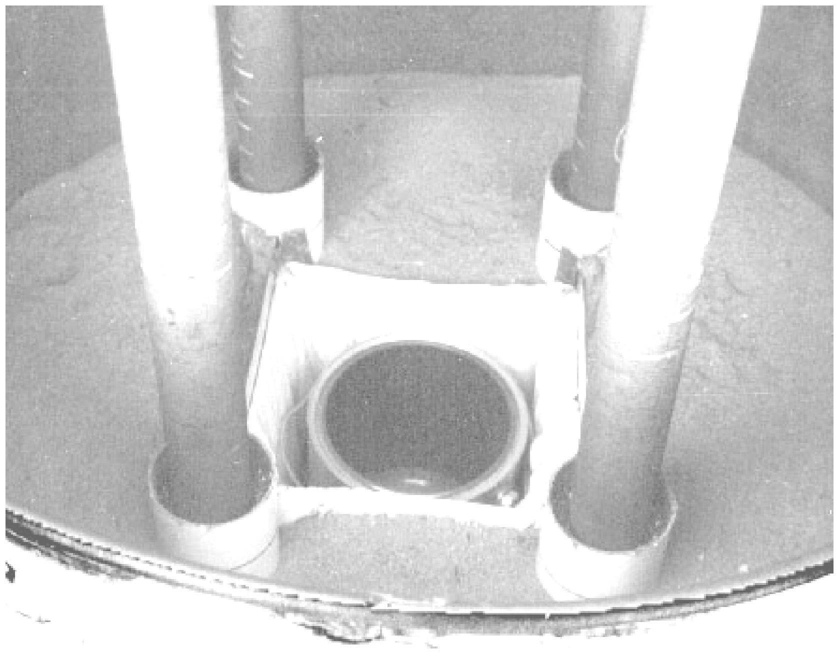

Figure 4: Placement of the DU Sample Canister Placed in Test Drum

Table I. Organic and Inorganic Characterization of Test Sample

CONSITUENT	SOLID PHASE (mg/kg)	LIQUID PHASE (mg/l)
ORGANICS		
Benzene	-	19
2-Butanone	-	300
TCE	-	2000
PCE	-	7.5
PCBs	-	480 mg/kg
HEAVY METALS		
Arsenic	16.8	0.2
Barium	176.6	28.1
Cadmium	1.56	0.05
Chromium	20.4	0.08
Lead	12.08	12.4
Mercury	0.02	0.734
Selenium	19.32	0.26
Silver	2.4	0.09

Table II. Radionuclide Characterization of Test Sample

CONSITUENT	SOLID PHASE (pCi/g)	LIQUID PHASE (pCi/ml)
U-234	280,000	680,000
U-235	1,900	5,168
U-238	280,000	680,000

TEST RESULTS

On August 30, 1999, Geosafe commenced the treatability test. Power to the electrodes was ramped up at a predetermined rate to a maximum level of 7.5 kW per phase (15 kW total) over a 3-hour period. The 15-kW power level was then maintained for the remainder of the test. Off-gas samples were pulled from the containment vessel at three times during the test. These samples were subsequently sent to a BHI-designated laboratory for analysis. After approximately 8-hours of operation, the target treatment depth was reached and power to the electrodes was shut off. The off-gas treatment system was operated for a period of time following this before being shut off.

The test consumed approximately 96-kWh of electrical energy and produced a 128-kg vitrified monolith. The specific energy consumption for this test was calculated to be 0.75-kWh/kg of material processed. This is considerably lower than the nominal 1-kWh/kg required in conventional, top-down ISV applications, despite the significant quantity of volatile, liquid materials processed in this test. This lower specific energy consumption is a direct result of the thermal efficiencies afforded by the subsurface, Planar-ISV approach to processing.

Due to economic considerations, it was elected not to collect continuous off-gas sampling data from this test. This decision was primarily based on the fact that the destruction of the organics has already been well documented for the ISV process. Off-gas grab samples were collected during the test to confirm that good destruction of organics was occurring in the melt treatment zone. Results from the off-gas sampling are presented in Table III. The results show that a low concentration of organics was measured in the off-gas after it exited the HEPA filter and before it entered the thermal oxidizer. Follow on treatment by a thermal oxidizer, which had a relatively long residence time, insured that good destruction of the organics was achieved. Airborne radiological samples obtained during the test, as well as radiological surveys performed after the test, indicated that the radioactive material was completely contained within the treatment zone.

Table III. Off-Gas Sample Results

ANALYTE	**ANALYTE CONCENTRATION (ppb)**		
	11:45 SAMPLE (BOW8V6)	**13:55 SAMPLE** (BOW8V7)	**16:10 SAMPLE** (BOW8V8)
Benzene	52000	5000	4300
Trichloroethene	1700	83	< 42
Toluene	20000	4100	3300
Ethylbenzene	2100	1000	690
m-xylene, p-xylene	4800	2000	1600
o-xylene	2200	1000	770
Styrene	870	390	180
1,3,5-trimethylbenzene	430	230	180
1,2,4-trimethylbenzene	1500	830	710

Samples of the vitrified product were subjected to the Toxicity Characteristic Leaching Procedure (TCLP)
to assess its quality and durability as a waste form. The results of this analysis are presented in Table IV indicated that, with the exception of barium, the concentrations of all analytes were below the detection limit for that element (i.e. – in the 0.1 to 50 parts per billion range). These results included hazardous elements such as arsenic, cadmium, chromium, lead, and mercury. The most stringent EPA Universal Treatment Standard (UTS) limits for these elements ranged from 18× to 250× higher than the detection limits listed. The barium concentration present in the leachate was also very low – less than ¼ the allowable level for the most stringent EPA UTS for

this analyte. As expected, PCB's were below detection limits (61-ppb) indicating that they were effectively destroyed. These results indicate that the PCBs present in the oil were effectively remediated by the Planar-ISV process.

Table IV. Vitrified Product Sampling Analysis Results

ANALYTE	**ANALYTE CONCENTRATION (ppb)**	
	GLASS SAMPLE (BOWBM6-001)	**TCLP LEACHATE** (BOWBM6-002)
Arsenic	< 270	< 24.2
Barium	1900	309
Cadmium	< 20	< 4.7
Chromium	270	< 5.3
Lead	190	< 30.9
Mercury	< 20	< 0.1
Selenium	570	< 45.4
Silver	< 80	< 3.6
PCBs	——	< 61

A sample of the vitrified product was analyzed using an electron microprobe. This analysis identified the structure and composition of the product. The glass composition was found to be relatively homogeneous – particularly given the small scale of the test. Moreover, the U_3O_8 concentration was measured at several locations within the sample. The average concentration was found to be approximately 9000-ppm, consistent with the projected theoretical concentration.

SUMMARY

Results from this treatability test indicated that GeoMelt Planar-ISV can safely process DU, as well as the high concentrations of oil and hazardous constituents that are also present with this waste. Geosafe's conceptual approach for processing the 1500+ drums present at the Hanford 618-4 Burial Ground involves staging the drums in a lined treatment cell. The drums would be placed in the treatment cell in layers, covered with soil and then breached. Oil present in the drums would then be absorbed by the surrounding soil. The drums of waste could then be safely processed by GeoMelt Planar-ISV. Geosafe estimates that up to 400 drums of DU waste could be processed in a 24-ft x 24-ft x 12-ft deep treatment cell. Following processing and a period of cooling, the vitrified monolith would be excavated and shipped to the nearby Hanford Environmental Restoration Disposal Facility.