IN-CONTAINER VITRIFICAITON OF CLASSIFIED MATERIAL

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ABSTRACT

The Waste Elimination Team teamed with the Nevada Test Site (NTS) and AMEC Energy & Environmental, Inc.-Geomelt Division to demonstrate the applicability of the In-Container Vitrification™ process to the desensitization of classified material. The subject material was came from Rocky Flats nuclear weapons research and production activities and is currently stored at NTS. AMEC conducted a drum-scale demonstration of the process on surrogate components made of graphite, stainless steel, and tool steel. The ICV process successfully destroyed the components opening a potential pathway for the treatment and disposal of the NTS classified material.

INTRODUCTION

The U.S. Department of Energy inherited many problematic materials and wastes from Cold War activities that require considerable thought and innovation before disposition pathways can be developed. The DOE's Waste Elimination Team was tasked with developing treatment and disposal paths for DOE's unique, difficult to solve waste problems. One of the problems brought to the team was finding a way to eliminate inventories of classified material that, if desensitized and treated to meet environmental regulations, could be disposed of. The classified material varies over a wide range of materials, radioactive and hazardous contaminants and configurations. In some cases the classification is based on the configuration of the component and in other cases the material of construction drives the classification. The WET needed a robust technology that could desensitize these components, while at the same time eliminating or stabilizing the contaminants. The WET teamed with the Nevada Test Site (NTS) and AMEC Earth & Environmental, Inc-GeoMelt to demonstrate the In Container Vitrification (ICV) process for the desensitization of classified material. This paper describes that demonstration and its results (AMEC 2003).

BACKGROUND

The WET served the DOE complex in an effort to treat and dispose of problematic and orphan wastes. The WET consisted of both DOE and contractor personnel from the DOE sites with mixed waste, combined with technical and regulatory experts from the Transuranic and Mixed Waste Focus Area. During the WET's short life, it attacked some of the worst mixed waste disposal problems, creating pathways for treatment that include both commercial and DOE capabilities. The WET met regularly to list the problems that the sites were having, and then, depending on available funding, created projects to attack similar, high-priority problems. One of the problems listed by several sites was how to dispose of radioactive classified material that had transuranic hazardous contaminants. Sites that have classified material include Rocky Flats, the Nevada Test Site, Lawrence Livermore National Laboratory, Pantex, and Y-12 in Oak Ridge.

Classified material cannot be disposed of without special controls until the material has been desensitized, eliminating the aspects of the material that required its classification. A federal judge had to declare Rocky Flats material waste, before it was eligible for disposal at the Waste Isolation Pilot Plant (WIPP). WIPP has been working on getting the safeguards in place to allow disposal of classified material there without desensitization. The Nevada Test Test site disposes of low-level classified material in a controlled cell, but cannot accept hazardous material there. The sites need a robust process that couples desensitization with treatment of hazardous constituents. Such a process would render the material suitable for disposal as non-radioactive, low-level, or transuranic waste, depending on the radioactivity present.

The WET initiated a project in fiscal year 2002 to demonstrate a robust technology that could make the classified material streams suitable for disposal. The WET first investigated a teaming effort with the Materials Recycling Center (MRC)at Oak Ridge to sort, segregate, decontaminate, and sanitize classified material contaminated with transuranic isotopes at greater than the transuranic waste concentration. The project would reduce the volume of material to be sent to WIPP, bringing major cost savings. The metals that could be sufficiently decontaminated would be recycled through the lead reuse program or converted to shield block. Low-level debris would be disposed at Envirocare, while the concentrated TRU stream will be prepared for WIPP disposal. Funding constraints forces the cancellation of this effort before it proceeded beyond planning stages.

The WET then focused on treatment of classified material from Pantex. Working with Pantex and the MRC, the WET prepared a request for proposal (RFP) (UT-Battelle) for a demonstration of a treatment process to address the Pantex material. The WET hosted a pre-bid meeting to discuss the type of technology and the criteria for successful treatment. Several vendors responded to the RFP with proposals, which were then evaluated by a selection team at Oak Ridge. Pantex reviewed the winning proposal and determined that there would be no substantial cost savings over the current process and that the technology proposed did not meet the requirements described at the pre-bid meeting. The bids associated with the other proposals that were more responsive in regard to the technology were well beyond the available funding. The Pantex work was stopped at that point.

The WET made a final attempt to demonstrate a process that could desensitize and stabilize contaminated classified material, this time teaming with NTS and AMEC. AMEC had been trying to establish a treatment facility at NTS. NTS and AMEC had been discussing treatment of several of the problematic NTS streams at that facility, including the classified material. NTS gladly accepted the WET's offer to conduct a demonstration of the ICV process and consented to assist in the preparations for it.

NTS Classified Material Description

The NTS classified material originated at Rocky Flats in the weapons production facilities. The drummed material was shipped to NTS for temporary storage, but had never been retrieved. The material has sufficient TRU contaminants to put it into the TRU waste category, if it could be considered waste. Stainless steel, tool steel, and graphite were selected as some of the most difficult to treat substances in the inventory. NTS requested that these three materials be used to make the surrogate components for the demonstration.

ICV Process

In-Container Vitrification is a technology developed by AMEC Earth and Environmental, Inc., GeoMelt Division, based on *in situ* vitrification (Buelt et al. 1987; Geosafe 1998; Spalding et al. 1992). In this technology, waste is mixed with soil and, if necessary, additional additives, and loaded into a refractory-lined metal container. The amount of soil added depends on the glass-forming characteristics of the waste and the soil. The treatment containers can vary in size and shape from 55-gal drums to large roll-off boxes. Graphite electrodes are positioned in the container before the waste is added. After the waste is charged, operators seal a gas collection hood onto the container. By maintaining a slightly negative pressure on the system, the hood funnels offgases to a treatment system that is designed to treat, through high-efficiency particulate filtration, chemical scrubbing and/or thermal processing, any hazardous residual material contained within the offgas.

Joule heating from electrical current passed through the electrodes melts the soil and metals in the waste, generating enough heat to oxidize or reduce the contaminants present, depending on the chemistry of the mixture and the additives present. When treatment is complete, the melt is allowed to solidify into a monolith in the container. After cooling, the monolith is sampled to verify that treatment objectives have been met. The solidified waste can then be removed from the container and the container reused. Alternatively, the container can be disposed after each melt. In this mode, after each batch of waste is treated, the vitrified waste solidifies, and the off-gas hood is removed, a lid is then placed on the container, readying it for transport to the disposal site.

The process requires the presence of certain alkali earth materials. These provide the cations necessary to support current flow through the melt. These too can be readily added to the waste if necessary. The amendments can also contain contaminants (e.g. – contaminated soils), further enhancing the throughput and efficiency of the process.

ICV DEMONSTRATION

Test Objectives

The demonstration agreed upon by the WET, NTS, and AMEC was a drum-scale surrogate test that would show that the process would desensitize material commonly found in the NTS waste by destroying objects that generally approximate the composition of classified materials. The test was designed and instrumented to facilitate characterization of operational aspects associated with ICV treatment of shapes composed of three different materials within a generic uncontaminated base soil. The materials were graphite, stainless steel, and tool steel. Verification of the final disposition of surrogate classified shapes and physical characterization of the resultant vitrified product were the primary post-test activities.

Surrogate Classified Shapes

Surrogate shapes used in the engineering-scale ICV test described in this report were machined from O1 tool steel, 304 stainless steel, and 0.250-in. grain electrode stock graphite. A total of six surrogate shapes, two of each material were processed. Each surrogate, regardless of material, was bowl-shaped. Neither the shape, nor the thickness of the surrogates were linked to actual components. However, treating the components successfully would give assurance that actual classified material could be treated.

ICV Demonstration Description

The soil for the test was obtained from the AMEC GeoMelt Horn Rapids Test Site (hereto after referred as HRTS soil) and combined with iron oxide in the form of powdered hematite ($Fe2O3$), at 20 percent by weight (wt-%). $Fe2O3$ was added in order to supplement the natural oxide content of HRTS soil to facilitate graphite destruction. Graphite oxidizes in the presence of oxygen, forming carbon monoxide

(CO) and carbon dioxide (CO2). Fe2O3, commonly used to color building materials and as a pigment in common paints, was chosen as an oxidizing agent because it is readily available and inexpensive. No other chemical amendments were used in preparation of the soil. Table 1 shows the natural oxide composition of HRTS soil. The total Fe2O3 content in the amended soil was 24.37 wt%.

Table 1 Major elemental oxide composition of HRTS soil.

Oxide Compound	**Mass Fraction**
Al2O3	13.96
CaO	5.50
Fe2O3	9.28
K2O	2.48
MgO	1.43
Na2O	3.31
P2O5	0.29
SiO2	62.42
TiO2	1.43

A slip form was used to ensure that the treatment zone was centrally positioned inside the ICV container and to separate the treatment zone from refractory materials during staging. Sixteen Type K thermocouples and one Type C thermocouple were verified operational and then staged in and around the target treatment zone to provide indication of the extent and progression of ICV processing. Type K thermocouples are used to monitor melt development and Type C thermocouples are used to determine melt temperature. Thermal failure of Type K thermocouples is used to monitor the progression of the melt as it develops. Type C thermocouples are staged into ICV melts in an attempt to measure true melt temperatures Each electrode was marked with painted lines at 1-inch intervals along its length to provide indication of their depth of insertion into the developing melt during processing. Tracking of electrode position combined with thermocouple burnout events allows for accurate monitoring of melt development during ICV operations.

After thermocouple staging, Fe2O3-ammended HRTS soil was added to the treatment zone inside the slip form. Steel, tool steel, and graphite shapes were staged at various locations within the treatment zone as soil was added. These locations were staggered, with the tool and stainless steel shapes located from 6 to 11 inches beneath a conductive starter path, and the graphite shapes located between 3 and 6 inches below the starter path. The one-inch starter path was placed directly above the treatment zone and covered with an additional inch of HRTS soil. The starter path was composed of a volumetric ratio of 1:2 HRTS soil to graphite flake. A total of approximately 108 kg of soil, Fe2O3, shapes, and starter path were staged in the treatment zone.

Operators gradually ramped-up in power during the first seven hours of testing until the target full power level of 20 kW (10 kW per phase) was achieved, after which that full power level was maintained for the duration of the test. The electrodes were allowed to gravity feed into the developing melt. Data obtained from thermocouples staged beside and below the treatment zone indicate that the entire treatment zone volume was molten by approximately 11 hours of operation. The test was continued for several hours after the melt had developed to its full extent within the confining refractory sand in order to sustain high-temperature, oxidative conditions conducive to graphite destruction.

The off-gas exhaust system was turned on shortly after initiation of ICV operations and was run until final termination of power to the melt. Hood vacuum was maintained consistently 1.2 inches of water throughout the duration of the test.

The electrodes were staged 4 inches below ICV container surface grade, leaving 12 inches of downward vertical migration to reach the base of the treatment zone. The electrodes were held in their initial position for approximately two hours, after which time they were released using pneumatic actuators located on the electrode feeder assembly. The electrodes were noted to begin their downward migration into the melt after approximately 4 hours of operation. All electrodes reached the base of the treatment zone after approximately 8 hours of ICV processing.

The 3-inch diameter graphite electrodes experienced significant oxidation as melting operations ensued. Electrode oxidation and necking is commonly experienced as a normal course of ICV processing. In the eventuality of a physical failure of an electrode, additional sections are simply threaded onto the top of the electrode and the entire electrode assembly lowered into the melt.

RESULTS

The melt was allowed to cool for a day, and then was removed from the ICV container for visual inspection. The volume reduction characteristic of ICV processing was evident from the location of the upper surface of the block relative to the test container rim. The level of the melt had subsided approximately 6 inches, incorporating lateral and lower refractory sand as a whitish, durable glassy rind. The block and cold cap glass were weighed, totaling 145 kg. This mass, combined with the 408 kWh consumed in during ICV operations, resulted in a specific energy consumption of 2.82 kWh/kg for this test.

The vitrified block and ancillary cold cap was sectioned for examination and characterization of post-test surrogate classified shape disposition. AMEC technical staff performed the examination with the assistance of NTS personnel. The block was dense and homogeneous. The entire block was reduced to pieces generally smaller than 1 inch in diameter. Metallic material was observed at the base of the block, appearing as balls ranging from 0.25 to 40 mm in diameter. Also, several larger amorphous lumps were observed. Most, but not all, of the visible metal was strongly magnetic. The total mass of the larger pieces of metal recovered from the melt was approximately 500 grams, well less than the mass of the steel shapes processed. The metal from the tool steel and stainless steel shapes, and from the reduction of the Fe by the $Fe2O3$-carbon reaction, appeared to be dispersed in an unquantifiable number of small droplets distributed throughout the block and concentrated at the bottom of the vitrified block.

Visual observation of the vitrified product during sectioning indicated the complete destruction of the graphite surrogate classified shapes. The only graphite discovered in the block was remnant electrode sections, which were easily identified due to their relative location within the melt and their cylindrical configuration. There were no visible remains of graphite surrogate classified shapes within the block or cold cap. In fact, the melt environment was so corrosive to graphite that, at the end of the test, only a minimal length of each of the four electrodes remained. Typically, the electrodes are fed down to the base of the melt, which was the case during this test; however, the $Fe2O3$ redox reaction proved to be very effective in consuming not only the surrogate shapes, but also a significant portion of the electrodes.

CONCLUSIONS

Based on the complete physical examination of the vitrified product, including the cold cap and the main block, the tool steel, stainless steel, and graphite surrogate classified shapes were destroyed beyond recognition and possible reconstruction by ICV processing. The metallic shapes were destroyed by melting, which resulted in droplets and agglomerations of various sizes dispersed throughout the block and at the base of the melt. The graphite shapes were completely destroyed by oxidation, proving Fe2O3 to be a suitable amendment to the process soil the treatment of graphite.

The successful destruction of the surrogate components demonstrated in part the applicability of the ICV process to the NTS TRU-contaminated classified material. Questions still remain regarding the partitioning of the transuranics in the melt, the control of radioactive offgas, and the leachability of RCRA metals from amorphous lumps that form at the bottom of the melt. If the treated material is going to WIPP, the leachability of RCRA regulated constituents is not a concern. However, if this treatment decreases the TRU concentration to a point where disposal at WIPP is not required, that leachability must be addressed before the waste can be disposed. In terms of the objectives of this demonstration, though, the ICV process was successful in destroying the surrogate components to an extent that the process' applicability for desensitization of the NTS components was fully proven.

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