VITRIFICATION DEVELOPMENT AND EXPERIENCES AT FERNALD, OHIO

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For presentation at the
Institute of Nuclear Materials Management
39th Annual Meeting

*Fluor Daniel Fernald with the U.S. Department of Energy, under Contract No. DE-AC24-92OR21972
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VITRIFICATION DEVELOPMENT AND EXPERIENCES AT FERNALD, OHIO

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ABSTRACT

Vitrification of radioactive wastes products have proven to produce an extremely stable waste form. Vitrification involves the melting of wastes with a mixture of glass-forming additives at high temperatures; when cooled, the wastes are incorporated into a glass that is analogous to obsidian. Obsidian is a volcanic glass-like rock, commonly found in nature. A one-metric ton/day Vitrification Pilot Plant (VITPP) at Fernald, Ohio, simulated the vitrification of radium and radon bearing silo residues using representative non-radioactive surrogates. These non-radioactive surrogates contained high concentrations of lead, sulfates, and phosphates. The vitrification process was carried out at temperatures of 1150 to 1350°C. Laboratory and bench-scale treatability studies were conducted before initiation of the VITPP. Development of the glass formulas, containing up to 90% waste, will be discussed in the paper. The VITPP processed glass for seven months, until a breach of the melter containment vessel suspended operations. More than 70,000 pounds of good surrogate glass were produced by the VITPP. Experiences, lessons learned, and the planned path forward will be presented.

BACKGROUND

The Fernald Environmental Management Project (FEMP) is a remediation project operated by Fluor Daniel Fernald (FDF) for the US Department of Energy (DOE). The FEMP is a former DOE production site for the extraction of uranium from ores and concentrates and the production of uranium metal for the DOE defense program. Residue materials from the uranium extraction and production activities were stored in three of four silos. The elemental analysis of the silo wastes is shown in Table 1. A fourth silo, Silo 4, was not used and remains empty.

Table 1 - Silo Waste Elemental Analysis (shown as oxides in wt%)

<table>
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<tr>
<th>Component</th>
<th>SILO 1 Measured</th>
<th>SILO 1 Normalized</th>
<th>SILO 2 Measured</th>
<th>SILO 2 Normalized</th>
<th>SILO 3 Measured</th>
<th>SILO 3 Normalized</th>
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<td>10.00</td>
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<td>3.40</td>
<td>4.02</td>
<td>9.30</td>
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<td>4.02</td>
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<td>3.00</td>
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<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.01</td>
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Totals 86.12 100.00 84.68 100.00 86.89 100.00
Figure 1
Schematic of the Melter
Figure 2

Schematic Process Flow Diagram of the Pilot Plant
oxidized glass, meaning the glass is rich in oxygen. Glass has commercially been made from feed containing sulfates since the 1800s. The sulfate glasses are low in oxygen and were classified as reduced glasses. Reductants, such as carbon, are added to the molten glass to reduce or destroy the sulfates because glass can only dissolve approximately 1 wt% sulfate without precipitation. If the molten glass also contains a high concentration of lead, strong reductants such as carbon, will also reduce the dissolved lead in the glass to lead metal or lead sulfide droplets. The droplets then can (depending and droplet size and flows through the melter) fall to the bottom of the glass melter and create a puddle. These puddles can short the melter electrodes and reduce the life of the melter through erosion of the melter refractory. In the VITPP operations, mild reductants, such as urea, were successful in the reduction of sulfates without precipitating lead. Urea is thirsty for oxygen and destroys sulfates by taking oxygen from the sulfates. Also, water in the melter feed slurry was helpful in removing sulfates from the molten glass. Water reacts with sulfates at high temperature to form sulfuric acid (H₂SO₄). Together, water and urea can compliment each other in the destruction of sulfates. The OU4 waste residues contain high concentration of sulfates and lead. Those silo constituents above the dotted line in Table 1 (shown previously) where simulated in the surrogate. Table 2 shows a typical surrogate blend of the waste for all three silos and the glass additives to make a glass processed in the melter at 1250 C.

**PROCESS SCALE UP**

The development of the glass formulas and the Melter are dependent upon each other. Both are significantly influenced by the waste materials in Silos 1 and 2. Characteristics of the glass that are key to developing glass formulas and Melter design include the concentration of sulfate and other components in the slurry feed, viscosity, liquidus temperature², redox state, foaming, and electrical conductivity of the resultant glass. This section presents a brief synopsis of the glass chemistry and process development for the vitrification of the Silos wastes in a chronological order of the following studies: (1) laboratory-scale; (2) bench-scale; (3) the pilot-scale VITPP. Process scale-up relationships between the development studies is presented.

1- **Silo Residue Characterization.** Elemental analysis was performed by Pacific Northwest Laboratories (PNL) in Richland, Washington to determine the makeup of the Silo Residues and develop surrogates³.

2- **Lab-Scale Development – Part One.** PNL made small 100 and 400 gram glass melts with the actual Silo Residues – only a small amount of actual Silo residues were available for testing. Surrogates, which simulate the actual residues where developed and most experimental melts were done with surrogates and only the best performing melts performed with actual materials. It was reported that high temperatures were required to destroy the sulfates. Therefore, most of the melts were performed around 1400 C and higher⁴.

3- **Laboratory Development – Part Two.** Potential vendors, that design and manufacture melters, indicated that melters were not available for the high temperature recommended in the previous lab studies. So, new glass recipes were developed for lower temperature
and the destruction of sulfates. Melts were performed to increase the ability to destroy sulfates and/or increase the glass’s ability to hold more sulfate while preventing the reduction of lead in the glass to lead metal or lead sulfide precipitates. Also, various techniques were tried to reduce (destroy) sulfates in the melts. The high phosphate content of the Silo residues was a concern, but adjustments in glass chemistry made that allowed sufficient solubility for the phosphates in the glass. All this work was done with surrogates. During these studies it was deduced that most of the sulfates were probably Barium Sulfate in Silos 1 and 2 and Magnesium Sulfate in Silo 3. This meant that the vitrification of Silo 1 and 2 would be more difficult than originally envisioned because barium sulfate has a high melting point and should be stubborn to destroy. Whereas, the magnesium sulfate in Silo 3 is easily destroyed at relatively lower temperatures.

4- Bench-Scale Development. The revised glass formulas were tried in the small three-chamber melter similar to the large three-chamber pilot melter to be used later. Some glass recipes were modified slightly during this stage of development. However, operating techniques and methods to handle and to destroy sulfates became the greatest challenge. It was found that urea and water were helpful in destroying and controlling sulfates. This development was done with surrogates at the Vitreous State Laboratory at The Catholic University of America in Washington, D.C. under contract of GTS Duratek.5

5- Pilot-Scale Development. The most successful glass recipes from the Bench-Scale Development activity were run in the VITPP at Fernald. Most of this paper centers on this development effort6.

THE PROCESS’S BOTTLENECK

The high concentration of sulfates can cause the molten glass bath to become supersaturated with dissolved SO₂/SO₃ gasses. When this happens, it becomes the bottleneck of the process – glass cannot be processed any faster without the formation of a sulfate layer. Likewise, any process upset or sudden increase in temperature can result in sudden foaming of the molten bath due to the release of the dissolved SO₂/SO₃ gasses. This became (other than mechanical problems with operating the melter and auxiliary equipment) the major challenge of vitrifying the silo residues. Through scale-up and operation of the pilot plant methods were developed to help control foaming. It was found that the addition of urea or water and/or in combination with temperature and power control were found to help eliminate or reduce the foaming problem. However, even with these adjustments, the handling of sulfates still proved to be a bottleneck in the process.

VITRIFICATION PILOT PLANT (VITPP) CAMPAIGNS

Development work for the VITPP program was divided into test campaigns. Each campaign processed a different combination of the waste residues from the silos. Startup of the melter (or Campaign 0)
started with a benign glass that contained no RCRA hazardous metals or sulfate.

The operational campaigns planned and the campaign objectives are listed below:

Campaign 0 - Bake-in of the melter was done with a benign glass frit.

Campaign 1 - Startup and learning to operate the melter was done with a benign glass feed slurry.

Campaign 2 - Acceptance of the melter from the vendor (known as The Acceptance Test), was a 36-hr continuous run using a feed slurry formulated high in sulfate and lead to test the capabilities of the melter. The second part of the campaign was done with surrogate slurries representing a realistic blend of the waste residue from all three of the silos. These runs were high in sulfate with moderately high lead content.

Campaign 3 - Glasses made from Silo 3 waste surrogates alone. Prior to initiation, this campaign was subsequently deleted from the VITPP scope.

Campaign 4 - Glasses made with Silo 1 and 2 feed slurry waste surrogates. These runs were high in lead with moderately high sulfate content.

Each campaign was planned to process roughly 20 metric tons of glass and lasted approximately one to two months depending on challenges encountered.

GETTING THE VITRIFICATION PILOT PLANT TO RUN

During startup of the pilot plant, significant difficulties were found with the systems. Consequently, the system was down frequently until corrections or modifications were made. The resulting uptime (the percentage of time that materials were being fed to the melter during a 24-hour period) experienced during Campaign 1 was 19%. Campaign 2 was 27% and Campaign 4 increased to 42%. Uptime estimates for the pilot plant were originally high but later estimated to be 20 to 30% when considering difficulties discovered during System Operability Testing and other facility operating efficiencies. Some delay time due to changes in testing direction and laboratory analyses also contributed to the low uptime. As reported in the VITPP Phase I Treatability Study Reports, the primary causes for the low uptime of the pilot plant were due to inadequacies in the slurry feed, the off-gas systems, and the melter discharge chamber.

The primary causes of problems in the VITPP feed system were due to:

- Sharp bends in the piping that restricted flow and provided areas for solids to collect
- Small diameter piping and long sections of piping that restricted flow
- Slurry pump design, seal design, and construction materials being inconsistent with
abrasive constituent in the waste slurry.

- Insufficient agitation of the clay-like cohesive material resulting in settling of solids in the bottom and sides of the slurry feed preparation tanks.
- Supersaturation of soluble components in the heated tank with subsequent recrystallization in the cooler downstream lines.

As a result, a significant amount of time was spent in removing blockages and performing repairs. Problems in the feed system affected other systems. For example, to help prevent blockage in the feed system, a more dilute feed slurry was used. The dilute slurry resulted in more water being boiled by the melter than was necessary. This action affected the off-gas system and resulted in less glass being produced due to the reduced waste solids content.

The off-gas system presented problems as well. The excess water vapor from the melter put an extra burden on the off-gas system and at times overwhelmed the system. To prevent unnecessary activation of the emergency off-gas system, waste slurry feed rates were kept low. Originally the pilot plant off-gas system design included a chiller to remove most of the moisture. However, the chiller was removed from the design (because of cost) and the off-gas system had to rely on a desiccant tower containing moisture-absorbing materials (desiccants) to remove the water. The desiccant tower experienced difficulties because there was too much water vapor to handle – the desiccant would gel/compact together and water would channel through the bed. Replacing the desiccant bed was time consuming and resulted in reduced plant uptime. In addition, carryover of particulates from the melter off-gas plenums partially plugged the system, reducing the off-gas flow. This condition required reducing the slurry feed to the melter. Frequent cleaning of the off-gas components further reduced the plant uptime.

There were difficulties in the operation of the melter discharge chamber. These difficulties resulted in downtime and hampered the ability to form the molten glass into the preferred final product form as gems. The primary causes of problems with the discharge chamber, as reported in the VITPP treatability reports, were:

- Pluggage in the melter discharge chamber due to excess outside air being drawn up into the discharge chamber. The melter chamber was maintained at negative pressure, but the upper part of the chamber wall, as seen in side view in Figure 1, was porous. This allowed air to be drawn through the discharge chamber into the main melter chamber. This caused the molten glass to (1) waver and make it hard to cut and form into gems and/or (2) freeze and cause plugging at the discharge.

- Migration of glass through the wall between the heated Main Chamber and the heated Discharge Chamber. Normally, glass freezes in a wall and will not advance. However, this wall was heated on both sides and allowed the glass to flow. The flow occasionally blocked the discharge port. Cooling was later used to limit the flow.

During Acceptance Testing, cracks developed or widened in the partition walls separating the Electrode Chambers and the Main Chamber, especially the West Partition Wall. These cracks allowed the Main Chamber glass to flow into the Electrode Chambers. The glass flowing through the cracks resulted in
reboil (the production of SO\textsubscript{x} gasses) and foaming in the side chambers. Foaming sometimes hampered production because the power had to be reduced to prevent the foam from carrying glass into the Main Chamber and exposing the electrodes to the air. The molybdenum electrodes will burn if exposed to air and greatly shorten their life. Glass frit was frequently added to the Electrode chambers to limit foaming and keep the electrodes covered.

FAILURE OF THE MELTER

Not directly related to the melter failure (which is described later), but factors reported in the VITPP Melter Incident Final Report\textsuperscript{8} that could have contributed to shortening the life of the melter were the materials of construction and design inadequacies. These factors were:

- A secondary Inconel™ liner was installed in the melter to provide a secondary containment for the molten glass. However, not realized by the vendor or the buyer, the liner actually increased the probability of failure. When molten glass migrates to the Inconel™ liner, the liner becomes an electrical short and a source of joule-heating of the wayward glass. This heating would accelerate the erosion of the refractory insulation and lead to early failure.

- Cracks in the partition wall between the Main Chamber and each Electrode Chamber appear to have formed or opened shortly after startup during the melter Acceptance Test overseen by the vendor's personnel. This lead excessive foaming in the electrode chambers and corrosion of the electrodes.

The partition wall was made from high-chromium content blocks. Cracks in the walls allowed the lead and sulfate-bearing Main Chamber molten glass to enter the Electrode Chambers. The Electrode Chamber molten glass was maintained in a reduced state because of the presence of the molybdenum metal electrodes. The reduced glass condition aids in the destruction of the sulfates, forming SO\textsubscript{2} gas as bubbles or foam. Also, reboil of the molten glass as it passes through the wall cracks, aids in the destruction of the sulfates. In defense of the situation, the vendor's scientists responded stating that the minimelter (the predecessor to the VITPP melter) during earlier stages of the development program, also developed a large hole in the partition walls. Foaming developed, but the minimelter electrodes appeared to be protected. And while the foaming in the pilot plant melter was an operational hindrance, it would not be destructive to the melter electrodes. However, FDF in an effort to control the situation responded with (1) flushing the Electrode Chambers with new benign glass and (2) replacing the Electrode Chamber glass with a denser glass formula to try to reverse the molten glass flow into the Main Chamber. Unfortunately, the cracks were too large and the efforts were to no avail and the upper electrodes did receive significant corrosion. One top electrode was essentially gone when inspected after the melter incident. In addition to erosion of the electrodes, molten lead metal formed from the leakage of the leaded waste glass into the Electrode Chambers as cited by the next bullet.
• The electrodes were eroding and producing metallic lead from the lead-bearing waste glass leaking into the Electrode Chambers. The mechanism is as follows:

\[
\begin{align*}
\text{Mo} + 3\text{PbO} & \rightarrow \text{MoO}_3 + 3\text{Pb} \\
1\text{ g} + 6.98\text{g} & \rightarrow 1.50\text{g} + 6.48\text{g}
\end{align*}
\]

(Equation 1)

According to Equation 1, 1 gram of molybdenum metal will produce 6.48 grams of molten lead metal. The lead metal could have aggravated the erosion of the melter refractory insulation.

The Pilot Plant was in the last run of the last campaign (Campaign 4) when a bottom mounted bubbler tube (which provided air injection to the inside of the melter Main Chamber for oxidation and agitation) failed on December 26, 1996. This event irreparably damaged the melter and allowed molten glass to leak into an emergency bottom drain container.

**ANALYSIS AND ROOT-CAUSE OF THE MELTER FAILURE**

According to the VITPP Melter Incident Final Report (the Report), the melter failed due to the melter's design and construction — not its operation. The identified main reasons for the melter failure were:

• The bubbler tubes in the bottom of the melter Main Chamber were made of molybdenum disilicide that quickly reduced to molten lead according to the following reaction:

\[
\begin{align*}
\text{MoSi}_2 + 7\text{PbO} & \rightarrow \text{MoO}_3 + 2\text{SiO}_2 + 7\text{Pb} \\
1\text{ g} + 10.27\text{g} & \rightarrow 0.95\text{g} + 0.79\text{g} + 9.53\text{g}
\end{align*}
\]

(Equation 2)

According to Equation 2, 1 gram of molybdenum disilicide produces 9.53 grams of molten lead metal.

• With the bubbler tubes gone, the molten glass found its way through the refractory and into the insulation understructure which was not designed to deal with the high temperature of direct exposure to molten glass. The bubbler air agitation allowed the exchange of the wayward molten glass with unreacted glass and helped erode away the understructure until the molten glass drained through the bubbler port. The glass migrated between the refractory and the liner and provided the mechanism for the melter breech.

The root cause as determined in the Report, was the wrong choice of construction material for the bubbler tubes. Other materials could have been chosen that would not have reacted to form lead when contacted by the lead-bearing molten glass. In addition, future designs should avoid any penetrations through the bottom of the melter. The bubbler tube material (molybdenum disilicide) does not hold up well under oxidizing conditions in the VITPP melter.
Initially it was believed that the melter could have failed because of glass chemistry problems producing metallic lead that caused early erosion of the melter refractories. However, this was shown not to be the case. Samples of glass from each campaign run were analyzed and the redox (ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$) was always below 0.2. Lab results show that the redox needs to be more than 0.6 before lead sulfide precipitation problems started. Only lead sulfide was formed during the glass redox studies. However, molybdenum and molybdenum sulfide was placed in molten glass and molten lead droplets formed at the points of contact with the molten glass overnight. It appears to take a strong reductant like molybdenum to form metallic lead. Therefore, the lead seen in the melter came from the molybdenum electrode and molybdenum disilicide reactions described above. For example, the amount of lead found in the melter was of the order of tens of pounds. This is verified by the lead mass balance done for the pilot operation; the mass balance was short about 50 pounds.

LESSONS LEARNED

The lessons learned were collated and distributed to other DOE sites to aid in their future vitrification and waste processing needs. This document is listed in the endnotes. Three main lessons learned were:

1. Handling slurries can be difficult and should not be underestimated.

2. Likewise, handling off-gases from a vitrification system can be difficult and should not be underestimated. Special attention should be given to (a) particulate dropout and buildup in lines and (b) the handling of excess moisture.

3. Materials of construction should not be taken for granted, but rather, the materials of construction should be tested for compatibility with the expected processing materials and conditions.

PATH FORWARD

Because of the VITPP experience, DOE at Fernald is reevaluating the remedy selected for treatment of the silo wastes. The main issues with any solidification/stabilization treatment methods that require resolution include:

- Can the radon gas be contained and controlled to meet shipping and disposal criteria?
- Can the treated waste form adequately contain and immobilize hazardous constituents to meet the disposal criteria?
- Can the stabilization method produce a satisfactory waste loading?
CONCLUSION

The failure of the bubbler tube on December 26, 1996, marked the end of two years of experience with the Fernald VITPP. Many facility and equipment design deficiencies were noted and corrected during the VITPP operating period. A significant amount of information was generated on the treatment of the silo waste and for the design of a final remediation facility. Experience was gained in vitrifying wastes and the operation of a unique three-chamber, high-temperature melter. Much of the information and experience from the VITPP operation has been documented and provided to other DOE sites for future work with vitrification throughout the DOE complex.

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ENDNOTES

1. The analysis shows the elements as oxides. The actual compounds may or may not be oxides. This format is a standard convention for showing ingredients for making glass. Sulfates, nitrates, and carbonates are shown as $\text{SO}_3$, $\text{N}_2\text{O}_5$, and $\text{CO}_2$. These, when combined with the oxide, form the traditionally known sulfate, nitrate, and carbonate formats. For example: $\text{CaO} + \text{SO}_3 = \text{CaSO}_4$.

2. The liquid temperature is the temperature where and if the glass is held at this temperature for a sufficiently long time can crystalized or constituents in the glass crystalize. Usually, the amount of time for this to happen is hours or days (not minutes).


5. Sabrina S. Fu., et al., "Vitrification Testing for Fernald CRU4 Silo Wastes – Final Report" The Vitreous State Laboratory at The Catholic University of America in conjunction with GTS Duratek, Columbia, Maryland, September 27, 1996.

