SAVANNAH RIVER SITE WASTE VITRIFICATION PROJECTS
INITIATED THROUGHOUT THE UNITED STATES: DISPOSAL AND RECYCLE OPTIONS

by

Carol M. Jantzen, Dennis F. Bickford, Kevin G. Brown, Alex D. Cozzi, Connie C. Herman, James C. Marra, David K. Peeler, John B. Pickett, Ray F. Schumacher, Mike E. Smith, John C. Whitehouse, and Jack R. Zamecnik
Westinghouse Savannah River Co.
Aiken, SC 29808

A paper proposed for publication in the Citizens for Nuclear Technology Awareness “Celebrating 50 Years of Excellence in Science and Engineering at the Savannah River Site”
May 17, 2000

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.
SAVANNAH RIVER SITE WASTE VITRIFICATION PROJECTS
INITIATED THROUGHOUT THE UNITED STATES: DISPOSAL AND RECYCLE OPTIONS

Carol M. Jantzen, Dennis F. Bickford, Kevin G. Brown, Alex D. Cozzi, Connie C. Herman, James C. Marra, David K. Peele, John B. Pickett, Ray F. Schumacher, Mike E. Smith, John C. Whitehouse, and Jack R. Zamecnik
Westinghouse Savannah River Co.
Aiken, South Carolina 29803

ABSTRACT

A vitrification process was developed and successfully implemented by the US Department of Energy’s (DOE) Savannah River Site (SRS)\(^1\) and at the West Valley Nuclear Services (WVNS) to convert high-level liquid nuclear wastes (HLLW) to a solid borosilicate glass for safe long term geologic disposal. Over the last decade, SRS has successfully completed two additional vitrification projects to safely dispose of mixed\(^2\) low level wastes (MLLW) (radioactive and hazardous) at the SRS and at the Oak Ridge Reservation (ORR). The SRS, in conjunction with other laboratories, has also demonstrated that vitrification can be used to dispose of a wide variety of MLLW and low-level wastes (LLW) at the SRS, at ORR, at the Los Alamos National Laboratory (LANL), at Rocky Flats (RF), at the Fernald Environmental Management Project (FEMP), and at the Hanford Waste Vitrification Project (HWVP). The SRS, in conjunction with the Electric Power Research Institute and the National Atomic Energy Commission of Argentina (CNEA), have demonstrated that vitrification can also be used to safely dispose of ion-exchange (IEX) resins and sludges from commercial nuclear reactors. In addition, the SRS has successfully demonstrated that numerous wastes declared hazardous by the U.S. Environmental Protection Agency (EPA) can be vitrified, e.g. mining industry wastes, contaminated harbor sludges, asbestos containing material (ACM), Pb-paint on army tanks and bridges. Once these EPA hazardous wastes are vitrified, the waste glass is rendered non-hazardous allowing these materials to be recycled as glassphalt (glass impregnated asphalt for roads and runways), roofing shingles, glasscrete (glass used as aggregate in concrete), or other uses. Glass is also being used as a medium to transport SRS americium (Am) and curium (Cm) to the Oak Ridge Reservation (ORR) for recycle in the ORR medical source program and use in smoke detectors at an estimated value of $1.5 billion to the general public.

THE GLOBAL MATERIALS CYCLE

Raw materials taken from the earth to produce a wide variety of products and processes must be disposed of safely back into the earth once declared a waste (Figure 1). The only other option is remediation for recycle into new products or new end uses. Technologies have been developed by the US Department of Energy’s (DOE) Westinghouse Savannah River Technology Center (SRTC) to convert a wide variety of hazardous and/or radioactive wastes to a solid stabilized glass via the process of vitrification. The vitrification technology has been shown to render hazardous wastes to be non-hazardous and/or convert non-hazardous sludges, asbestos, etc. into recyclable products or reusable raw materials.

\(^1\) The history of the development of the vitrification of HLLW at the SRS is the subject of another section of this proceedings [1]. To date over 3 million pounds of HLLW waste glass have been produced in the SRS Defense Waste Processing Facility (DWPF).

\(^2\) Wastes that are both hazardous under the Environmental Protection Agency (EPA) Resource, Energy and Recovery Act (RCRA) and radioactive, e.g. governed by the Atomic Energy Act (AEA).
Figure 1. The global materials cycle.

If a waste cannot be recycled due to its radioactive content then it must be safely disposed of back into the earth (Figure 1). Stabilizing such wastes into glass by fusing the waste with glass forming oxides (\(\text{SiO}_2\), \(\text{Na}_2\text{O}\), \(\text{B}_2\text{O}_3\)) at elevated temperatures in an electric melter\(^3\) atomistically bonds the hazardous and/or radioactive species in the solid glassy matrix ensuring safe disposal for thousands (\(10^6\)) years. In addition, large volume reductions (up to 97%) allow for large associated cost savings for such wastes during interim storage, shipping, and/or long term permanent disposal.

**WHAT KIND OF WASTES CAN BE VITRIFIED?**

Development of “cradle-to-grave” vitrification processes have been investigated and initiated by SRTC for a wide variety of wastes, which include, but are not limited to, the following:

- spent filter aids from waste water treatment
- waste sludges and/or liquid supernates including EPA hazardous sludges from harbors
- mining industry wastes, sludges, and/or mill tailings
- incinerator ash, incinerator off-gas blowdown, or combinations of the two
- lead paint
- cement formulations in need of remediation
- ion exchange resins and zeolites
- soils, geologic material/media including Naturally Occurring Radioactive Material (NORM)
- asbestos containing material (ACM) or inorganic fiber filter media

\(^3\) Joule heated or induction heated melters. Joule-heated melters vitrify waste in a refractory-lined vessel containing diametrically opposed electrodes. The electrodes are used to heat the glass by passing an electric current through the material. The process is called Joule heating.
- radioactive materials including Transuranic (TRU), plutonium (Pu), and other actinide wastes, e.g. Am and Cm

Mixed low level waste (MLLW)\(^4\) in any of the above categories must meet the regulatory requirements imposed on hazardous waste by the EPA Resource Conservation and Recovery Act (RCRA) and the regulatory requirements imposed on radioactive materials governed by the US Department of Energy (DOE) orders or Atomic Energy Act (AEA) regulations. Untreated wastes that Fail the U.S. Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP) for any of the inorganic species listed in Table I (Column A) or any organic species listed in the Resource Conservation and Recovery Act are considered characteristically hazardous.\(^3\) Prior to May 28, 1998 characteristically hazardous wastes could be treated so that they would meet the TCLP leachate levels given in Column A. The U.S. EPA promulgated a regulation on May 28, 1998 that characteristically hazardous wastes must be treated to the Universal Treatment Standards (UTS)\(^5\) shown in Table I (Column B). The final vitrified glass must not release any of the species listed in Table I above the limits given in Column B whether the waste is non-radioactive or radioactive.

The need to provide MLLW treatment has been driven by the RCRA Land Disposal Restrictions (LDR) that require the treatment of the existing MLLW stockpiles. As of 1992 the MLLW waste volumes were ~250,000 m\(^3\) and projected to increase to 1,200,000 m\(^3\) by 1997 [2]. A schedule for DOE to come into compliance with RCRA was mandated by the passage of the Federal Facilities Compliance Act (FFCAct) of 1992. Large volumes of MLLW must, therefore, be converted to a solid stabilized waste form for permanent disposal. Since vitrification vaporizes EPA hazardous organics into CO\(_2\) and H\(_2\)O, the final waste form quality is assessed using the EPA Toxic Characteristic Leaching Procedure (TCLP) for the inorganic hazardous species listed in Table I.

Seventy six percent of the existing mixed wastes in the DOE complex are candidates for electric and/or Joule heated vitrification [2]. Several RCRA listed MLLW wastewater sludges at SRS [3-5] and ORR [6] were identified as the first candidates for demonstration of Joule heated vitrification. Several radioactive simulated RCRA wastes have also been shown to be candidates for vitrification and include incinerator ash and blowdown from SRS [3,7], waste sludge from Rocky Flats admixed with Portland cement, sludge from Los Alamos National Laboratory, and mill tailings from the Fernald Environmental Management Project (FEMP) K-65 site. Non-radioactive RCRA wastes made successfully into glass include waste water treated sludges from mining operations in Colorado, Pb paint from the Triborough bridge in New York City, and New York City harbor sludge. All of these were rendered non-hazardous by the vitrification treatment and the waste product could be recycled rather than disposed of. Vitrification studies of non-RCRA wastes have also been initiated by SRS. These include both non-contaminated ("clean") as well as radioactively contaminated asbestos containing material (ACM) from the DOE complex [9-10], some ion-exchange resins from commercial and government nuclear reactors [8], recycle of SRS americium and curium wastes to ORR for medical applications [11-19], and vitrification of weapons grade and scrap plutonium [11-12] from the DOE complex.

---

\(^4\) waste that contains source, special nuclear, or byproduct material subject to regulation under the Atomic Energy Act and hazardous waste species subject to regulation under the Resource Conservation and Recovery Act waste as defined in 40 CFR 261 (U.S. Code Title 42, Section 2011)

\(^5\) Federal Register, V.63, #100, p.28748-9.
Table I
Environmental Protection Agency Concentration Limits for Inorganic Constituents of Hazardous Wastes

<table>
<thead>
<tr>
<th>RCRA Inorganic Species</th>
<th>Column A Characteristically Hazardous Limits (TCLP; mg/L)</th>
<th>Column B Universal Treatment Standards (UTS) Limits (TCLP; mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5.0</td>
<td>0.14</td>
</tr>
<tr>
<td>As</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Ba</td>
<td>100.0</td>
<td>21</td>
</tr>
<tr>
<td>Be</td>
<td>-</td>
<td>1.22</td>
</tr>
<tr>
<td>Cd</td>
<td>1.0</td>
<td>0.11</td>
</tr>
<tr>
<td>Cr</td>
<td>5.0</td>
<td>0.60</td>
</tr>
<tr>
<td>Pb</td>
<td>5.0</td>
<td>0.75</td>
</tr>
<tr>
<td>Hg</td>
<td>0.2</td>
<td>0.025</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>1.15</td>
</tr>
<tr>
<td>Se</td>
<td>1.0</td>
<td>5.7†</td>
</tr>
<tr>
<td>Tl</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>V**</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>Zn**</td>
<td>-</td>
<td>4.3</td>
</tr>
</tbody>
</table>

** not underlying hazardous constituents
† Se must be treated to the characteristic limit (1.0 mg/L) to be non-hazardous, although it may be land disposed as a hazardous waste if <5.7 mg/L TCLP

WHY VITRIFY?

Vitrification of radioactive and/or hazardous wastes into glass is an attractive option because it atomistically bonds the hazardous and radioactive species in a solid glassy matrix. The waste forms produced are, therefore, very durable and environmentally stable over long time duration. The Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste [20] and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste [21].

Vitrification processes are flexible to process chemistry variations and can accommodate dry or wet wastes, e.g. the process is very robust. Vitrification is an ancient, well established, and well studied technology used in many commercial applications. A new generation of high throughput Joule heated melters, available from the commercial glass industry, allow for rapid vitrification of large volumes of waste. These vitrification systems are compact enough to be transportable, e.g. the SRS Transportable Vitrification System (TVS) [22-23] (Figure 2). This enables the Joule heated melter to be transported from waste site to waste site. Induction melters with high throughput, also used in the commercial glass industry, are robust and compact enough to handle high throughput vitrification of TRU wastes in glove box applications and/or canyon operations. Compact melter technology minimizes capital and operating costs, making vitrification cost effective on a life cycle basis compared to other stabilization technologies which do not support recycle uses (Figure 3).
Figure 2. Transportable Vitrification System (TVS) in the field. Composed of 5 modules, a feed batch preparation module (left) with an exterior waste tank or hopper, a melter module (center double story), an off-gas module (along front face of concrete pad with a 40 foot tall off-gas stack), a control/power supply module (behind the off-gas and melter module). Co-designed by EnVitco Corporation and SRTC [24].

18 Drums (55 gallon) of cement vs. 1 Drums (55 gallon) of glass

1,440,000 (55 gallon) drums/year cement

7930 (55 gallon) drums/year glass

Figure 3. Ninety four percent (94%) volume reduction for mining wastes vitrified at a conservative waste loading of 35wt% compared to alternative stabilization in cement. Only 1 drum of glass which can be recycled instead of 18 drums of cement which cannot be recycled.
Vitrification produces large waste volume reductions, e.g. up to 97% [3], using cheap sources of glass former, e.g. sand, soil, crushed scrap fluorescent bulbs, crushed reagent bottles, etc. Large reductions in volume minimize long-term storage/disposal costs if the waste cannot be recycled. Often the alternative stabilization technologies such as cement stabilization cannot produce a waste form that is durable enough, e.g. cement does not thermally decompose the EPA RCRA hazardous organics and the porosity often allows the RCRA inorganic species to leach at greater than the UTS values listed in Table I. Therefore, alternative stabilization technologies often cannot produce a waste form that can be recycled (Figure 3).

DEVELOPING A VITRIFICATION PROCESS

Development of each vitrification process follows the protocol shown in Figure 4 and below:

- Analyze wastes
- Surrogate "proof-of-principle" laboratory scale studies (optional if actual waste is readily available)
- Actual waste "proof-of-principle" laboratory scale studies
- Surrogate “pilot-scale” demonstration (optional if actual waste is readily available)
- Actual waste “pilot-scale” demonstration
- Production scale (“field-scale or full-scale”) testing of melter with surrogate waste (necessary for initial check-out of equipment, otherwise optional)
- Actual waste processing, e.g. “field-scale or full-scale

The first step, “proof-of-principle” laboratory scale testing, uses a systems approach to glass formulation and process optimization. The systems approach simultaneously evaluates product performance and processing considerations [25-26]. Parameters affecting the product performance, such as chemical durability, are optimized relative to processing considerations such as melt temperature, volatility of hazardous species, melt viscosity, melt corrosivity, electrical resistivity, waste solubility, etc. The process/product models which form the basis for the statistical process control systems developed for HLLW [27] and MLLW [28] vitrification, allow this optimization to be based on melter feed composition.

“Proof-of-Principle” laboratory scale crucible testing is often performed with surrogates (1) in order to optimize glass product performance and processing considerations and/or (2) if the amount of waste available is limited. “Proof-of-Principle” laboratory scale crucible studies are necessary with actual waste whether or not a surrogate is available. “Proof-of-Principle” laboratory scale crucible testing should evaluate the following parameters:

- waste loading
- melt temperatures
- reduction/oxidation (redox) reactions between the waste and the additives
- varying types of silica additives, e.g. Reactive Additive Stabilization Process (RASP)\(^6\) using high surface area sources of silica such as various filter aids, perlite, precipitated silica, rice husk ash, etc. vs conventional vitrification with granular sand, soil, scrap glass from light bulbs reagent bottles, etc.
- corrosion of melter materials of construction (refractories and electrodes)
- determination of glass homogeneity, e.g. crystallization and/or phase separation

---

\(^6\) Reactive Additive Stabilization Process (RASP), U.S. Patent 5, 434,333. Reactive high surface area silica, used as a waste form additive, was determined to greatly enhance the solubility and retention of hazardous, mixed and heavy metal species in glass [5-6]. Vitrification using this Reactive Additive Stabilization Process (RASP)\(^6\) was found to increase the solubility and tolerance of Soda(Na\(_2\)O)-Lime(CaO)-Silica(SiO\(_2\)) glass (SLS) to atomistically bond waste species. Highly reactive silica lowers classification temperatures, increases waste loadings which provides for large waste volume reductions, minimizes melt line corrosion, and produces EPA acceptable glasses.
• waste form performance (durability) evaluation using the Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP) and/or the Product Consistency Test (PCT) developed for HLLW and MLLW waste glass durability testing (ASTM C1285-97).
• utility of existing statistical process/product control models [27,28]

“Proof-of-scale-up” testing is usually necessary in a pilot scale melter. “Pilot-scale” testing with actual waste allows the following parameters, which cannot be assessed in crucible scale testing, to be determined:
• data on actual vitrified waste forms for input to Delisting Petitions for final disposal of listed wastes
• confirmation of the processability of the glass compositions optimized in the “proof-of-principle” studies
• determination of off-gas emissions\(^7\) as a function of melt temperature
• verification of melter behavior as a Continuously Stirred Tank Reactor (CSTR) to ensure that waste and glass formers are homogenized during melting
• demonstration of recycle of secondary waste condensate produced
• utility of existing statistical process/product control models [27,28]
• demonstration of decontamination of the off-gas system/condensate tank
• evaluation of melter refractory and electrode corrosion
• determination of glass homogeneity, e.g. crystallization and/or phase separation

The same steps were used to develop the vitrification process for High-Level Liquid Waste (HLLW) vitrification at SRS and at West Valley Fuel Services (WVFS). Although development of the process for vitrification of HLLW took ~25 years to develop, and the process for the M-Area waste sludges took ~7 years, the development of the ORR waste vitrification was completed in ~3 years. Tables II-IV show the various vitrification projects initiated by SRS within the DOE complex and in the commercial sector. All of these vitrification projects were applications of the vitrification technology developed for HLLW disposal.

SUCCESSFUL DEMONSTRATIONS OF WASTE VITRIFICATION: CASE STUDIES

A. RCRA LISTED RADIOACTIVE WASTE SLUDGES (SOMETIMES ADMIXED WITH SPENT FILTER AIDS, SOILS, AND/OR CEMENTS)

SRS M-Area Sludge + Spent Filter Aid - 3,500,000 kgs

• Analyze wastes (SRS) - high SiO\(_2\) (~45 wt%), Al\(_2\)O\(_3\) (~20 wt% as Al(OH)\(_3\)), NaNO\(_3\) (~20 wt%) RCRA listed F006 nickel plating line sludge mixed with spent filter aid, Ni at ~1.2 wt% is the primary hazardous constituent, while the prime radioactive constituent is ~4.2 wt% U [3].
• Actual waste "proof-of-principle" studies (SRS) - 44 glass formulations (alkali borosilicate\(^8\) and alkali-lime-silica\(^8\) glasses); waste loadings between 70-90 wt%; melt temperatures between 1150-1350°C; varied composition of waste from high alkali to high silica; one to three glass forming

---

\(^7\) The EPA, as part of the Clean Air Act, Title III, National Emissions Standards for Hazardous Air Pollutants (NESHAP) has imposed Maximum Achievable Control Technology (MACT) standards on hazardous species such as Cr, Pb, Cd, Hg, Be, and As and a host of organics from all types of high temperature thermal treatments from incineration to vitrification to cement kiln operations.

\(^8\) Soda-lime-silica glass is common window glass. Lithium oxide was used preferentially over sodium as a glass forming flux additive and various silica sources were investigated since recent studies had shown that the known glass forming region in the SLS system could be expanded using reactive sources of SiO\(_2\) and or reactive fluxes like Li\(_2\)O [3-5, U.S. Patent 5,434,333, Lithia Additive Stabilization Process, LAMP\(^\text{TM}\), patent pending].
additives; volume reductions of 86-88%; all glasses passed [3-5] the TCLP Land Disposal Restriction
Universal Treatment Standards (LDR/UTS [29]) in 1994 which were more stringent for Ni than the
1998 standards given in Table I
Figure 4. Steps in developing a vitrification process for any type of radioactive or hazardous waste. For some types of wastes certain steps are optional (see text).

Table II
Vitrification Projects Initiated by Savannah River Site at the SRS

<table>
<thead>
<tr>
<th></th>
<th>DWPF HLLW(^9) SLUDGES</th>
<th>SRS M-AREA SLUDGES</th>
<th>SRS CIF(^{10}) ASH</th>
<th>SRS Am/Cm SOLUTIONS</th>
<th>SRS ASBESTOS COVERED PIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surrogate</td>
<td>1987</td>
<td>5/92</td>
<td>12/98</td>
<td>4/96</td>
<td></td>
</tr>
<tr>
<td>“Proof of Principle”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Proof of Principle”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surrogate</td>
<td></td>
<td>12/93</td>
<td>2/94</td>
<td>In progress</td>
<td>*</td>
</tr>
<tr>
<td>Pilot Scale Testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual Waste</td>
<td></td>
<td>9/94</td>
<td>*</td>
<td>N/A</td>
<td>*</td>
</tr>
<tr>
<td>Pilot Scale Testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>3/95</td>
<td>V (4/96)</td>
<td>*</td>
<td>12/98</td>
<td>*</td>
</tr>
<tr>
<td>Integrated Testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Processing</td>
<td>3/96</td>
<td>V (10/96)</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Recycle or Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
<td>Recycle</td>
<td>Recycle</td>
</tr>
</tbody>
</table>

\(^{9}\) DWPF HLLW=Defense Waste Processing High Level Liquid Waste  
\(^{10}\) CIF=Consolidated Incinerator Facility  
\(^{11}\) ORR WET=West End Treatment Facility  
\(^{12}\) CNF=Central Neutralization Facility  
\(^{13}\) CPCF=Central Pollution Control Facility  
\(^{14}\) LANL=Los Alamos National Laboratory  
\(^{15}\) FEMP=Fernald Environmental Management Project

Table III
Vitrification Projects Initiated by Savannah River Site at/for Other DOE Sites

<table>
<thead>
<tr>
<th></th>
<th>ORR K-25 ±CNF(^{12}) SLUDGES</th>
<th>ORR CPCF(^{13}) SLUDGES</th>
<th>LANL(^{14}) SLUDGES</th>
<th>ROCKY FLATS (RF) SLUDGES</th>
<th>FEMP(^{15}) MILL TAILINGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyze Waste</td>
<td>1/94</td>
<td>1/94</td>
<td>7/95</td>
<td>1/94</td>
<td>1/94</td>
</tr>
<tr>
<td>“Proof of Principle”</td>
<td>2/95</td>
<td>1/96</td>
<td>8/95</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Actual Waste</td>
<td>4/95</td>
<td>11/95</td>
<td>*</td>
<td>9/94</td>
<td>6/94</td>
</tr>
<tr>
<td>“Proof of Principle”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surrogate</td>
<td>V</td>
<td>4/97</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Pilot Scale Testing</td>
<td>*</td>
<td>10/96</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Actual Waste</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pilot Scale Testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated Testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Processing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recycle or Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
<td>Disposal</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- COMPLETED BY SRS,
- COMPLETED BY OTHER ORGANIZATION,
- IN PROGRESS BY SRS,
- VENDOR PRIVATIZED,
- PROGRAMATIC/BUDGETARY HOLD
Table IV
Vitrification Projects Initiated by Savannah River Site at/for Commercial Firms

<table>
<thead>
<tr>
<th></th>
<th>COMMERCIAL REACTOR RESINS</th>
<th>COLORADO MINING INDUSTRY</th>
<th>Pb PAINT REMOVAL BY THERMAL SPRAY VITRIFICATION (TSV)</th>
<th>NEW YORK HARBOR SLUDGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surrogate</td>
<td>4/96</td>
<td>N/A</td>
<td>1995</td>
<td>N/A</td>
</tr>
<tr>
<td>Actual Waste</td>
<td>*</td>
<td>8/98</td>
<td>N/A</td>
<td>1996</td>
</tr>
<tr>
<td>Recycle or Disposal</td>
<td>Disposal</td>
<td>Recycle</td>
<td>Recycle</td>
<td>Recycle</td>
</tr>
</tbody>
</table>

- **COMPLETED BY SRS**
- **IN PROGRESS BY SRS**
- **VENDOR PRIVATIZED**
- **PROGRAMATIC/BUDGETARY HOLD**

- Surrogate “pilot-scale” demonstration (SRS/Clemson DOE/Industry Waste Vitrification Center) - 6 sodium borosilicate glass formulations; one glass forming additive; waste loadings between 70-95 wt%; melt temperatures 1150-1500°C; all glasses passed TCLP LDR/UTS limits [30]

- Actual waste “pilot-scale” demonstration (SRS) - 2 alkali borosilicate glass formulations; waste loadings of 80 wt%; processed 400 kgs of waste; all glasses passed TCLP LDR/UTS limits; TCLP and Multiple Extraction Procedure (MEP) which is multiple TCLP tests used for “Delisting” listed RCRA wastes; first Delisting Petition in the DOE complex for vitrified mixed waste [31]

- Production/integrated “full-scale” testing (GTS Duratek) - first commercial vitrification of MLLW in DOE complex; contract awarded November1993, design, construction, and a Readiness Review completed April 1996, simulant testing completed November, 1996 [32,33] (see Figure 5).

- Actual “full-scale” waste processing (Duratek) - fixed unit price treatment contract; all construction and operations costs borne by sub-contractor until waste treated to meet delisting standards; treatment of M-Area wastes completed in February 1999 [32,33]

- M-Area Vitrification Summary – first completed privatized vitrification project in the DOE complex. It was under budget, all proposed wastes were treated successfully, and the final glass met all product criteria (TCLP leaching on every batch). The volume of waste was reduced from >760,000 to >200,000 gallons (as glass “gems” in 71-gallon square drums), which will be delisted and disposed as Low Level Radioactive waste. From an SRS prospective, it was completely and totally successful privatization [33].
Figure 5. GTS Duratek Duramelter™ 5000 at the SRS M-Area Vitrifying RCRA Listed Waste Sludges from Ni Plating Line Operations. First vendor privatization of vitrification in the DOE complex.

**ORR West End Treatment Facility (WETF); ~ 8,000,000 kgs**

- **Analyze wastes (ORR).** - wastes contain 60-75% CaO from CaCO₃, and 2-10wt% Fe₂O₃ from FeOOH) RCRA listed waste from treatment of solvent residues plating line operations; nickel (~0.25 wt% is the primary hazardous species of concern while U at ~0.42 wt% and traces of Tc⁹⁹ and TRU (Np²³⁷, etc.) are the radioactive species of concern [34].
- **Surrogate waste "proof-of-principle" studies (SRS).** 120 alkali-lime-silica glass formulations; waste loadings of 20-70 wt%, melt temperatures between 1150-1350°C; no more than three glass forming additives; severe melt line and general refractory corrosion at high waste loadings and high temperatures; sources of alkali and silica varied; glass viscosity vs temperature studied; all glasses passed TCLP LDR/UTS limits and PCT durability testing [6].
- **Actual waste "proof-of-principle" studies (SRS/ORR).** ~60 alkali-lime-silica glass formulations with Tank 8 and Tank 13 due to the large known immiscibility gap in the CaO-B₂O₃-SiO₂ system [35] where glasses are known to phase separate (form immiscible liquid phases); waste loadings between 20-70 wt%; melt temperatures between 1150-1350°C; no more than three glass forming additives; volume reductions of 73-87%; sources of alkali and silica varied; all glasses passed TCLP LDR/UTS limits.
- **Surrogate “pilot-scale” demonstration (SRS/Clemson DOE/Industry Waste Vitrification Center).** 2 alkali-lime-silica glass formulations; three glass forming additives; waste loadings 20-40 wt%; melt temperature 1050-1350°C; 20 wt% glass passed TCLP LDR/UTS limits [36]; 40 wt% glass crystallized in the canister but passed TCLP.
• Actual waste “pilot-scale” demonstration - vendor privatized by ORR
ORR K-25 B&C Pond Waste (Valley of the Drums); ~ 16,000,000 kgs

- Analyze wastes (ORR) - B&C Pond Waste contained high SiO₂ (wt%) and CaO (~25 wt% from Ca(OH)₂) sludge with Fe₂O₃ (~16 wt%) from admixed clay basin liner, RCRA listed mixed F006 wastes derived from plating line activities. Ag and Ni (~0.51 wt%) are primary hazardous components; ~0.30 wt% U is the primary radioactive constituent, trace concentrations of Te⁹⁹ [34]; the relative proportions of SiO₂, Ca(OH)₂ and Fe₂O₃ vary greatly from drum to drum since clean RCRA closure of the basins in 1988-89 involved intermixing pond sludge with dredged clay pond liner and some partially successful stabilization efforts with Portland cement. The B&C Pond Waste was co-vitrified with CNF wastes containing high P₂O₅, high CaF₂, and high Fe₂O₃ (see discussion of CNF wastes below).

- Surrogate waste "proof-of-principle" studies (SRS) - 120 alkali-lime-silica glasses made with waste extremes; waste loadings of 40-90 wt%, melt temperatures between 1150-1350°C; a maximum of three glass forming additives; sources of alkali and silica varied; general refractory corrosion studied, PO₄ solubility studied, glass viscosity vs. composition examined; all glasses passed TCLP LDR/UTS limits and PCT durability testing; crystallization and liquidus vs. composition studied.

- Actual waste "proof-of-principle" studies (SRS/ORR) - 70 alkali-lime-silica glass formulations with waste from the rotary drier used in K25 B/C pond remediation efforts in 1991-92; waste loadings between 40-90 wt%; melt temperatures between 1150-1350°C; no more than three glass forming additives; volume reductions of 70-90%; sources of alkali and silica varied; all glasses passed TCLP LDR/UTS.

- Surrogate "pilot-scale" demonstration (SRS/Clemson DOE/Industry Waste Vitrification Center) - high SiO₂ B/C simulant developed by SRS; 1 alkali-lime-silica glass; three glass forming additives; waste loading 50 wt%; melt temperature 1250°C; glass passed TCLP LDR/UTS limits and PCT testing.

- Actual waste “pilot-scale” demonstration (SRS/CETL) - at the Clemson Environmental Technologies Lab (CETL) during May and June of 1997. Melted two different waste streams: surrogate B&C pond waste and a blend of surrogate B&C pond waste with actual ORR Central Neutralization Facility (CNF) waste sludge (see discussion of CNF waste below). 865 kgs. of actual CNF waste sludge (see next section) was processed with a mix of B/C sludge making about 460 kg of glass.

- Production/integrated “field-scale” testing (SRS) - high SiO₂ B/C simulant developed by SRS; SRS Transportable Vitrification System (TVS); waste loading 50 wt%; melt temperature 1150°C. An extensive surrogate waste test program was conducted on the TVS at Clemson during January and February of 1996. A total of 11,614 kgs. of surrogate waste glass was produced. Additional surrogate testing was performed at ORR in the fall of 1996.

- Actual “field-scale” waste processing (SRS) - The TVS treated a total of 7345 kgs. of actual mixed waste composed of B&C pond waste and CNF waste. During the campaign at ORR’s East Tennessee Technology Park (formerly ORR’s K-25 site) 3797 kg of B/C sludge and 3532 kg of CNF sludge were co-vitrified producing 7970 kgs. of mixed waste glass during September and October of 1997 [28]. Air pollution emissions did not exceed authorized limits and the glasses produced easily passed TCLP limits. The estimated volume reduction was 60%.

ORR Central Pollution Control Facility (CPCF); ~ 186,200 kgs

- Analyze wastes (ORR). - There are three categories of CPCF wastes: oily, wet non-oily, and dry non-oily; oily RCRA listed plating line sludges containing 20-30% organics and ~0.50 wt% U and 0.2 wt% Ni. The oily CPCF wastes studied are high in SiO₂ (~50% on a dry oxide basis), ~4 wt% CaO as Ca(OH)₂, ~12 wt% Fe₂O₃ from FeOOH, and ~30-40 wt% organics.

- Actual waste "proof-of-principle" studies (SRS/ORR) - 30 alkali-lime-silica glasses tested with oily CPCF waste and 3 glass formulations in the alkali-borosilicate system; waste loadings between 70-90 wt%; melt temperatures between 1150-1350°C; three glass forming additives; volume reductions of
85-90% sources of alkali and silica varied; organics driven off with slow heat up ramps; all alkali-lime-silica glasses passed TCLP LDR/UTS; 3 borosilicate glass formulations phase separated [35] and had poorer overall durability.

- **Actual waste “pilot-scale” demonstration (SRS/CETL) –** not completed because a pretreatment technique such as solvent extraction, wet oxidation, or incineration was needed to destroy the 30-40% organics before vitrification (the maximum safe organic content for a Joule heated melter is <10 wt% organics).

**ORR Central Neutralization Facility (CNF); ~ 900,000 kgs**

- **Analyze wastes (ORR).** - CNF wastes are listed RCRA wastes resulting primarily from the treatment of ORR TSCA incinerator scrubber blowdown solution.
- **Surrogate waste “proof-of-principle” studies (SRS).** - 15 alkali-lime-silica glass compositions tested with waste loadings ranging from 15 to 40 wt%; melt temperature was 1250°C; glasses with higher Li₂O content produced more homogeneous glasses.
- **Actual waste “proof-of-principle” studies (SRS/Clemson) –** 6 glass compositions tested in the ALS system with waste loadings ranging from 30 to 40 wt%; melt temperature was 1250°C; glasses were visually homogeneous
- **Actual waste “pilot-scale” demonstration (SRS/CETL)** - co-vitrified with B&C pond waste (see previous section).
- **Actual “field-scale” waste processing (SRS)** - Performed as part of the TVS campaign on B&C pond waste in 1997. See discussion above.

**Los Alamos National Laboratory (LANL) Liquid Waste Processing Plant; ~324,000 kgs**

- **Analyze wastes (ORR).** - ~50 wt% CaO (on an oxide basis) from CaCO₃ processing and admixed Portland cement and gypsum, high SiO₂ (38 wt% from filter aids such as perlite and diatomaceous earth), and Fe₂O₃ (8 wt% from FeOOH) RCRA from treatment of solvent residues; U at ~0.23 wt% and traces of Pu²³⁹ and Am²⁴³ are the radioactive species of concern and the hazardous species of concern are not well documented except for Cd [34]
- **Surrogate waste “proof-of-principle” studies (SRS).** - 19 alkali borosilicate glasses were tested, as well as glasses in the CaO-Al₂O₃-SiO₂, the CaO-Fe₂O₃-SiO₂, and the soda-lime-silica glass (SLS) forming systems [37]; waste loadings of 25-75 wt%, melt temperatures between 1150-1500°C; two glass forming additives; severe crystallization was noted in certain composition regions in all systems with the in the SLS glasses. Glasses doped with Ba, Cd, Cr and Ni; all glasses passed TCLP LDR/UTS limits and PCT durability testing [37].
- **Surrogate “pilot-scale” demonstration (SRS/Clemson DOE/Industry Waste Vitrification Center).** - 1 glass formulation at 65 wt% loading in the CaO-Al₂O₃-SiO₂ system at 1350°C, the glass was difficult to pour due to high viscosity, TCLP and PCT testing indicated durable glass was produced

**Rocky Flats By-Pass Sludge**

- **Analyze wastes (ORR).** - ~36 wt% Fe₂O₃ from Fe(OH)₃, ~25 wt% CaO from CaSO₄, and ~12 wt% Na₂O from NaNO₃ creating about 12 wt% NOₓ and >20 wt% SO₃ gaseous species upon vitrification; some waste admixed with up to 30% Portland cement; RCRA listed nickel plating line waste; listed for Cd, Cr, Pb, Ag, and Ni hazardous species; Pu as primary radioactive species of concern [34]
- **Surrogate waste ”proof-of-principle” studies (SRS).** - 10 sodium-borosilicate glass formulations were tested at waste loadings of 25 – 75 wt% but required charcoal additions to get rid of the sulfate layer that formed on the glass surface. Only two glass forming additives plus charcoal were necessary to
stabilize the waste. The homogeneous glasses passed TCLP LDR/UTS limits and PCT durability testing [37]

- **Surrogate “pilot-scale” demonstration (SRS/Clemson DOE/Industry Waste Vitrification Center)** - 1 glass formulation at 75 wt% loading in the sodium-borosilicate system at a melt temperature of 1350°C.

### B. INCINERATOR WASTES (ASH AND/OR OFF-GAS BLOWDOWN)

**SRS Consolidated Incinerator Facility (CIF); ~ 800 m³/year blowdown and 124 m³/year ash generation for 25+ years**

- **Simulate wastes (SRS)** - ~65 wt% Na₂O (primarily from NaCl in the waste) and ~32 wt% CaO (on a dry oxide basis) in a mixture of 68 wt% blowdown and 32 wt% bottom ash [3]; RCRA for all inorganic species of concern and Zn; radioactive constituents include Cr⁵¹, Sr⁹⁰, Cs¹³⁷, traces of Pu
- **Surrogate waste “proof-of-principle” studies (SRS) - 20 alkali-lime-silica glasses tested with surrogates [3]; waste loadings of 30-50 wt%; melt temperatures between 1150-1250°C to avoid volatilization of hazardous species such as chlorides; 94-97% volume reduction; one glass forming additive, SiO₂; sources of alkali and silica varied; all glasses passed TCLP LDR/UTS limits; pyrohydrolysis investigated to remove Cl as HCl plus steam [3].

### C. ION EXCHANGE RESINS AND ZEOLITES

**Commercial Reactor Resins ~220,000 kgs Boiling Water Reactor (BWR) and 66,000 kgs Pressurized Water Reactor (PWR) Ion Exchange (IEX) resins per reactor per year**

- **Analyze wastes (SRS/EPRI)** - samples of six ion exchange resins from EPRI undergoing wet chemical analysis for cationic and anionic species; undergoing Differential Thermal Analysis (DTA) with coupled mass spectrometry to identify inorganic and organic volatile components
- **Surrogate waste “proof-of-principle” studies (SRS) - preliminary data indicates 50 wt% waste loading for PWR wastes which gives a 77% volume reduction and a 35 wt% waste loading for BWR wastes which gives a 66% volume reduction [8]; 35 glass compositions tested with 6 different resin types with a borosilicate glass composition; waste loading (24 to 42 wt%) limited by salt formation and glass redox; melt temperature of 1150°C; glasses passed PCT durability testing.

- **Surrogate “pilot-scale” demonstration (SRS)/Clemson** - 1 borosilicate glass formulation tested at 33 wt% waste loading for a 64% volume reduction; melt temperature of 1050°C; glass was homogeneous and passed PCT durability testing; retention of radioactive surrogates was greater than 93% [38].

**National Atomic Energy Commission of Argentina (CNEA) Resins – 42 m³ with 2.83 m³ generated/year of Atucha and 130 m³ with 9.5 m³ generated/year of Embalse**

- **Analyze wastes (SRS/CNEA)** - resins analyzed by the CNEA; surrogate radionuclides added by SRS and the CNEA for vitrification testing.
- **Surrogate waste “proof-of-principle” studies (SRS) – a borosilicate glass composition tested with both resins at various waste loadings; optimum determined to be ~30 wt% waste loading for both resins with associated volume reductions of >65%; melt temperature of 1050°C; glasses were homogeneous and durable.
• Surrogate “pilot-scale” demonstration (SRS/Clemson) – three melter demonstrations completed with simulated and actual CNEA supplied resin; melt temperature of 1050°C; homogenous and durable glasses produced.
D. SOILS, GEOLOGIC MATERIAL/MEDIA

Fernald Environmental Management Project (FEMP) K-65 silos of depleted uranium (mill tailings from processing pitchblende ore) for atomic bomb development ~10,000,000 kgs (~10,000 metric tons)

- Analyze wastes [39] - Residues from processing pitchblende ores from 1949-1958, high in SiO2 (~63 wt%), BaO (~6.5 wt%), Pb (~12.5 wt%), and Fe (~5 wt%).
- Surrogate waste "proof-of-principle" studies (SRS) - 2 alkali-lime-silica glass formulations; waste loadings of 80-90 wt%, melt temperature 1050°C; two glass forming additives; both glasses passed TCLP limits [40].

E. ASBESTOS AND/OR GLASS FIBER FILTERS (UNCONTAMINATED OR CONTAMINATED)

Decommissioning and Decontamination (D&D) throughout the DOE, DOD, and commercial sectors [10]

- Analyze wastes (SRS) - analysis of asbestos coated pipe indicates that asbestos containing materials (ACM) are admixed with up to 50 wt% MgCO3 and/or CaSO4 as cementitious binder material.
- Surrogate waste "proof-of-principle" studies (SRS) - use of patented [9] caustic dissolution process to remove ACM from adhering pipe; allows pipe or other adhering metal to be sold/recycled; 10 glass formulations of high Mg silicate glasses render ACM non-crystalline and non-hazardous; waste loadings of 60-70 wt%; melt temperatures between 1150-1350°C; volume reductions of 90-99.7% for asbestos covered pipe; non-contaminated glass can be sold for recycle.

F. RADIOACTIVE MATERIALS INCLUDING TRANSURANIC (TRU), PLUTONIUM (Pu), AND OTHER ACTINIDE WASTES

Am/Cm - 15,000 liters to be stabilized in glass for shipment to ORR for reuse as medical target sources [12-19]

- Analyze wastes (SRS) - dilute 4N nitric acid solution containing approximately 10.1 kgs Am and 2.7 kgs Cm
- Surrogate waste "proof-of-principle" studies (SRS) compositional variability studies have demonstrated the production of glasses with 30–47 wt% feed loadings, coupled with a lanthanide borosilicate based frit, that meet specific process and product performance specifications. The resulting glass form can be safely shipped to ORR as a solid for their Isotope Sales Program; SRS waste reclaimed as a source of revenue for DOE complex; full (100%) recovery of all rare earth oxides (including La2O3, CeO2, Er2O3, Eu2O3, and Nd2O3) from glass demonstrated by nitric acid extraction; >90% volume reduction.
- Surrogate waste “full scale” demonstration (SRS) – Actinide and lanthanide oxalates precipitated from solution with oxalic acid and then washed to lower the nitric acid concentration; oxalate precipitate is then transferred to a Pt/Rh induction melter, which is preloaded with glass-making additives; the mixture is dried and heated to approximately 1450°C in the induction heated Cylindrical Induction Melter (CIM) (see Figure 6); glass is poured through a drain tube into a stainless steel cylinder for shipment.
G. **RCRA HAZARDOUS MINING INDUSTRY WASTES [41]**

- Analyze wastes (SRS) - ~7 wt% Al₂O₃, ~7 wt% CaO, ~20 wt% (Fe₂O₃ + FeO), ~12 wt% MnO, ~25 wt% ZnO, and ~8-9 wt% SiO₂: RCRA hazardous for CdO which only comprises 0.12 wt% of the waste
- Surrogate waste "proof-of-principle" studies (SRS) - 9 soda-lime-silica glasses tested, waste loadings of 35-50 wt%, volume reductions of 90-94% (see Figure 3); melt temperatures of 1250-1350°C; 2 basalt glasses tested, waste loadings of 35 wt%; volume reductions of 90-94%, melt temperatures of 1300-1500°C; one borosilicate glass tested, waste loadings of 28 wt%, volume reductions of 87%, melt temperatures of 1150-1250°C; mill tailings from mine used as cheap source of glass forming additives; glasses rendered non-hazardous by TCLP and acceptable for recycle.

H. **RCRA HAZARDOUS NEW YORK HARBOR SLUDGE [42]**

- Analyze wastes (WSTC) - Westinghouse Science and Technology Center ~60 wt% SiO₂ and ~15 wt% Al₂O₃; waste RCRA hazardous for organics such as dioxins and heavy metals such as Pb from fuel used in ships and boats
- Surrogate waste "proof-of-principle" studies (SRS) - 3 soda-lime-silica glasses tested, waste loadings of 85 wt%; melt temperature 1350°C; volume reductions of >90%; glasses rendered non-hazardous by TCLP and acceptable for recycle.

![Figure 6. Schematic of the Batch Vitrification Process.](image-url)
I. RCRA HAZARDOUS Pb PAINT REMOVAL [43]

- Analyze wastes (SRS) - not applicable
- Surrogate waste "proof-of-principle" studies (SRS)-4 alkali borosilicate, 1 sodium barium silicate, 1 lead iron phosphate, and 1 commercial lead silicate (leaded glass) glass formulas were tested; the borosilicate glasses containing lithium oxide were the most successful in stabilizing the hazardous Pb constituents
- Actual waste “full scale” demonstration (USACERL)-the U.S. Army Corps of Engineers Construction Engineering Research Laboratory performed a full scale demonstration of the Thermal Spray Vitrification (TSV) on the Triborough Bridge in New York City; removed multiple layers of paint that had accumulated on the bridge abutment over a 30 year period of time (Figure 7).

CONCLUSIONS

Vitrification is a viable option for a large variety of wastes in the DOE complex and the commercial sector. The SRS has initiated and completed vitrification projects in both stationary and transportable vitrification facilities as well as via thermal spray vitrification (TSV). A wide variety of waste types can be stabilized and/or recycled with this robust technology. In addition to the case studies presented in this review, the SRS has recently initiated vitrification programs with the Idaho National Engineering and Environmental Laboratory (INEEL) for vitrification of their HLW calcines and with British Nuclear Fuel Ltd. (BNFL) for vitrification of HLW and MLLW Hanford wastes. One of the most recent endeavors has been the adaptation of TSV for decontamination of radioactive species from duct work and hoods throughout the DOE complex.
REFERENCES

1. C.Randall and S.L. Marra, This proceedings


Development (U),” Materials Research Society, Symposium on the Scientific Basis for Nuclear Waste Management XXII.


