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R.F. Schumacher, A.L. Kielpinski, D.F. Bickford, A. Applewhite-Ramsey, C.A. Cicero, T.L. Spatz, and J.C. Marra

Westinghouse Savannah River Co.
Savannah River Technology Center,
Aiken, SC 29808

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R. F. Schumacher 2/95
Author's Signature

M. John Plodinec
Derivative Classifier's Signature

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ABSTRACT

The U.S. Department of Energy (DOE) weapons complex has numerous radioactive waste streams which cannot be easily treated with joule-heated vitrification systems. However, it appears these streams could be treated with certain robust, high-temperature, melter technologies. These technologies are based on the use of plasma torch, graphite arc, and induction heating sources. The Savannah River Technology Center (SRTC), with financial support from the Department of Energy, Office of Technology Development (OTD) and in conjunction with the sites within the DOE weapons complex, has been investigating high-temperature vitrification technologies for several years. This program has been a cooperative effort between a number of nearby Universities, specific sites within the DOE complex, commercial equipment suppliers and the All-Russian Research Institute of Chemical Technology. These robust vitrification systems appear to have advantages for the waste streams containing inorganic materials in combination with significant quantities of metals, organics, salts, or high temperature materials. Several high-temperature technologies were selected and will be evaluated and employed to develop supporting technology. A general overview of the SRTC "High-Temperature Program" will be provided.

BACKGROUND

From the beginning of World War II, the various sites within the present DOE weapons complex, including the Savannah River Site (SRS), have been involved with the production of special nuclear materials for military and other purposes. The pursuit of these missions has resulted in the accumulation of a wide range of radioactive wastes which require disposal. The waste streams include high-level wastes (HLW) from the separations of the special nuclear materials, common materials contaminated with transuranics (TRU), and low-level radioactive wastes (LLW). A portion of these waste streams can also contain hazardous or reactive materials. These waste streams are referred to as "mixed" waste and may be either HLW, TRU, or LLW. Investigations by the Environmental Protection Agency have concluded that vitrification is the "Best Demonstrated Available Technology" (BDAT) for immobilizing high-level radioactive waste.[1] In the light of the present trends within the United States toward stronger environmental regulations, it has become more apparent that vitrification may also be the most appropriate means of treating other types of radioactive waste streams.

At SRS the HLW is stored either in a slurry form or as a partially dry salt cake in steel tanks at the Tank Farm. This waste will be pretreated in the Tank Farm. At the Defense Waste Processing Facility (DWPF) individual HLW streams will be mixed with commercial glass frit and melted or vitrified in a specially designed, Joule-heated electric melter. The melted mixtures are then poured directly into stainless steel canisters and temporarily stored at SRS. The DWPF will begin radioactive operation in 1996 after 15 years of extensive process research and development.[2]

There are many other waste streams at SRS and around the DOE weapons complex which could require extensive processing or pre treatment prior to disposal and which are not compatible with the DWPF vitrification process. The use of vitrification technologies other than Joule heating have been thoroughly discussed.[3] These vitrification systems include Joule heated, In-Situ Joule heated, Plasma heating, Microwave heating, Induction heating, Resistance heating, Electric Arc heating, and Incineration with fossil fuels.

Under the DOE program for buried waste at Idaho National Engineering Laboratory (INEL), INEL concluded that certain robust high-temperature processes should be the most adaptable to their buried waste. The retrieved buried waste would contain a portion of the local basaltic soil, the steel drum, and the radioactive heterogeneous waste. After employing a "systems" approach to narrow the number of vitrification technologies, it was reasonably well established that some type of plasma arc or graphite arc melting of these mixtures was acceptable for producing an iron enriched basaltic glass-ceramic material.[4] Recent efforts at INEL demonstrated that although the feed composition could not be tightly controlled, the resulting glass-ceramic durability was as good as the HLW glass limit. [5]

The DOE-OTD also initiated a large effort toward the treatment of mixed low-level waste (MLLW) and concluded that approximately 75% of the MLLW streams could be treated by Joule heating and plasma vitrification.[6] This assumption along with the vast amount of data from the HLW program and the buried waste program provided an excellent basis for the selection of high-temperature vitrification systems for many of the mixed waste streams.[7] In addition, the robust technologies reduced the requirement to thoroughly characterize the waste as was required for the Joule-heated process.

Based on these previous DOE programs, the Savannah River Technology Center at SRS set a course toward technology development and the eventual high-temperature melter selection for the site. The following will provide an over-view of this program.

HIGH-TEMPERATURE PROGRAM

The high-temperature program was divided into two portions. One portion was the acquisition of experimental equipment based partially on findings from the Buried Waste and Mixed Waste Programs and partially on the extensive experience of SRTC scientists. The remaining portion of the funding was aimed at developing control technologies to support the high-temperature vitrification and some initial scoping trials using existing equipment which was available within nearby Universities.

Scoping Trials

A series of "scoping trials" were conducted at the Georgia Institute of Technology, Plasma Applications Research Facility (PARF), in Atlanta, Georgia.[8] The heating system employed was a 100 KVA, non-transferred plasma torch built by Plasma Energy Corp, a fixed graphite crucible melting chamber, and a wet scrubber off-gas system. The chamber was preheated prior to feeding and the feed materials were placed in cardboard tubes for feeding through a sealed plunger chamber. The general observations obtained for each of the waste streams are summarized:

- *Southeastern United States Soil*

Vitrification of the very refractory southeastern soils (high silica) require very high temperatures or the addition of flux materials. These soils would be obtained from spill sites or from seepage basins at SRS. Vitrification with the plasma torch required the addition of lime or other flux materials. A significant portion of the fine powder was entrained in the off-gas.

- *Crushed Electronic Circuit Boards*

Crushed surplus electronic circuit boards are an extremely difficult waste stream to vitrify. The waste contains many different types of metal, ceramic, glass and highly aromatic organic resins. The trial with the torch produced a non-homogeneous metallic portion in the bottom of the crucible and a semi-vitreous portion at the top. Some of the metallic and glassy phase was remelted in an induction unit at SRTC to homogenize the materials. This second stage melting was quite helpful in producing two homogeneous waste forms (metal-glass).

- *Tyvek™ Filter Paper with attached filtrate*

The Tyvek filter paper was composed of polypropylene fiber and a small amount of simulated M-area sludge. This is a waste stream obtained from water purification in the fuel element fabrication area of SRS. While the volume was reduced dramatically a great deal of solid material was captured in the scrubber off-gas system. This resulted in a good deal of secondary waste.

- *High Efficiency Particulate Air Filters (HEPA)*

HEPA filters are widely used at SRS and other sites for the removal of sub-micron particulate from off-gas systems. The filters are constructed of stainless steel or wood frames, glass fiber filter material, some organic materials and trapped radioactive particles. This waste stream was well suited for volume reduction and destruction in the plasma furnace.

- *Heterogeneous Debris Waste*

A surrogate composite waste representative of the standard Mixed Waste Integrated Program (MWIP) "Heterogeneous Debris" recipe [9] was prepared and vitrified. This recipe contained various common ingredients (e.g. charcoal, PVC, glass, metal, etc.) as well as RCRA metals and radioactive surrogates.

The plasma provided a very intense high temperature flame but the temperature fell quite rapidly with distance from the flame. The thermal energy of the plasma torch destroyed the organics and reduced the volume of the metals and inorganics.

Due to funding limitations only a few chemical analyses or evaluations of the waste forms were performed. However, a number of general conclusions were drawn from these preliminary scoping trials. Overall the plasma torch system showed great promise. In all cases the torch effectively destroyed the original waste and generated a fused, reduced volume waste form plus residuals. Some type of controlled mechanical metering system for the waste steam would be required. In the absence of three dimensional movement of the torch the plasma system would require an additional controlled secondary heat source to homogenize the glass and metal phases. It is believed from a thermodynamic and practical basis that many of the radioactive contaminants would migrate to the glass phase. Because of this concentration effect, the metal phase could possibly be disposed of as a low level waste or reclaimed for limited uses. e.g. radioactive shielding or radioactive containers. The ability to separate the glass stream from the metal stream would be an advantage. Any high-temperature system would require a robust off-gas system and off-gas monitoring capability. When the waste stream contained a large fraction of organic materials, such as the Tyvek material, the limits of a marginal off-gas system were exceeded.

Table 1

Recipe for Heterogeneous Debris Briquettes	
Water	20.0wt%
Starch	7.5
Activated Carbon	4.5
Pecan Shell Flour	10.0
PVC Granules	10.0
Iron Powder	10.0
Glass Beads (SLS)	10.0
Portland Cement	4.0
Alumina	7.25
Aluminum Powder	1.5
Silica Sand	4.0
Pearlite (Harborlite)	10.0
Total	98.75
RCRA Metals	
Cadmium Chloride	0.23
Lead Chloride	0.23
Chromic Chloride	0.23
Nickel Chloride	0.23
Total	0.92
Radionuclide Surrogates	
Cesium Chloride	0.23
Cerium Chloride	0.12
Total	0.35
Total	100.02

* Developed by Georgia Tech Research Institute R.A. Newsom,(404-894-8047) and K.R. Komarek Briquetting Research Inc., Anniston, AL

As a portion of the effort at the Georgia Institute of Technology, approximately 5,000 lbs. of compacted briquettes were produced based on the formula for the MWIP Heterogeneous Debris recipe.[9] The actual briquette recipe is shown in Table 1. These briquettes will be used as a standard material to characterize different melters and for certain other specific tests. Briquetting is one of the few mechanisms capable of providing essentially homogeneous debris type feed to a melter.

Several additional scoping trials were conducted at the Mississippi State University Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Starkville, Mississippi. A nominal 250 KVA Torch, supplied by Plasma Energy Corporation was used. The torch was attached to the melt chamber by a gimbals mount to allow for complete x, y, z mobility.

- *Southeastern United States Soils*

A series of studies were performed with soil from the SRS. The nominal composition of the soil is 55% sand, 30% kaolinite clay and 15% silt [10]. Limestone was added to the soil at 11%. The addition was made as a well mixed feed and as an unmixed addition in the melter For the localized addition, the torch was manually manipulated in the x and y plane to enhance mixing. The mixed material, of course, formed a more homogeneous waste form. The unmixed addition did not produce a homogeneous product. The Product Consistency Test[11] was performed on several samples and indicated that the glasses formed were significantly more durable than the Environmental Assessment[12] (EA) glass as measured by the silica release. The EA glass is used as a benchmark glass for the HLW glass program.

- *Refractory Trials*

A series of refractory material trials were also conducted at the DIAL facility. It was known from work at SRTC, that the glass/metal melts and off-gas products could be very corrosive at the very high temperatures encountered in these systems. Corrosion testing of numerous different refractory materials was performed in the plasma vitrification system using the surrogate heterogeneous debris briquettes described previously.

Corrosion coupon testing at SRTC on typical materials used in Joule heated melters was completed with glass compositions with high salt contents. The presence of chloride in the melts caused the most severe attack and the rate of corrosion increased with increasing temperature.[13] In the metal alloys, oxidation was the predominant corrosion mechanism, while in the refractory materials, enhanced dissolution of the refractory into the glass was observed.

The heterogeneous debris waste is very likely the most challenging waste stream to be treated due to its varied composition. A total of 33 different refractory materials were identified and obtained from refractory manufacturers for testing.[14] The refractory materials are presented in Table 2. Initially a thermal cycling evaluation was employed to evaluate thermal shock resistance. The different test materials were placed in the graphite crucible.

After several hours most of the samples had fallen into the melt and, upon examination of the intact samples, were severely corroded at the melt line and were covered by deposited salts. The aluminum nitride, high chromium fused cast refractory, and one silicon nitride material appeared to perform the best in this trial. The high surface area samples, e.g. fiber boards and castables, were completely consumed during the tests. Other oxide, carbide, and fused cast refractories showed evidence of thermal shock. Corrosion of samples in the vapor space was relatively insignificant in comparison to the melt line corrosion.

Table 2
Candidate Materials for Waste Vitrification Systems

Ceramics	Identification
Oxides	Alumina - high purity, fiber board
Carbides	Silicon carbide - hot pressed, sintered
Nitrides	Silicon nitride - reaction bonded, sintered
	Aluminum nitride - varying additive levels
	Boron nitride - pyrolytic, hot pressed
	Sialon
Borides	Titanium diboride - sintered
Graphite	Pyrolytic graphite
Fused-cast Refractories	Magnesia - alumina
	Very high chromium-alumina
	High chromium-alumina
Composites	Aluminum nitride + silicon carbide whiskers
	Zirconia + alumina
	Boron Nitride + titanium diboride

Based on the results of the cycling test, only the best performing materials were exposed in the continuous operation test. Three aluminum nitride samples, three fused cast refractory samples and one reaction bonded silicon nitride sample were installed in the graphite crucible. After the four hour test only the high chromium refractory and the aluminum nitride sample with 0.25 wt% Yttria additive remained intact. Based on these observations it was suggested that either a very large chamber or a cold wall process might be required.

After these refractory evaluations it was concluded that the use of refractories to contain the heterogeneous wastes in a plasma process would be difficult. Very high quality refractories, large diameter melt chambers or extensive water cooling would be required to insure refractory survival over any extended period of time.

Acquisition of Melter Vitrification Systems

DC Graphite Arc Melting System

The electric arc furnace was first developed for the metals industry and often employs three graphite electrodes and three phase AC power. Electro-Pyrolysis Inc.(EPI), the Massachusetts Institute of Technology (MIT), and Pacific Northwest Laboratory (PNL), developed a DC, single graphite electrode, arc melting system under the buried waste program which showed promise for the vitrification of buried waste drums.

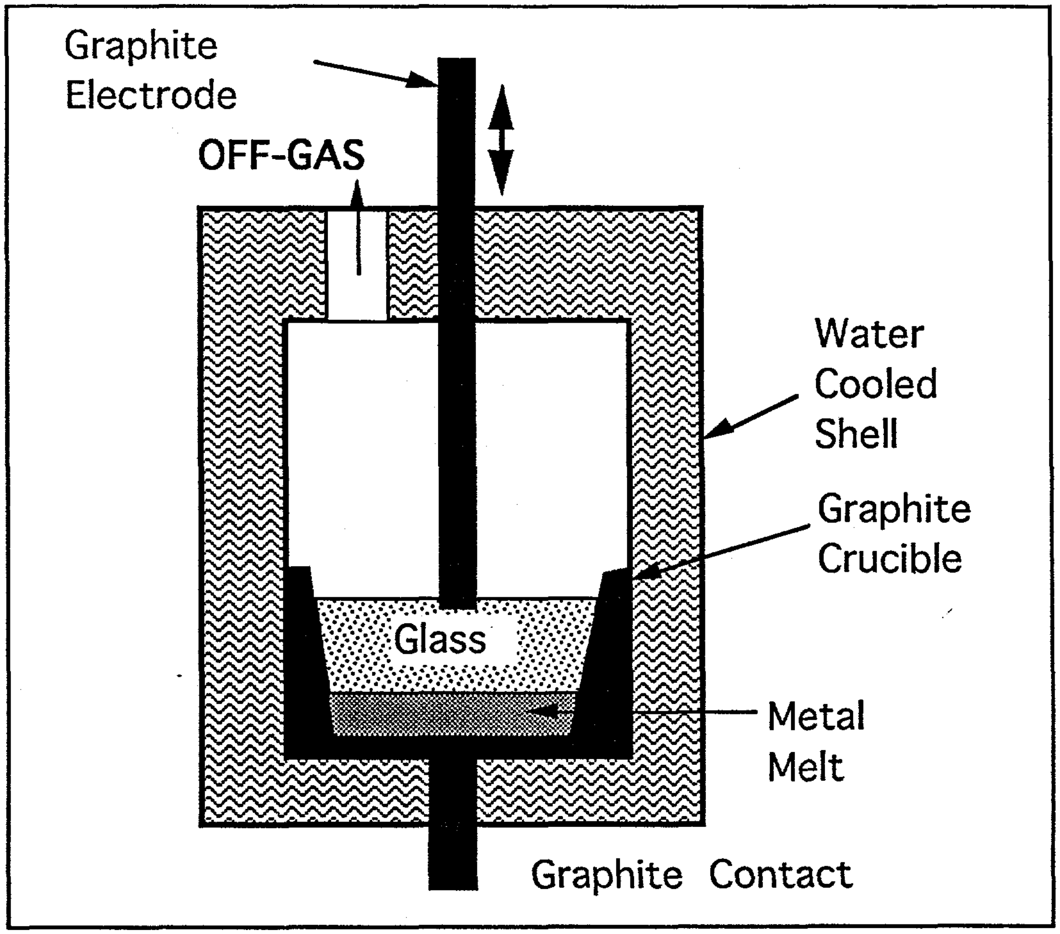

Figure 1 Electro-Pyrolysis Inc. DC Graphite Arc Melter

A small engineering scale unit was purchased under the SRS Special Vendor Solicitation program from EPI and installed at the Clemson DOE /Industrial Center for Vitrification Research. This unit is represented in Figure 1. This system will be used as a test-bed for trials on waste streams, testing off-gas systems, and developing improvements for the DC arc melting technology. A Cooperative Research and Development Agreement between EPI and SRTC is being considered at this time. This EPI unit has the following advantages :

- Single Electrode
- Clean Utility Load
- Ease of Power Control
- Lower Refractory Wear than an AC System
- Higher Energy Transfer Efficiency than Plasma Torch or Induction

Initial trials at Clemson have been performed largely with the Southeastern United States soils with flux additions of lime and soda. A very homogeneous melt was prepared using these additions. The sealed unit was operated under inert nitrogen atmosphere.

A similar, but unique two graphite electrode DC arc system is presently being fabricated by INEL and will be shipped to SRTC for insertion in a radioactive glove box. This unit will be capable of performing radioactive partitioning tests and off-gas studies which are crucial to demonstrating radioactive operation.

Hybrid Plasma-Induction Cold Crucible Melting System

During 1994, D.F. Bickford traveled to Russia as part of a cooperative program between the DOE and the Russian Ministry of Atomic Energy. During the visit he evaluated a demonstration unit in Moscow and determined that it may be the very suitable technology for treating SRS transuranic waste. A combination of plasma heating with induction heating of metal in a cold wall crucible was available. This system had been developed in Russia in the middle 70's and was used for producing chemically active high-purity metals such as zirconium, titanium, uranium, and rare-earth metals alloys. A cooperative program between SRTC and the All-Russian Institute of Chemical Technology is underway at this time. A simple schematic of this system is presented as Figure 2.

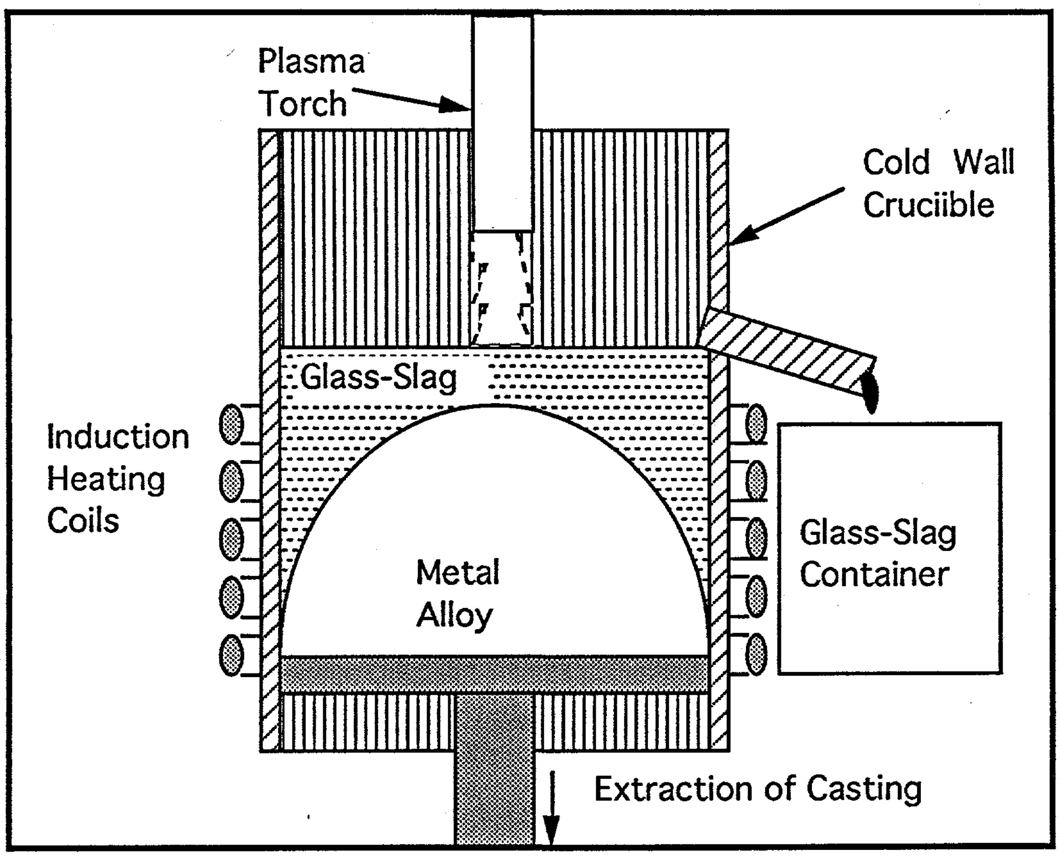

Figure 2. Hybrid Plasma/Induction Cold Crucible Melting System

The cold crucible technology partially resolves the previously discussed problem of developing refractories that can survive in both the metallurgical and the glass evnvironments found in many high temperature heterogeneous debris melter systems. This solution is obtained at the expense of low-efficiency of energy transfer via electromagnetic field generation to the metallic portion of the melt. Energy concerns are not primary concerns when considering radiological safety. The cold crucible design has been shown to survive for five or more years with a minimum of repair. The electromagnetic fields create intense stirring within the metal portion of the melt. This stirring produces a homogeneous metal melt and transfers heat to the bottom of the glass melt. The metal melt is water cooled at the sides and bottom and this permits continuous casting of solid metal from the bottom by lowering the bottom plate. It is believed that most of the radioactive impurities will be concentrated in the vitreous phase and the metal ingot can be recycled or disposed of as low level waste. The plasma torch inserted in the top of the melter furnace supplies sufficient energy to maintain the molten state of the glass phase and to enhance the glass discharge.

This furnace is presently being fabricated in Russia and will be shipped to the United States early in 1996. It is presently estimated that six months will be required to set up and test out this unit.

Path Forward

All efforts within this program will be aimed at supporting the high temperature vitrification efforts under the INEL Mixed Waste and the SRS Landfill Stabilization Focus Areas.

The EPI graphite arc system at Clemson will be entering a formal test evaluation program in FY96 to characterize the melter system. Future trials will include SRS soil mixtures, heterogeneous debris and other simulated waste streams. If the CRADA is established, equipment modifications, mathematical modeling of the unit, and additional simulated waste stream demonstrations will be initiated.

Upon the arrival at SRS of the small DC arc melter from INEL, the system will be installed in a suitable glove box and various treatability studies initiated. A major portion of these studies will concentrate on the partitioning of the radionuclides.

After the hybrid induction/plasma melter system is installed and evaluated, consideration will be given to obtaining a full size unit for actual mixed waste treatability studies at SRS.

Additional efforts will be aimed at advanced computer methods of controlling the high-temperature vitrification product and systems.

ACKNOWLEDGMENTS

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