55

FEMP-2541

RECEIVED

APR 02 1998

OSTI

VITRIFICATION PILOT PLANT EXPERIENCES AT FERNALD, OHIO

BY

Nina Akgunduz, Department of Energy-FEMP
Rod F. Gimpel, Fluor Daniel Fernald
Dr. Donald Paine, Fluor Daniel Fernald
Vernon H. Pierce, Fluor Daniel Fernald

July 18, 1997

DTIC QUALITY INSPECTED 8

Fluor Daniel Fernald, Inc.
Fernald Environmental Management Project
P.O. Box 538704
Cincinnati, Ohio 45253-8704

For presentation at Science and Technology for Disposal of
Radioactive Tank Wastes Symposium, September 1997

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

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.

VITRIFICATION PILOT PLANT EXPERIENCES AT FERNALD, OHIO

Nina Akgündüz¹, Rod F. Gimpel, Dr. Donald Paine, Vernon H. Pierce²

¹Department of Energy -- Fernald Field Office
P.O. Box 538705
Cincinnati, Ohio 45253-8705

²Fluor Daniel Fernald³
P.O. Box 538704
Cincinnati, Ohio 45253-8704

ABSTRACT

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 containing high concentrations of lead, sulfates, and phosphates. The vitrification process was carried out at temperatures of 1150 to 1350°C. The VITPP processed glass for seven months, until a breach of the melter containment vessel suspended operations. More than 70,000 pounds of surrogate glass were produced by the VITPP. Experiences, lessons learned, and 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 1⁴. The fourth silo, Silo 4, was not used and remains empty. Silos 1 and 2, also known as the K-65 silos, contain radium-bearing, radioactive waste.

³Fluor Daniel Fernald with the U.S. Department of Energy, under Contract No. DE-AC24-92OR21972.

⁴The 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 SO₃, N₂O₅, and CO₂. These, when combined with the oxide, form the traditionally known sulfate, nitrate, and carbonate formats. For example: CaO + SO₃ = CaSO₄.

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

SILO 1			SILO 2			SILO 3		
Component	Measured	Normalized	Component	Measured	Normalized	Component	Measured	Normalized
SiO ₂	50.00	58.06	SiO ₂	51.00	60.23	SO ₃	15.00	17.26
PbO	12.00	13.93	PbO	6.20	7.32	SiO ₂	14.00	16.11
BaO	6.30	7.32	Fe ₂ O ₃	6.10	7.20	MgO	10.00	11.51
CO ₂	3.20	3.72	Al ₂ O ₃	3.40	4.02	P ₂ O ₅	9.30	10.70
Al ₂ O ₃	2.60	3.02	CO ₂	3.40	4.02	Fe ₂ O ₃	8.00	9.21
Fe ₂ O ₃	2.50	2.90	BaO	3.00	3.54	N ₂ O ₃	6.10	7.02
Na ₂ O	1.80	2.09	CaO	2.50	2.95	Na ₂ O	5.90	6.79
SO ₃	1.80	2.09	MgO	1.70	2.01	Al ₂ O ₃	5.30	6.10
MgO	1.20	1.39	SO ₃	1.70	2.01	CaO	4.70	5.41
K ₂ O	0.68	0.79	Na ₂ O	0.88	1.04	CO ₂	1.90	2.19
P ₂ O ₅	0.62	0.72	K ₂ O	0.68	0.80	K ₂ O	1.80	2.07
MoO ₃	0.43	0.50	P ₂ O ₅	0.68	0.80	MnO ₂	0.67	0.77
La ₂ O ₃	0.42	0.49	N ₂ O ₃	0.62	0.73	NiO	0.52	0.60
NiO	0.42	0.49	UO ₂	0.47	0.56	V ₂ O ₅	0.50	0.58
Ce ₂ O ₃	0.41	0.48	NiO	0.36	0.43	Li ₂ O	0.47	0.54
CaO	0.37	0.43	Ce ₂ O ₃	0.33	0.39	CuO	0.41	0.47
N ₂ O ₃	0.29	0.34	TiO ₂	0.33	0.39	CoO	0.36	0.41
TiO ₂	0.28	0.33	La ₂ O ₃	0.29	0.34	UO ₂	0.34	0.39
CoO	0.19	0.22	CoO	0.21	0.25	ThO ₂	0.31	0.36
Nd ₂ O ₃	0.19	0.22	Nd ₂ O ₃	0.16	0.19	As ₂ O ₃	0.29	0.33
SrO	0.08	0.10	ZrO ₂	0.14	0.17	TiO ₂	0.22	0.25
Cl	0.08	0.09	CuO	0.08	0.10	PbO	0.19	0.22
V ₂ O ₅	0.06	0.07	Cr ₂ O ₃	0.08	0.10	MoO ₃	0.18	0.21
CuO	0.06	0.07	V ₂ O ₅	0.08	0.10	Cr ₂ O ₃	0.08	0.10
ZrO ₂	0.05	0.06	MoO ₃	0.08	0.09	F	0.07	0.08
SeO ₂	0.05	0.05	SrO	0.06	0.07	ZnO	0.07	0.08
Cr ₂ O ₃	0.02	0.02	As ₂ O ₃	0.05	0.06	Y ₂ O ₃	0.04	0.04
MnO ₂	0.01	0.02	SeO ₂	0.04	0.05	BaO	0.03	0.04
BeO	0.01	0.01	MnO ₂	0.03	0.04	SeO ₂	0.03	0.03
F	0	0.01	ZnO	0.01	0.01	SrO	0.03	0.03
As ₂ O ₃			Cl	0	0.01	Ce ₂ O ₃	0.02	0.02
CdO			F	0	0.01	ZrO ₂	0.02	0.02
Li ₂ O			BeO			Cl	0.02	0.02
ThO ₂			CdO			Nd ₂ O ₃	0.01	0.01
UO ₂			Li ₂ O			La ₂ O ₃	0.01	0.01
Y ₂ O ₃			ThO ₂			BeO	0.01	0.01
ZnO			Y ₂ O ₃			CdO	0	0.01
Totals	86.12	100.00		84.68	100.00		86.89	100.00

The major characteristic toxic metal compounds of concern in the K-65 wastes are the high concentrations of lead and barium. Silo 3 contains dry, radioactive, metal oxide waste. The major characteristic toxic metal compounds in the Silo 3 wastes are cadmium, chromium, arsenic, lead, and selenium. Silo 3 contains most of the silo's sulfates, phosphate and nitrates. Each silo contains more than 3000 m³ of waste (almost 1 million gallons). The K-65 material is classified as by-product material consistent with the Atomic Energy Act. When the silo was filled, a bentonite clay cap was placed over the residues in Silos 1 and 2. Collectively the four silos are known as Operable Unit 4 (OU4). The Fernald site is operating with five signed Records of Decisions (RODs) for each of the operable units being remediated under the Comprehensive Environmental Response Compensation and Liability Act, as amended, (CERCLA) and agreements between the DOE, the United States Environmental Protection Agency (EPA), and the Ohio EPA (OEPA).

THE SILO WASTES AND THEIR VITRIFICATION

Vitrification of radioactive wastes produces one of the most stable waste forms known. 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 which is a volcanic glass-like rock commonly found in nature. The VITPP was designed and constructed to support the final full-scale treatment facility for the remediation of the Silo wastes. Laboratory and bench-scale treatability studies were conducted before the VITPP. The VITPP facility was designed for a production rate of one metric ton per day for vitrification of K-65 (Silos 1 and 2) and Silo 3 waste residues.

The VITPP primary component was a unique joule-heated melter (see Figure 1) designed for high-temperature service with waste residues that contain significant concentrations of lead and sulfates. The melter was unique due to its three-chamber design. The center, or Main Chamber, contains the corrosive waste slurries, while the melter electrodes were housed in Electrode Chambers on each side of the Main Chamber. Each Electrode Chamber contained benign glass and was designed to isolate five molybdenum electrodes from the corrosive and oxidizing molten glass in the Main Chamber.

The VITPP contains the vitrification melter (furnace) and systems for feed preparation, off-gas treatment, wastewater treatment, a control room, and product-forming and handling which includes a gem-making system. The gem making system cuts the continuous stream of molten glass from the melter into discrete "gobs," which then cool into their final vitrified waste form (called "gems" because of their squashed marble size and shape). A schematic process flow diagram of the VITPP is shown in Figure 2.

TREATMENT OF WASTE WITH HIGH LEAD AND SULFATES

Glass can easily be made from feed that contains lead or sulfate, but in combination is more of a challenge. Commercial glass that contains 36 wt% lead is called crystal which is an 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

Figure 1
Schematic of the Melter

Figure 2
Schematic Process Flow Diagram of the Pilot Plant

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. The lead metal or sulfide can fall to the bottom of the glass melter, 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 (H_2SO_4). 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 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.

Table 2.
All Silo Waste and Glass Composites

Basis: 100 lbs Glass from Slurry

<u>Melter Input -- Feed</u>			Silo 1	Silo 2	Silo 3	Surrogate	Additives	Batch
Oxide	Glass wt%	Moisture wt%	Surrogate lbs	Surrogate lbs	Surrogate lbs	Total lbs		
Al ₂ O ₃	14.03	2.71	0.84	0.96	1.26	3.05	10.72	13.78
B ₂ O ₃	8.82							
H ₃ BO ₃							6.00	6.00
BaO	2.80							
BaCO ₃			1.15			1.15		1.15
BaSO ₄		1.17	1.66	1.27		2.93		2.93
CaO	13.84			0.14		0.14		0.14
CaCO ₃		0.72		0.93		0.93	21.41	22.34
CaSO ₄		20.93		0.08	3.33	3.41		3.41
Fe ₂ O ₃	4.45		0.78	1.68	1.58	4.04		4.04
Fe ₂ (SO ₄) ₃		1.98			0.68	0.68		0.68
K ₂ O	0.85							
K ₂ CO ₃		6.56	0.33	0.29		0.63		0.63
KNO ₃		2.19			0.91	0.91		0.91
Li ₂ O	1.15							
Li ₂ CO ₃		0.96			0.27	0.27	2.60	2.88
MgO	3.40							
MgCO ₃			0.95	1.39		2.33		2.33
MgSO ₄		51.16			2.93	2.93		2.93
Mg ₃ (PO ₄) ₂			0.36	0.35	3.98	4.68		4.68
MnO ₂	0.16				0.15	0.15		0.15
Na ₂ O	6.28							
Na ₂ B ₄ O ₇		30.90					11.38	11.38
Na ₂ SO ₄					1.00	1.00		1.00
Na ₂ CO ₃		3.53	1.00	0.26	0.70	1.95	2.75	4.70
NaNO ₃		0.71		0.27	1.48	1.75		1.75
NiO	0.12				0.12	0.12		0.12
P ₂ O ₅	2.53							
PbO	5.46		3.75	1.71		5.46		5.46
SiO ₂	35.47		15.63	14.04	3.23	32.90		32.90
TiO ₂	0.01							
V ₂ O ₅	0.13				0.13	0.13		0.13
Bentonite	--	14.23				4.53		4.53
CO(NH ₂) ₂	--						3.32	3.32
SO ₃ in glass	0.50							
Total Solids	99.98	na	26.44	23.36	21.75	76.08	58.19	134.27

Note:

Glass elemental composition shown as oxides.
The surrogates that were used for the silo residues is shown in the columns above. Another column shows the additives that were used for making the glass.
Amounts are shown with moisture.
Bentonite adds to the Al₂O₃, SiO₂, etc.

Later runs substituted:

Chemicals for bentonite to help prevent blockage in the feed system.
CaSO₄ substituted for BaSO₄ to determine different sulfate behavior.
H₃BO₃ and Na₂CO₃ substituted for Na₂B₄O₇ to help prevent blockage in feed system.

Water for average 34 wt% Solids 260.65

Total 394.92

Melter Output

Glass 100.00
CO₂ (to off-gas system) 14.41
SO_x 3.45
NO_x 1.58
Urea decomposition products 3.32
Water (H₂O to off-gas system) 272.16
Subtotal 394.92

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 done with 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. 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.

GETTING THE VITRIFICATION PILOT PLANT TO RUN

During startup of the pilot plant, significant difficulties were found with the systems discussed below. 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% uptime 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 Reports⁵, the primary causes for the low uptime of the pilot plant were due to inadequacies in the slurry feed, the off-gas systems, and melter discharge chamber.

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

⁵Operable Unit 4 Vitrification Pilot Plant Phase I Interim Treatability Study Report, Campaign 2, Report No. 40110-WP-0002, Revision 1, December 13, 1996. Operable Unit 5 Vitrification Pilot Plant Phase I Interim Treatability Study Report, Campaign 4, Report No. 40110-WP-0003, Revision 1, March 1997.

- Sharp bends in the piping that restricted flow and provided areas for solids to collect
- Too small diameter piping and too 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.

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, diluting slurries that 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 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 and the off-gas system relied 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 cause channeling through the bed. Replacing the desiccant bed was time consuming and resulted in reduced plant uptime. 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 Center 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 caused blockage of 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_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. Glass frit was frequently added to the Electrode chambers to limit foaming and keep the electrodes covered.

FAILURE OF THE MELTER

Melter problems were mostly the result of the design of the melter and materials of construction -- not its operation. Not directly related to the melter failure (which is described later), but factors reported in the VITPP Melter Incident Final Report⁶ 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, this 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. Without the secondary liner, the glass may freeze and stop advancing as it approaches the cool side of the melter wall.
- Cracks in the partition wall between the Main Chamber and each Electrode Chamber appear to have formed or opened during the melter Acceptance Test during Campaign 1. The Acceptance Test was overseen by the melter vendor's personnel around the clock. The partition wall was made from high-chromium 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 to be 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 SO₂ 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. Similarly, 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.
- The electrodes were eroding and producing metallic lead from the lead-bearing waste glass leaking into the Electrode Chambers. The mechanism is as follows:

⁶ Vitrifaction Pilot Plant Melter Incident: Final Report, Report No. 40100-RP-00019, February 1997.

- Sharp bends in the piping that restricted flow and provided areas for solids to collect
- Too small diameter piping and too 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.

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, diluting slurries that 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 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 and the off-gas system relied 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 cause channeling through the bed. Replacing the desiccant bed was time consuming and resulted in reduced plant uptime. 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 Center 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 caused blockage of 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_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. Glass frit was frequently added to the Electrode chambers to limit foaming and keep the electrodes covered.

FAILURE OF THE MELTER

Melter problems were mostly the result of the design of the melter and materials of construction -- not its operation. Not directly related to the melter failure (which is described later), but factors reported in the VITPP Melter Incident Final Report⁶ 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, this 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. Without the secondary liner, the glass may freeze and stop advancing as it approaches the cool side of the melter wall.
- Cracks in the partition wall between the Main Chamber and each Electrode Chamber appear to have formed or opened during the melter Acceptance Test during Campaign 1. The Acceptance Test was overseen by the melter vendor's personnel around the clock. The partition wall was made from high-chromium 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 to be 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 SO₂ 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. Similarly, 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.
- The electrodes were eroding and producing metallic lead from the lead-bearing waste glass leaking into the Electrode Chambers. The mechanism is as follows:

⁶ Vitrification Pilot Plant Melter Incident: Final Report, Report No. 40100-RP-00019, February 1997.

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. A small portion of the molten glass overflowed the container.

ANALYSIS AND ROOT-CAUSE OF THE MELTER FAILURE

The melter failed because of the melter's design and construction — not its operation. The VITPP Melter Incident Final Report identified the main reasons why the melter failed as:

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

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 down into the refractory insulation understructure of the melter. 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. Note that the understructure material in the melter was not selected for corrosion control, but for the insulation properties.

The root cause as determined in the melter incident 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. Plus, the material 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 lead metal that caused early erosion of the melter refractories. However, this appears not to be the case. Samples of glass from each campaign run were analyzed and the redox (ratio of $\text{Fe}^{+2}/\text{Fe}_{\text{total}}$) was always below 0.2. Lab results show that the redox needs to be more than 0.6 before lead precipitation problems start. 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.

PATH FORWARD

Because of the VITPP experience, DOE-FEMP 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 corrected during the VITPP operating period. A good deal of information was generated on the treatment of the silo waste and for the design of a final remediation facility. Experience gained was first-of-a-kind vitrification with a three chamber, high-temperature melter. Much of the information and experience from the VITPP operation will be useful for future work with vitrification throughout the DOE complex.

This technical information was prepared as an account of work sponsored by an agency of the United States Government. Reference herein to specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not 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, or Fluor Daniel Fernald, its affiliates or its parent companies.

M98004663

Report Number (14) FEMP-2541

Publ. Date (11)

19970718

Sponsor Code (18)

DOE/EM, XF

UC Category (19)

UC-2000, DOE/ER

DOE