The Treatment of Mixed Waste with GeoMelt In-Container Vitrification

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ABSTRACT

AMEC's GeoMelt® In-Container Vitrification (ICV)™ has been used to treat diverse types of mixed low-level radioactive waste. ICV is effective in the treatment of mixed wastes containing polychlorinated byphenyls (PCBs) and other semi-volatile organic compounds, volatile organic compounds (VOCs) and heavy metals. The GeoMelt vitrification process destroys organic compounds and immobilizes metals and radionuclides in an extremely durable glass waste form. The process is flexible allowing for treatment of aqueous, oily, and solid mixed waste, including contaminated soil. In 2004, ICV was used to treat mixed radioactive waste sludge containing PCBs generated from a commercial cleanup project regulated by the Toxic Substances Control Act (TSCA), and to treat contaminated soil from Rocky Flats Environmental Technology Site. The Rocky Flats soil contained cadmium, PCBs, and depleted uranium. In 2005, AMEC completed a treatability demonstration of the ICV technology on Mock High Explosive from Sandia National Laboratories. This paper summarizes results from these mixed waste treatment projects.

INTRODUCTION

AMEC's GeoMelt process has been used to treat radioactive and mixed waste since the mid 1980s. GeoMelt originated as an in-situ method to treat contaminated soils at U.S. Department of Energy (DOE) sites. In the late 1990s GeoMelt was developed to include an ex-situ method (In-Container Vitrification) to treat stockpiled and excavated wastes. ICV is a batch waste treatment process that is performed in a refractory-lined steel container. The waste is blended with soil (an inexpensive source of glass-formers) and melted using Joule (resistive) heating generated by electrical current supplied by graphite electrodes positioned in the waste. Because soil at ambient temperatures is not sufficiently conductive, the melting process is initiated by placing a conductive pathway between the electrodes. The Joule heat generated in this pathway elevates the temperature of soil surrounding the path to the point where it becomes molten. Once molten, the soil is conductive and the electrical current is transferred throughout the waste material as the melting process propagates. Most ICV melts realize temperatures ranging from 1400 to 1800°C. The melt temperature is determined by the chemical make-up of the soil and waste materials being processed. Melts have been performed at temperatures as high as 2000 °C.

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™ In-Container Vitrification (ICV) is a trademark of AMEC

ICV containers may serve as the disposal container or may be reused, depending on project demands. The refractory lining used in the container may be as simple as refractory silica sand, which is easily recycled into subsequent melts, thus minimizing secondary waste generation. Alternatively, pre-cast refractory linings are used in some ICV configurations to allow for extended treatment durations and feeding additional waste into active melts to increase disposal package payloads. The ICV process can be initiated either in a top-down fashion or from the base of the staged waste payload. In the top-down application, the container is preloaded with waste and then treated from the surface downward. As the melt depth increases with time, the electrodes are allowed to gravity-feed into the developing melt, thereby insuring widespread distribution of electrical current through the molten mass. In the base melting method, the melt is initiated beneath an initial batch of preloaded waste. As melting and volume reduction (from densification) occurs additional waste is added to the ICV container. This material is incorporated into the melt below.

Off-gases generated during ICV processing are contained by a steel hood structure and off-gas treatment system that is maintained at a negative pressure during processing. These off-gases are then routed through this treatment system that traps and removes any particulates present in the flow, and scrubs any condensable (e.g. – water vapor) and non-condensable (e.g. – CO_2, NO_x, etc.) gases from the flow. The treated off-gas flow is finally released to the atmosphere.

A broad range of organic contaminants has been treated successfully in commercial ICV operations. Concentrated organic wastes up to 33 weight percent (wt%) in soil have been treated with the process. Organic contaminants such as dioxins, pesticides and PCBs are destroyed via pyrolysis and dechlorination reactions at the elevated temperatures and reducing conditions of the melt [1]. No organic contaminants remain in the melt due to the inability of organics to exist in the melt at such high temperatures. ICV has been successfully demonstrated for the treatment of hexachlorobenzene, nuclear fuel holding pond sludge, and currently is being evaluated by DOE for the treatment of low activity Hanford tank waste. ICV is especially suited for the treatment of "difficult" mixed waste streams because 1) it is a high-temperature thermal treatment technology capable of destroying all organic wastes, 2) it results in a vitrified waste form with superior leach characteristics for metals and radionuclides, and 3) can be configured to treat nearly any waste or combination of wastes in most conceivable forms (e.g., solid, aqueous, oily, sludge, etc.). The destruction and removal efficiency (DRE) for organic contaminants achieved is greater than 99.9999%. This DRE includes the percentage destroyed by the melt (typically 90-99.9%) and the percentage destroyed and/or removed from the off-gas stream by the off-gas treatment equipment.

The vitrified product normally consists of a mixture of glass and crystalline materials and often has an appearance similar to volcanic obsidian. The product is typically ten times stronger than concrete and is extremely leach resistant. The vitrified product readily satisfies the requirements of the US Environmental Protection Agency's (EPA) Toxicity Characteristic Leaching Procedure (TCLP). The vitrified product is normally 10 to 100 times more durable and leach resistant than typical borosilicate glasses used to immobilize high-level nuclear waste. The durability and leach resistance of the glass is due to a high concentration (60-90 wt%) of glass formers (SiO_2 and Al_2O_3) and the ability to treat soil and wastes without large amounts of temperature-lowering additives such as sodium.

TSCA MIXED WASTE TREATMENT

The waste treated in this project was a three-phase mixture (aqueous, oil and sludge) generated by material exiting low-level radioactive waste containers as they were compacted during the course of a TSCA spill cleanup/remediation project. A total of twenty-five 208-liter (55-gallon) drums containing 4,490 kg of mixed low-level radioactive waste were treated. PCB levels in the waste were between 443 and 496 mg/kg. The waste also contained detectable concentrations of various VOCs and heavy metals, all of which were below treatment standards. The goal of the project was to destroy the PCBs while converting the waste materials into a non-leachable product that would meet land disposal restrictions (LDRs).

Waste Preparation

The waste ranged from 25-90 % by volume liquid with the remainder as a semi-solid sludge. The waste was pretreated by blending with sand and other additives in order to achieve adequate melt chemistry and to allow batch staging into the melt container. A portion of the waste was blended for Melt 1 to allow modifications to the blending chemistry for subsequent melts based on melting characteristics of the first batch. Table I provides blended waste compositions. Sand containing 80.5 weight percent (wt%) silica (SiO_2) was used to provide glass formers in order to enhance vitrified waste form leaching characteristics. Zeolite and montmorillonite are clay minerals that were used to absorb water and oil, respectively. Sodium carbonate (Na_2CO_3) was used to provide additional sodium to optimize processing conditions as it improves the electrical properties and moderates temperatures of the melt. All of these additives are readily available and inexpensive.

Table I. Blended TSCA Mixed Waste Composition

Melt 1		
Component	Mass (lbs)	Wt%
Waste Material	619	35.5
Sand	483	27.7
Na_2CO_3	157	9.1
Zeolite	483	27.7
Total	1,742	100
Melts 2-5		
Component	Mass (kg)	Wt.%
Waste Material	3,870	36.2
Sand	395	3.7
Na_2CO_3	855	8.0
Zeolite	1,120	10.5
Montmorillonite	4,447	41.6
Total	10,687	100

Waste Processing

A schematic diagram of the ICV process is shown in Figure 1. The ICV container, baghouse, and HEPA pre-filters were located within an airlocked indoor treatment facility (Figure 2) and the off-gas treatment system was located outside of this facility in a 14-meter trailer that also contained the process controls and the transformer that supplies electrical power to the melt. The off-gas treatment system cools, scrubs and filters emissions from the ICV treatment. A thermal oxidizer was added to the standard GeoMelt off-gas treatment system for this project

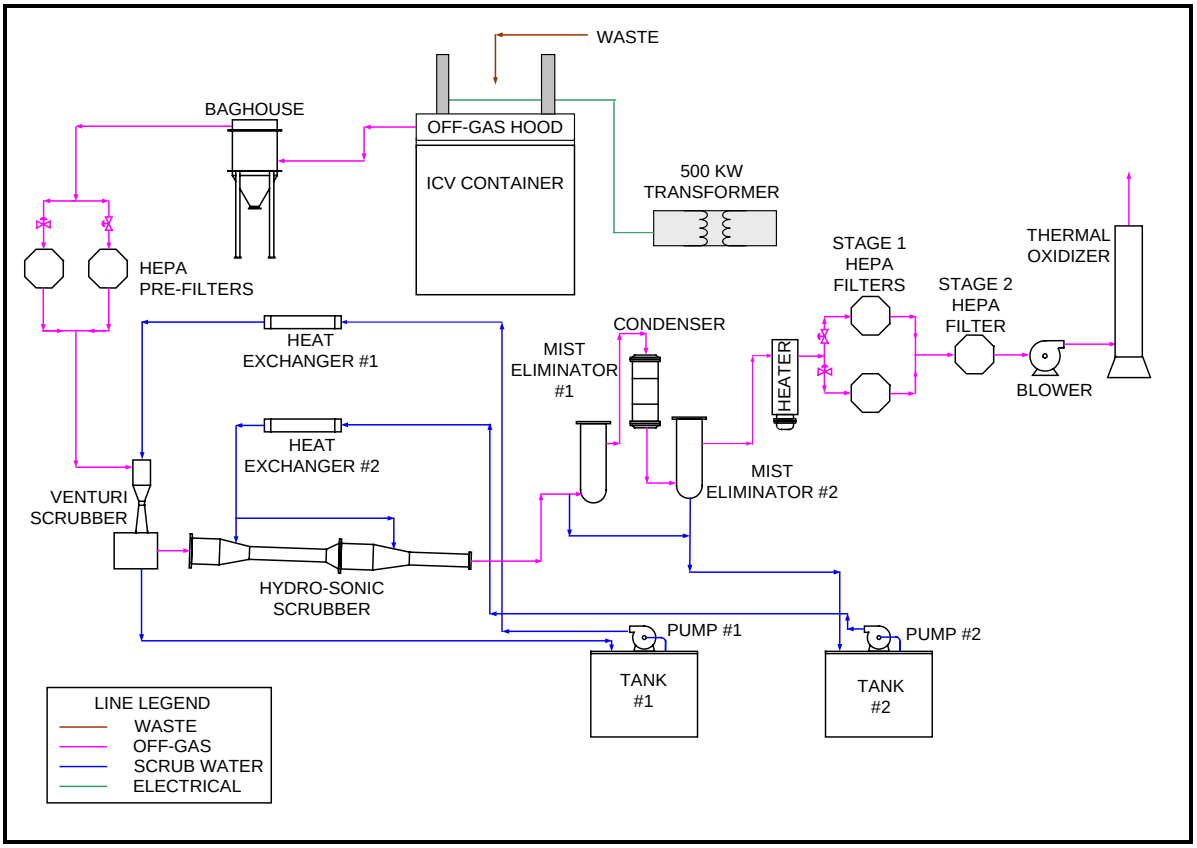

Fig. 1. GeoMelt pilot-scale system process flow diagram

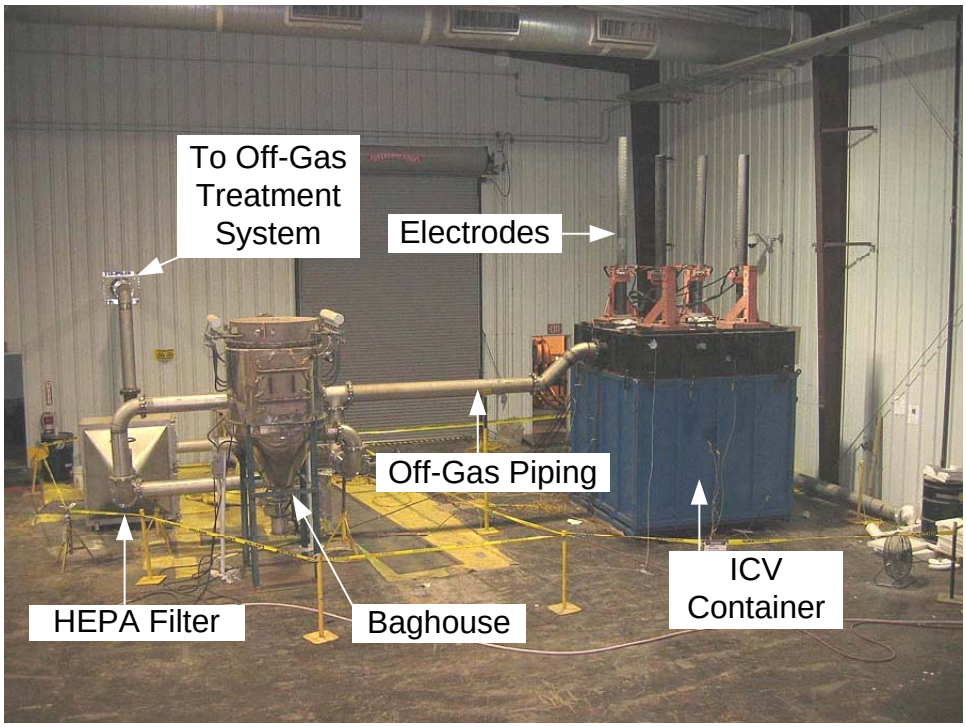

Fig. 2. GeoMelt pilot-scale ICV container and initial off-gas treatment components

As indicated in Table I, the TSCA mixed waste was treated in 5 successive melts. Process parameters of each melt are summarized in Table II. Melt duration was primarily a function of waste mass. Power levels were relatively low until Melt 5, which was significantly greater in mass than previous melts. The average and maximum power levels for Melt 5 were well within the transformer capacity (500 kW). Waste processing efficiency ranged from 1.36 to 3.37 kilowatt-hours per kilogram (kWh/kg). The greatest efficiency was realized while treating the largest batch. In all of the melts, the target vertical processing rate of 2.5 cm per hour or less was maintained. The processing rate is controlled by moderating power levels to the melt.

Table II. TSCA Mixed Waste Vitrification Process Parameter Summary

Parameter	Melt 1	Melt 2	Melt 3	Melt 4	Melt 5
Treated Mass (kg)	1,742	2,214	1,179	2,204	5,080
Melt Duration (hr.)	73	47.5	34.5	52.5	59.5
Electrode Separation (in.)	36	36	36	36	52
Expended Energy (kWh)	5,849	4,269	3,659	4,290	6,938
Ave. Power (kW)	82.5	102	112	90	126
Max. Power (kW)	134	126	135	139	220
Processing Efficiency (kWh/kg)	3.37	1.93	1.41	1.95	1.36
Processing Rate (cm/hr)	1.8	2.4	2.5	2.3	2.2

Stack Sampling

Isokinetic air sampling for PCBs and polychlorinated dibenzodioxins/dibenzofurans (PCDDs/PCDFs) was conducted in the off-gas piping immediately before the thermal oxidizer during Melt 5. PCDDs and PCDFs are compounds produced by combustion of PCBs, and often are noted as problematic by-products of PCB incineration. Although combustion is not a primary destruction mechanism in GeoMelt (pyrolysis and dechlorination reactions are responsible for PCB destruction in the GeoMelt process), the sampling was undertaken to satisfy TSCA regulatory requirements. The PCB analysis was performed for each of the 209 individual isomers with the results compounded into each of the ten congener classes representing degree of chlorine substitution. The measured flow rate at the sampling location and the sample duration are used to calculate a PCB mass emission rate. DRE is calculated by the following formula:

$$DRE = \left[1 - \left(\frac{W_{out}}{W_{in}}\right)\right] x\ 100$$

where W_{in} is the blended waste treatment rate multiplied by the PCB concentration and W_{out} is the PCB mass emission rate. The DRE calculated for total PCBs prior to the thermal oxidizer was 99.3%, which is within the range typical for GeoMelt. Monitoring during previous GeoMelt operations has indicated that the melt accounts for 97.1 to 99.7 % destruction of PCBs [2]. The standard GeoMelt off-gas treatment system (used primarily to abate radioactive particulates within the off-gas) is augmented with a thermal oxidizer in order to achieve ≥99.9999% DRE at the exhaust stack, which is required by TSCA. PCDDs and PCDFs were not positively identified or were below laboratory detection limits in the off-gas.

Vitrified Waste Characterization

After each melt was complete, the treated waste was allowed to cool into a glass block in the shape of the refractory liner inside which it was produced. The cooling generally took only 2-3 days for each block, after which time the block was removed through a removable sidewall in the ICV container. It should be noted that although the vitrified mass was solid, the exterior temperatures were still quite hot (>200 °C). The blocks were fractured to allow product samples to be obtained, and to facilitate packaging for transport for permitted landfill disposal. Figure 3 depicts the Melt 2 block. In this figure, the vitrified waste is seen as dense, homogenous, dark glass, surrounded by light colored silica refractory sand. This siliceous layer is formed through the partial dissolution of the refractory silica sand lining into the molten glass resulting in a durable silica-rich rind. Dissolution of silica from the ICV lining into the glass is not detrimental to the vitrified product leach characteristics. In fact, refractory lining silica dissolution has been shown to improve leach responses under TCLP and under other, more aggressive procedures (i.e., Vapor Hydration Test [VHT] and Project Consistency Test [PCT]) used in determining the chemical durability of nuclear waste glass [3, 4].

Fig. 3. Vitrified monolith from TSCA mixed waste melt 2

Table III summarizes laboratory analytical results of the vitrified product samples from each demonstration melt. The table shows reduced concentrations of radionuclides in the vitrified product, which is due to convective mixing and the consequent distribution of the contaminants throughout the volume of vitrified material. The analytical results indicate destruction of PCBs, which cannot survive in the melt owing to the extreme temperatures (≥1,500 °C).

Concentrations of PCBs and other organic contaminants were not detected above laboratory reporting limits in the resulting glass. The vitrified waste was shipped to Envirocare of Utah, LLC (Envirocare) for land disposal.

Table III. TSCA Mixed Waste Glass Sample Analytical Results

Waste Inventory			Melt 1	Melt 2	Melt 3	Melt 4	Melt 5	Melt 5	Regulatory
Component	WP17332	WP17392	Glass	Glass	Glass	Glass	Glass	Glass	Levels [a,b]
Radionuclides pCi/g									
Co-60	59,000	18,000	ND	145	329	69	94	94	30,000
Co-58	3,690	1,000	ND	ND	ND	ND	ND	ND	4.4e+08
Co-57	720	370	0.4	1.47	0.86	ND	ND	ND	4.4e+08
Cs-137	20,300	22,000	135	269	114	211	423	423	60,000
Cs-134	1,000	7,300	12.9	19.7	8.4	15.2	24.9	24.9	4.4e+08
Mn-54	2,600	710	ND	ND	ND	1.08	ND	ND	4.4e+08
Sb-125	1,680	450	ND	ND	ND	ND	ND	ND	4.4e+08
Zn-65	1,530	390	ND	ND	ND	ND	ND	ND	4.4e+08
Am-241	ND	135	0.28	ND	ND	0.59	1.39	1.39	1,000
Ag-110M	1,330	270	ND	ND	ND	ND	ND	ND	4.4e+08
Zr-95	ND	330	ND	ND	ND	ND	ND	ND	4.4e+08
PCBs (mg/kg)									
Aroclor 1242	443	496	ND	ND	ND	ND	ND	ND	10

[a] Maximum average radionuclide concentrations from Envirocare of Utah License UT 2300249 amendment 13
[b] Universal Treatment Standard for PCB (US EPA Land Disposal Restrictions CFR 268-48)

DEPLETED URANIUM MIXED WASTE TREATMENT

This section discusses AMEC's treatment of depleted uranium mixed waste from a burial trench at Rocky Flats Environmental Technology Site Trench. This trench was used from 1954 to 1962 to dispose approximately 171 208-liter drums containing depleted uranium chips and turnings, the byproduct of manufacturing nuclear weapons components. The trench was remediated in 1998 and 1999 when approximately 30 tons of contaminated soil and depleted uranium were excavated and packaged. The trench was backfilled with clean soil and the surface was reseeded. Most of the waste was shipped to the Nevada Test Site for disposal. However, a significant amount of the waste from this project was characterized as mixed waste requiring treatment before land disposal. AMEC was selected to perform a series of trial melts to establish the suitability of ICV for treating this waste stream. The treatability tests were performed in 2004.

Waste Description

The waste was composed of approximately 65% soil, 30% depleted uranium (DU) chips and turnings, and 5% steel drum fragments with ICV. In addition the contaminated soil contained PCBs, trichloroethylene (TCE), tetrachloroethylene (PCE) and cadmium in excess of land disposal restriction (LDR) levels. Whole rock compositional analysis of the waste indicated that it was suitable for treatment without blending additives or extra soil. The waste was loaded directly from the B-12 shipping containers to the ICV container (Figure 4).

Fig. 4. Loading Rocky Flats mixed DU waste into ICV container for GeoMelt processing

The Rocky Flats DU mixed wasted treatment demonstration was accomplished in 2 melts. Table IV provides a summary of process parameters associated with these melts. The vitrified monolith from Melt 1 is depicted in Figure 5. The monoliths from each melt were removed from the processing container, sampled, and packaged for shipping to Envirocare for land disposal.

Table IV. Rocky Flats DU Mixed Waste Vitrification Process Parameter Summary

Parameter	Melt 1	Melt 2
Treated Mass (kg)	4,741	5,031
Melt Duration (hr.)	59	74
Electrode Separation (in.)	38	39
Expended Energy (kWh)	5,849	4,269
Ave. Power (kW)	135	127
Max. Power (kW)	180	170
Processing Efficiency (kWh/kg)	1.56	1.88
Processing Rate (cm/hr)	2.7	2.3

Fig. 5. The Rocky Flats DU mixed waste melt 1 vitrified monolith

The following conclusions summarize the Rocky Flats DU mixed waste post-test analysis:

- The treatment resulted in monolithic blocks approximately 80 ft^3 in size, indicating greater than 50 percent volume reduction of the waste during treatment.

- Radionuclide concentrations in the vitrified product samples were significantly lower than in the pre-demonstration waste. This is in part because the pre-treatment waste sampling was biased towards higher activity areas in the waste (according to the waste profiles), and also because of the homogenizing effect of the vitrification process.

- PCBs and VOCs were not detected in the post-demonstration vitrified product samples.

- Leachable cadmium was reduced from 26.74 to 0.398 milligrams per liter (mg/L), in the Melt 2 vitrified product. This represents a 98.5 % reduction, well within 40 CFR 268.49 alternative treatment LDR for contaminated soil that requires a 90% reduction in leachable concentrations of underlying hazardous constituents (UHC) such as cadmium and other naturally occurring metals to allow land disposal.

SANDIA MOCK HIGH EXPLOSIVES TREATABILITY TEST

In 2005, AMEC completed a demonstration to establish the suitability of GeoMelt ICV in the treatment of Mock High Explosive 900-10 (mock HE) for Sandia National Laboratories. Table V Mock HE is non-detonating low-grade propellant. Mock HE bears similar physical properties (texture, density, cohesion, etc.) to actual explosives, and is used at DOE weapons laboratories to represent explosives in equipment testing. For this treatability demonstration a sample of non-radioactive mock HE was vitrified. Mock HE contains 24 wt% percent barium (as barium nitrate). The Mock HE is not suitable for land disposal without treatment because it is a strong

oxidizer and because of the barium content. Sandia has a stockpile of waste Mock HE that is also contaminated with Pico curie levels of H-3, Pb-214, Pb-212, Ra-224, Tl-208, Th-232, and Bi-214.

Table V. Mock HE Composition

Component	Wt. %
Pentaerythritol	48.0
Barium Nitrate	46.0
Tris (2-chloroethyl) Phosphate	3.2
Nitrocellulose	2.8

Waste Preparation

Sandia National Laboratories shipped 4.5 kg of Mock HE to AMEC for use in the treatability demonstration. The Mock HE was size-reduced to a consistency of coarse sand by Sandia prior to shipping to AMEC. AMEC mixed approximately 40.73 kg of soil with the entire batch of Mock HE resulting in a 10 wt% waste loading. Mixing was carried out in the 114-liter drum in which the mock HE was shipped, using an electric drum mixer. Thermometric monitoring of the mixture was performed during mixing to ensure that no adverse exothermic reactions occurred. The Mock HE as shipped and then mixed with soil is shown in Figure 6.

Fig. 6. Mock HE before (left) and after blending with soil (right).

Melting Operations

AMEC's ICV engineering-scale equipment consisting of a power supply, electrode feeder assemblies, ICV container and hood, associated piping, and off-gas filtration components, was used for the Sandia Mock HE demonstration. The ICV container used during this test is cylindrical; 3 feet high and 6 feet in diameter (Figure 7). An off-gas containment hood, 2-inch diameter exhaust piping, a high efficiency particulate (HEPA) filter and a single-phase 2.5 hp blower were installed on the treatment container in order to exhaust off-gas produced during the melting operations. The blended waste was loaded into this container and surrounded by a lining of refractory silica sand.

Fig. 7. Engineering-scale ICV test container

Nominal full power for this test was 15 kW. This equates to a power density (the applied power divided by the surface area of the melt) of approximately 161 kW/m^2, consistent with larger-scale ICV power densities, which are typically between 100-175 kW/m^2. A slight vacuum was applied to the treatment container and off-gas was drawn through a HEPA filter and exhausted to the environment. Figure 8 depicts the melt surface during operations. Visual observations of the off-gas outlet stack were performed in accordance with AMEC's air emissions permit. No visible plume was observed during the test. Emission samples collected with NO_2-specific colorimetric tubes indicated NO_2 concentrations in excess of 50 parts per million (ppm) during the course of the test. The test was concluded after approximately 8 hours. A total of 120 kWh of electrical energy was delivered to the melt during operations. Figure 8 depicts the melt surface during operations.

Fig. 8. Mock HE melt surface during operations.

Vitrified Waste Characterization

After allowing two days to cool, the vitrified monolith was removed from the ICV container for examination and sampling. Figure 9 depicts the vitrified block after it was removed from the ICV container, and then after it was broken open for sampling. Measurement of the block indicated approximately 50% volume reduction. A siliceous layer formed on the exterior of the block, which is typical of ICV melts when silica sand is used as a refractory lining adjacent to the melt (see previous discussion).

Fig. 9. The Sandia Mock HE vitrified block (left) and after it was fractured for sampling (right).

AMEC collected two samples of vitrified product for TCLP analytical testing. The analytical results indicated that leachate from these samples did not contain barium above the applicable Universal Treatment Standard (UTS) of 21 mg/L. In fact, barium was not detected above the laboratory reporting limit of 0.5 mg/L.

CONCLUSIONS

In 2004 and 2005, AMEC treated a variety of commercial and DOE mixed wastes using its GeoMelt ICV waste treatment technology. All of these projects resulted in waste forms that were suitable for land disposal. The successes of these projects reflect the flexibility and effectiveness of GeoMelt ICV in treating mixed wastes. The technology is suitable for treating liquid wastes as well as solids. Soil is used to provide glass formers that make up the superior leach-resistant matrix of the vitrified waste product of ICV. As in the case of the Rocky Flats DU mixed waste, contaminated soil often does not need amending prior to ICV processing. In the case of the TSCA mixed waste, soil and other inexpensive additives facilitate ICV processing and also results in a superior leach-resistant waste form. ICV is effective because it combines thermal treatment and immobilization. These dual treatment mechanisms result in the destruction of organic wastes and the retention of toxic metals and radionuclides in a geologically stable waste form.

REFERENCES

1. AMEC, 2000, *Destruction of Hexachlorobenzene Wastes with the GeoMelt Process, Final Report of Demonstration Trials,* Prepared for Orica Australia Pty. Limited and SHE Pacific Pty. Limited.
2. Geosafe Corporation, 1995, *TSCA Demonstration Test Performance Report,* Prepared for US EPA Office of Toxic Substances, Chemical Regulation Branch, PCB Disposal Section, May 1995.
3. AMEC, 2003, *Bulk Vitrification Project-Engineering-Scale ICV Test Results,* Prepared for CH2M HILL Hanford Group, August, 2003.
4. AMEC, 2003, *Bulk Vitrification Project-Large-Scale Bulk Vitrification Test Results*, Prepared for CH2M HILL Hanford Group, December, 2003.