

Transportable Vitrification System Demonstration on Mixed Waste

CONF-980905--

by

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A document prepared for SPECTRUM '98 at Denver, CO, USA from 9/13/98 - 9/18/98.

DOE Contract No. DE-AC09-96SR18500

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Publication Date: April 22, 1998

Keywords: vitrification, mixed waste, wastewater sludge, glass,
Oak Ridge Reservation, melter

Retention: Permanent

A paper to be presented at:

Spectrum '98
Denver, CO
September 13-18, 1998

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ABSTRACT

The Transportable Vitrification System (TVS) is a large scale, fully integrated, vitrification system for the treatment of low-level and mixed wastes in the form of sludges, soils, incinerator ash, and many other waste streams. It was demonstrated on surrogate waste at Clemson University and at the Oak Ridge Reservation (ORR) prior to treating actual mixed waste. Treatment of a combination of dried B&C Pond sludge and CNF sludge was successfully demonstrated at ORR in 1997. The demonstration produced 7616 kg of glass from 7328 kg of mixed wastes with a 60% reduction in volume.

Glass formulations for the wastes treated were developed using a combination of laboratory crucible studies with the actual wastes and small melter studies at Clemson with both surrogate and actual wastes. Initial characterization of the B&C Pond sludge had not shown the presence of carbon or fluoride, which required a modified glass formulation be developed to maintain proper glass redox and viscosity. The CNF sludge challenged the glass formulations due to high levels of phosphate and iron.

The demonstration was delayed several times by permitting problems, a glass leak, and electrical problems. The demonstration showed that the two wastes could be successfully vitrified, although the design glass production rate was not achieved. The glass produced met the Universal Treatment Standards and the emissions from the TVS were well within the allowable permit limits.

I. INTRODUCTION

The stabilization and disposal of mixed wastes, which contain both hazardous and radioactive materials, is a significant waste management challenge to the Department of Energy (DOE) complex. A large portion of

these wastes is suitable for treatment by vitrification as demonstrated by laboratory and small-scale melter demonstrations on both actual and surrogate wastes. The Department of Energy's Office of Science and Technology together with DOE's Oak Ridge Operations Office sponsored a demonstration of the TVS on actual mixed waste. Westinghouse Savannah River Company worked with Lockheed Martin Energy Systems to apply field scale vitrification to actual mixed waste at Oak Ridge Reservation's East Tennessee Technology Park (ETTP, formerly the K-25 Site). Prior to the application of the TVS to actual mixed waste it was tested on surrogate K-25 B&C Pond waste.

The TVS is a large scale, fully integrated, vitrification system for the treatment of low-level and mixed wastes in the form of sludges, soils, incinerator ash, and many other waste streams. The unit is designed to be transportable and easily decontaminated. Equipment is primarily housed in modules that can be sealed for over-the-road transportation. Major modules include feed preparation, melter, offgas, and control/services. Slurried or dry feed is introduced to the feed preparation module where it is blended with glass forming additives. A slurry feed system then pumps the waste/additives mixture to the melter. The melter module contains a joule-heated cold-top melter manufactured by EnVitCo Inc. of Toledo Ohio. The melter is refractory lined, with a separate chamber for the glass drain. Offgas is processed in a separate emissions control module. Glass product is poured into steel containers that are stored for eventual disposal.

II. PROJECT HISTORY

In 1993, DOE identified a need to move mixed-waste vitrification technology from the laboratory to the field as rapidly as possible and felt that the technology was mature enough to allow field-scale demonstration on actual

wastes using units that would be prototypic of full-scale waste treatment equipment. The DOE Office of Science and Technology Mixed Waste Focus Area then sponsored Westinghouse Savannah River Company (WSRC) and Lockheed Martin Energy Systems (LMES) to specify, procure, test, and operate a field-scale demonstration using transportable equipment.^{1,2}

The original specification for the TVS was issued by WSRC and preliminary proposals for the TVS were solicited in September 1993. A technical evaluation team reviewed and ranked the proposals. After additional reviews, EnVitCo Inc. was selected to provide a detailed proposal. The contract for the TVS was then awarded to in August 1994. In parallel, WSRC opened a dialogue with LMES to explore candidate waste streams at the ORR for the first TVS vitrification campaign. After some preliminary work, a group of wastewater treatment sludges was selected.

After fabrication and acceptance testing of the TVS at EnVitCo's facility in Erwin TN, the TVS containing solidified glass was disassembled and transported to Clemson SC, where it was reassembled for surrogate testing by WSRC and Clemson University's Environmental Systems Engineering personnel in September 1995. A series of modifications and upgrades was completed prior to surrogate operations at Clemson. The TVS was operated from December 1995 through early March 1996, processing about 7600 kg of surrogate B&C pond waste to produce 11600 kg of glass. Following this surrogate waste campaign, the melter was flushed with glass cullet because laboratory testing had suggested that the waste glass composition could devitrify (crystallize) in the melter during cooldown.

Modifications associated with Oak Ridge site-specific requirements and repairs were then completed and the TVS was transported to the Oak Ridge K-25 Site in June 1996. LMES assumed responsibility for TVS assembly at Oak Ridge, which was completed in September 1996, with WSRC and EnVitCo providing technical assistance. The TVS started up in September 1996 for further testing with surrogate B&C Pond waste feed and training of LMES operators. WSRC provided 24 hour technical oversight during operations.

Following surrogate operations, a demonstration processing 80,000 kg of actual mixed waste was planned. A temporary authorization (TA) for the mixed waste demonstration was issued by the state of Tennessee in October 1996, but contained unexpected requirements that could not be met. Uncertainty about these permitting issues resulted in a decision to place the TVS in cold shutdown following completion of the B&C surrogate run by again flushing the melter with glass cullet.

A glass leak incident occurred in November 1996 while flushing the melter with cullet following two months of surrogate feed operation. The cause of the glass leak was determined and a decision was made to repair the melter and continue with the planned mixed waste demonstration in late 1997 following repair of the TVS. Design modifications to prevent another glass leak were identified and melter repairs were completed in April 1997. The melter was filled with glass cullet and preparations were made for restarting.

During the delay period resulting from the glass leak, additional testing conducted at WSRC, ORR, and at Clemson in crucibles and small melters provided a basis for including mixed waste sludge from the ETTP Central Neutralization Facility (CNF) in the demonstration by vitrifying a blend of B&C Pond and CNF sludges.

A revised final TA was issued by the state of Tennessee in July 1997. The repair expenses and delays from the glass leak created time and funding limitations that would not allow completion of processing the originally planned 80,000 kg of mixed waste. Heatup of the melter and additional surrogate operations were then started in late July. Resolving a series of equipment problems that occurred during these surrogate operations delayed the start of actual mixed waste operations until mid-September 1997. Due to this additional delay, DOE decided to extend support for TVS mixed waste melter operations through the end of October 1997. From September 26–October 19, 1997, twenty feed batches containing 7328 kg (16,158 lb) of actual mixed waste were successfully vitrified in the TVS.

III. WASTE CHARACTERIZATION, GLASS FORMULATION AND PROCESS CONTROL

The approximate compositions of the B&C Pond and CNF wastes are shown in Table I. For the B&C Pond waste, the initial characterization did not identify the presence of carbon or fluoride, so the surrogates used for initial glass formulation development and for melter testing, including the extensive surrogate testing at Clemson, did not contain these. Moreover, treatment of the CNF sludge had not been considered, so the need to handle high levels of iron, sulfate, and phosphate was not considered.³ This table also shows the variability of the compositions of both wastes. For example, the glass formers CaO and SiO₂ in B&C Pond sludge varied from 17-22% and 40-54%, respectively. This wide variation in waste glass formers from batch to batch mandated adjustment of the glass formers added to each batch.

The glass system chosen for immobilization of these wastes was the soda-lime-silica (Na₂O-CaO-SiO₂, or SLS) system. This glass was chosen because of the high calcium

Table I. Compositions of Actual B&C Pond and CNF Sludges Processed (Weight Percent Oxide Basis)

Oxide	B&C Pond Sludge		CNF Sludge	
Ag ₂ O	~0.002		NA	
Al ₂ O ₃	11.0	(8.2-15.0)	3.14	(2.86-3.60)
As ₂ O ₃	0.045	(0.035-0.050)	0.055	(0.040-0.091)
BaO	0.033	(0.027-0.042)	0.100	(0.041-0.122)
CaO	19.8	(17.1-22.2)	14.9	(13.4-16.3)
CdO	0.002	(0.002-0.003)	0.008	(0.008-0.010)
Cr ₂ O ₃	0.068	(0.062-0.084)	0.112	(0.105-0.117)
CuO	0.057	(0.049-0.071)	0.390	(0.364-0.416)
Fe ₂ O ₃	6.29	(5.05-8.01)	31.0	(29.3-32.5)
FeO	1.41	(1.14-1.80)	6.97	(6.59-7.30)
K ₂ O	1.71	(1.25-2.28)	0.62	(0.44-1.00)
Li ₂ O	0.045	(0.012-0.045)	0.015	(0.009-0.024)
MgO	1.22	(1.09-1.46)	0.94	(0.85-1.05)
MnO	0.49	(0.17-0.84)	1.11	(0.84-1.71)
Na ₂ O	0.42	(0.31-0.50)	2.01	(1.49-2.63)
NiO	0.40	(0.35-0.45)	0.068	(0.059-0.073)
P ₂ O ₅	1.10	(0.87-1.44)	20.5	(18.5-21.9)
PbO	0.037	(0.029-0.041)	0.31	(0.29-0.34)
Sb ₂ O ₃	~0.002		NA	
SiO ₂	49.6	(39.6-53.5)	11.1	(9.7-12.9)
SrO	0.019	(0.016-0.023)	0.035	(0.033-0.036)
TiO ₂	0.87	(0.73-1.06)	0.34	(0.33-0.36)
UO ₂	0.17	(0.11-0.25)	1.89	(1.64-2.03)
ZnO	0.043	(0.025-0.070)	1.07	(1.00-1.18)
ZrO ₂	~0.004		NA	
Total C	~3.950		~2.214	
Cl ⁻	0.159	(0.046-0.159)	0.141	(0.010-0.188)
F ⁻	3.96	(3.16-5.19)	1.26	(0.94-1.44)
NO ₃ ⁻	~0.208		~0.190	
SO ₄ ²⁻	1.02	(0.72-1.38)	1.95	(1.69-2.23)
Solids	~97.350		~17.10	
Calcine	~81.200		~14.20	

Ranges shown in parentheses, NA= not analyzed

and silicon contents of the wastes. Process control of the glass composition and properties is designed to meet both glass processing and waste acceptance criteria.^{4,5,6,7} Glass processing criteria that were applied to the TVS demonstration are given in Table II. Models developed by WSRC were used to predict the glass viscosity, liquidus temperature, and redox ratio ($\text{Fe}^{+2}/\Sigma\text{Fe}$) as a function of the feed and glass compositions. Waste acceptance criteria include the Toxic Characteristic Leaching Procedure (TCLP), precipitation of the metals listed below, and devitrification. Although the TVS was designed to handle formation of a molten salt layer, it was still undesirable to form one, so the limits on chloride, fluoride, and sulfate were applied.

For initial surrogate work, the glass additives used were Na₂CO₃, Li₂CO₃, and SiO₂. Lithium was used for

about one half of the alkali requirement to reduce the glass viscosity. The constraints on the Fe+Mn oxides, phosphate, sulfate, and fluoride were not required as none of these components had been determined to be present in any significant amount. Redox control was not considered critical during the initial surrogate testing activities since there were no species identified that would adversely affect the glass redox.

After completion of the surrogate testing of the TVS at Clemson, additional characterization of the B&C Pond waste was performed and the CNF sludge was identified as a waste for which treatment was desired. This characterization of these wastes showed that B&C Pond waste contained significant amounts of carbon and fluoride that had not been previously identified. CNF sludge was found to contain substantial amounts of iron, phosphate, sulfate, carbon, and fluoride.

In crucible melting tests, waste loadings of B&C Pond waste in the glass of up to 80% could be achieved, but the presence of carbon gave unacceptable redox values greater than 0.5; therefore, an oxidizing agent would be required to adjust the redox into the acceptable range of $0.09 < \text{Fe}^{+2}/\Sigma\text{Fe} < 0.50$. Sodium nitrate is commonly used for redox control, but operating permit constraints were expected to preclude its use. Use of MnO₂ as an oxidant was then successfully demonstrated.

Tests of vitrification of CNF waste showed that waste loadings of only 20% or less could be achieved due to the high phosphate content which, at higher loadings, resulted in devitrification and/or phosphate-silicate glass phase separation. Because of the low waste loading, treatment of a mixture of B&C Pond and CNF sludges was examined. Crucible tests with the actual sludges and minimelter tests with surrogate B&C Pond sludge and actual CNF sludges demonstrated that a 70%/30% waste ratio of B&C/CNF could be successfully vitrified with a total waste loading of about 40-50%.⁸ MnO₂ was again used as the oxidant for redox control. The total waste loading was limited mostly by the phosphate content and the Fe+Mn content. Also, lithium, which was used to reduce glass viscosity, was removed from the glass formulation since the fluoride from both wastes resulted in reduced viscosity.

IV. OPERATIONAL EXPERIENCES

Before beginning the surrogate demonstration at Clemson, modifications and upgrades to the TVS were performed. These included electrical upgrades and improvements to the slurry pump system, offgas system, and dry glass former addition system. Upon completion of the surrogate demonstration, it was determined that additional upgrades would be required prior to mixed waste operations.⁹ Improvements made at ORR included

Table II. Glass Processing Composition Control Criteria

Glass Property or Species	Acceptable Range	Concern
Melting Temperature, T_M	1200-1250 °C	corrosion, volatility
Viscosity	20-100 poise	pourability, corrosion, melt rate
Liquidus Temperature, T_L	$T_M - T_L > 100$ °C	crystallization (devitrification)
Redox	$0.09 < Fe^{+2}/\Sigma Fe < 0.50$	foaming, metals precipitation, electrode wear, electrode alloying, corrosion
Cr ₂ O ₃	<0.5 wt %	precipitation
CuO	<1.0 or	Cu metal precipitation
Fe ₂ O ₃ , FeO, MnO	$Fe_2O_3 + FeO + MnO < 20\%$	spinel formation
NiO	<1.0%	Ni metal precipitation, eutectic melting of Mo
P ₂ O ₅	<2-10%	phase separation, devitrification
TiO ₂	<1.0%	glass devitrification
Cl ⁻	<0.6%	molten salt layer
SO ₄ ⁻²	<1%	molten salt layer
F ⁻	<2%	molten salt layer

installation of a variable frequency drive (VFD) on the offgas system main fan, a dry waste vacuuming system for transfer of waste from drums to the feed hopper, a liquid waste feed system, and improvements to the feed hopper system.

The addition of the VFD for the offgas fan was done to reduce the amount of vacuum on the melter and thus reduce the amount of air inleakage and heat loss.¹⁰ The reduction in air inleakage achieved by improvements made at ORR (see Section V) made it desirable to reduce the fan speed to further reduce inleakage while maintaining an adequate vacuum. However, after the melter rebuild, the air inleakage had increased, so the usefulness of the VFD was not as great as it might have been. The offgas system was generally operated with the main fan operating at 85 or 100% speed. The VFD was useful during melter heatup, where the speed was set low to maintain only a very slight vacuum and minimize heat losses.

The dry waste vacuum system was used to transfer the dry B&C Pond sludge from drums into the waste hopper. This system worked reasonably well with very dry material, but plugged if drums of slightly damp material was vacuumed. The vacuum system used a HEPA vacuum to pull the waste from the drum to a cyclone separator, where the waste fell down into the waste hopper. Some material was collected in the HEPA vacuum and was periodically recycled to a waste drum. The liquid waste addition system operated well, provided the CNF sludge was diluted about 1:1 with water. This sludge, as received, had a consistency similar to peanut butter.

The waste hopper (a square conical hopper with a bottom auger feeder) was modified to add two "air

blasters" to help eliminate bridging that was a problem during surrogate operations. The surrogate B&C waste was a mixture of "Indian red pottery clay", a fine artists clay, and a number of technical grade carbonates, oxides, etc. This mixture was very fine and was susceptible to bridging, especially when damp. The addition of the "air blasters", along with the existing vibrator, worked well to solve these problems. However, when the actual B&C Pond sludge was used, the "air blasters" were rarely needed since the real waste did not bridge like the surrogate had. The actual waste consisted of a substantial amount of dredged soil, which had a much larger particle size than the surrogate. These results show the importance of using surrogates that are not only chemically representative of the waste, but physically representative.

A glass leak occurred from the TVS melter just prior to a planned shutdown in November 1996. The TVS was being shutdown due to delays in receiving the required permits for mixed waste operation. The leak occurred at a joint between refractory blocks in the main melter chamber. The cause of the leak was determined to be due to a combination of design factors and operating methods. The TVS melter uses binding steel to maintain compression on the refractory; during heatup and cooldown, the compression must be adjusted appropriately to eliminate gaps between refractory blocks. During previous heatup and cooldown cycles, the refractory compression may not have been maintained adequately. Improved operating procedures were written to address this problem. The refractory design was also such that it made it difficult to maintain refractory contact. When the melter was rebuilt, design modifications were made to improve refractory compression and fit.

The start of mixed waste operations was delayed about four weeks by offgas system electrical problems that were difficult to diagnose. These problems were finally traced to defective programmable logic controller (PLC) cards that may have been damaged by an electrical transient during the extended outage.

V. MIXED WASTE DEMONSTRATION

The mixed waste demonstration was originally planned to treat 80,000 kg of mixed waste. However, due to the time and funding limitations caused by the glass leak and repairs and the late issuance of the TA in July 1997, the scope of the demonstration had to be limited to less waste. Restart of the TVS occurred on July 30, 1997. One to two weeks of surrogate operation was planned prior to mixed waste operation, but was extended when the offgas system electrical problems occurred. These problems were described in Section IV. Mixed waste operation was started on September 26, 1997.

Utilizing the information from the crucible and minimelter tests, a process control method for control of the glass properties and composition was developed. The quantities of the B&C Pond and CNF wastes, the glass formers (Na_2CO_3 , SiO_2) and the oxidizer MnO_2 were adjusted based on the measured composition and predicted properties of the glass poured from the melter. This type of feedback control system is appropriate where rework of the product (remelting of the glass) is possible (although not desirable). Feedback control can be contrasted with the feedforward control used in the Defense Waste Processing Facility (DWPF), where rework of the glass is not possible. In the DWPF, each batch fed to the melter is well characterized to assure that the glass product will meet the specifications. Feedback control in the TVS is also more acceptable due to the relative size of the melter to the feed batch; one feed batch makes about $1/8^{\text{th}}$ of a melter volume of glass, so an off-spec batch does not have a great effect on the glass produced. In the DWPF, one feed batch makes more than two melter volumes of glass.

The first four batches of mixed waste treated in the TVS contained only B&C Pond waste. The remaining 16 batches contained both B&C Pond and CNF wastes. It was quickly discovered that to control the redox of the glass produced, the quantity of MnO_2 required would eventually cause the $\text{MnO}_2 + \text{Fe}_2\text{O}_3 + \text{FeO}$ limit of 20 wt% to be exceeded. The Fe content of the glass increased with each batch from the iron in both of the wastes. After the fourth batch, the state of Tennessee was contacted for permission to add small quantities of NaNO_3 to the melter feed in place of MnO_2 as an oxidant. Figure 1 shows the glass redox and relative amounts of MnO_2 and NaNO_3 added to each batch.

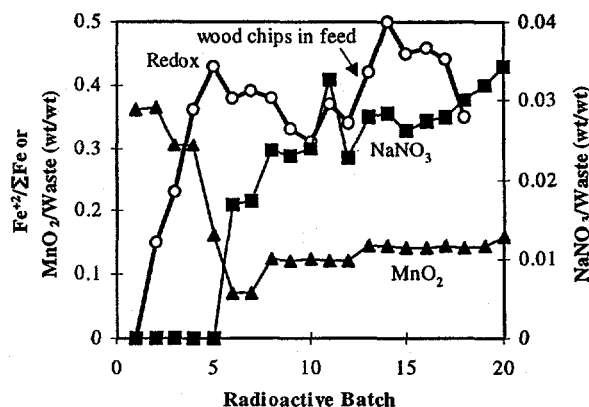


Figure 1. Glass Redox, MnO_2 , and NaNO_3 .

The glass redox measured for glass poured during a given batch is shifted back two batches in Figure 1 because the glass poured during feeding of batch "X" is actually the glass that was produced during feeding of batch "X-2". This delay is due to the construction of the melter; the main chamber where the feed is introduced behaves like a well-stirred tank, whereas the flow in the throat and glass drain chamber is closer to plug flow.¹¹ This plug flow is what introduces the delay. The sharp rise in glass redox from batch 12 to 14 was attributed to a significant amount of wood chips that were found in the B&C Pond sludge.

The desired melter temperature range was 1200-1250°C. To maintain this temperature, the power to the main electrodes was adjusted accordingly. As the demonstration proceeded, the concentration of iron increased from zero to about 7 wt%. The B&C and CNF wastes contained about 7 wt% and 39 wt% Fe_2O_3 on an oxide basis. As the iron content increased, radiant heat transfer within the glass became reduced since iron absorbs infrared radiation. Figure 2 shows the mean power required to maintain 1200-1250°C versus Fe_2O_3 concentration; the data plotted is for both increasing concentration during waste feeding and decreasing concentration during flushing with cullet. The electrode

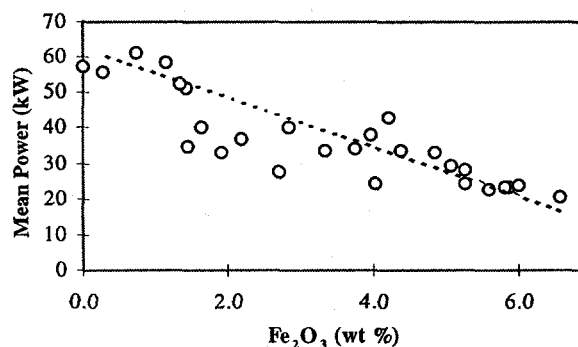


Figure 2. Mean Power to Maintain 1200-1250°C versus Iron Oxide Concentration

configuration of the TVS melter is such that most of the energy is concentrated in the center of the melter. With less radiant heat transfer away from the center, the power required to maintain the center temperature became less. As the radiant heat transfer decreased and the center temperature was maintained constant, the glass temperatures away from the center began to drop.

The glass production rates achieved in the TVS for several different situations are given in Table III. The design rate for slurry feeding is 1640 kg/d. During the surrogate testing at Clemson, a maximum rate of only 1200 kg/d was achieved. This low rate was attributed to high air inleakage (inversely proportional to melter vacuum) into the main melter chamber that resulted in more heat loss than was desirable. At ORR, improvements were made that reduced air inleakage and a maximum rate of 2075 kg/d was found. However, after the melter rebuild after the glass leak, the inleakage had increased, resulting in lower production rates.

for avoidable delays, the production rate would have been about 550 kg/d.

Higher processing rates could have likely been achieved during the mixed waste demonstration by increasing melting temperature. The only measurement of in-glass temperature in the TVS is at the center of the melter where the maximum temperature occurs. A conservative operating approach was taken in not significantly exceeding 1250°C measured at this location. The purpose of the 1250°C limit was to minimize refractory wear. Crucible testing had indicated that excessive refractory wear would occur with the mixed waste glass compositions used at temperatures above 1250°C. However, as the melting rate decreased with increasing glass Fe content, the temperature at the glass-refractory interface would have also decreased. Glass level was drained down ~20 cm at the end of the mixed waste operations and visual examination indicated that no significant refractory wear had occurred.

Table III. Glass Production Rates

Situation	Feed	Maximum Glass Production Rate (kg/d)	Melter Vacuum (inwc)
Design- Slurry Fed	"50 wt% slurry"	1640	
Before Inleakage Improvements	B&C Pond sludge surrogate	1200	0.1-0.3
After Inleakage Improvements	B&C Pond sludge surrogate	2075	1.0-1.6
After Melter Rebuild	Actual B&C Pond Sludge Actual B&C + CNF	1525	0.4-0.6
		1185	
		550 ^a	
		325 ^b	

^a Demo average accounting for outages ^b Demo average

The first four batches fed during the mixed waste demonstration were comprised of B&C Pond waste only. During this time, the maximum glass production rate was about 1525 kg/d, which approached the design rate and was higher than expected based on the previous feeding of surrogate after the rebuild. Visually, the B&C only feed was incorporated into the glass very quickly and it was difficult to build a cold cap on the glass.

Starting with the fifth batch, a mixture of B&C Pond and CNF sludges was fed. Soon after, the maximum achievable melt rate began to decrease due to the radiant heat transfer limitations from the increasing iron content. The maximum rate, calculated from data for batches 13-15 was about 1185 kg/d. The overall processing rate during the demonstration was about 325 kg/d. Contributing to this lower rate were lack of timely analytical turnaround, maintenance, unavailability of feed, offgas line pluggages, shift changes, and site considerations such as housekeeping. Limited personnel availability contributed to all of the delays. Accounting

Overall, the demonstration produced 7616 kg of glass from 3797 kg of dry B&C Pond sludge and 3531 kg of CNF sludge. The volume reduction achieved was approximately 60%, with ~7.8 m³ of waste being converted into ~3.2 m³ of glass.

During feeding of mixed waste, the offgas line directly exiting the melter became plugged four times. No previous plugging problems had been seen with surrogate feeds. In three cases, processing had to be stopped and the plug removed. In one case, the plug was seen to fall out into the melter. Analysis of one of the plugs showed a composition similar to the feed, but enriched in fluoride, sulfate (or sulfur), calcium, magnesium, lithium and sodium. These materials are the more volatile species in the feed; the plug was also found to be relatively depleted in the least volatile species, such as the transition metals and silicon. Carbon was also found in the plug. The actual wastes appear to be more likely to cause pluggage than the surrogates. The likelihood of plugging may have been

increased by a misalignment of the offgas line relative to the melter offgas outlet.

VI. REGULATORY PERFORMANCE

The mixed waste demonstration was subject to a number of permitting requirements, including offgas emissions and wastewater handling. Wastewater generated was treated at the ETTP Central Neutralization Facility. Offgas emissions were subject to maximum allowable generation rates for metals, acid gases, and radionuclides. The metals, hexavalent chromium, halides, and total particulate were measured by EPA methods.

Measured emission rates and the regulatory limits are shown in Table IV. The melter outlet values were for sampling from the offgas line from the melter to the quencher. Rates indicated by "<" were below the detection limit. Except for Ba and Hg, all of the stack metals were below the detection limits, so the actual removals of these were higher than the reported values. Several of the metals (Ag, As, Be, Cd, Co, Se, Tl) were below the detection limits at both the melter outlet and stack. The removal found from actual operation ranged from 95.87 to 99.96% for metals, except for Ba and Hg. The low value for Hg is expected since the offgas system was not designed to remove mercury, but the low value for Ba was unexpected and is assumed to be due to undetermined contamination or measurement error. Overall, the TA limits for all species were easily met.

Radionuclide emissions were monitored to determine the Effective Dose Equivalent (EDE), which is an estimate of the dose to the nearest receptor from the stack. The TVS operated within radionuclide emission limits specified for the system. The operation of the stack continuous radionuclide emissions sampling system did, for the most part, operate within expected design parameters. Problems were encountered with the ability to obtain continuous stack velocity readings with the original in-situ pitot tube system due to high moisture content of the effluent. Additionally, throughout the mixed waste operation, stack temperature measurements identified that during the course of daily operations the stack temperature varied sufficiently resulting in occasional problems maintaining isokinetic sampling conditions.

The measurement of individual radionuclides included identifying all that contributed >10% of the total EDE. Based on actual stack emission measurements, Tc-99, Th-228, and U-234 contributed about 27, 31, and 13%, respectively, whereas Th-228, Th-230, and Np-237 were predicted to contribute >10%. The difference between the predicted and the actual radionuclides emitted is not unexpected. The retention of the radionuclides in the vitrified material, the offgas pollution control system removal efficiencies, and the actual radionuclide contents of the waste streams impacted the actual radionuclide emissions.

Table IV. Offgas Emissions. *Italicized values indicate both melter outlet and stack below detection limit.*

Species		Melter Outlet	Stack	TA Limit	Percent Removal
Ag	μg/s	<9.59 ± 0.2	<0.396 ± 0.005	212	95.87
As	μg/s	<95.9 ± 1.8	<3.96 ± 0.05	323	95.87
Ba	μg/	50.1 ± 7.7	33.7 ± 7.9	4950	32.69
Be	μg/s	<9.59 ± 0.18	<0.396 ± 0.005	17.1	95.87
Cd	μg/s	<9.59 ± 0.18	<0.396 ± 0.005	61.8	95.87
Co	μg/s	<9.10 ± 0.18	<0.214 ± 0.002		97.64
Cr	μg/s	60.2 ± 6.2	<1.49 ± 0.19		>97.52
Hg	μg/s	157 ± 19	<104 ± 76	2860	34.11
Mn	μg/s	12813 ± 12923	8.60 ± 11.88		99.93
Ni	μg/s	362 ± 34	<2.14 ± 0.02	84.2	>99.41
Pb	μg/s	61.8 ± 8.2	<0.214 ± 0.002	1300	>99.65
Sb	μg/s	31.3 ± 2.8	<0.396 ± 0.005	1480	>98.74
Se	μg/s	<192 ± 4	<7.92 ± 0.11	91.4	95.87
Tl	μg/s	<9.59 ± 0.18	<0.396 ± 0.005	21900	95.87
U	μg/s	601 ± 63	<0.213 ± 0.002	None	>99.96
Cr ⁺⁶	μg/s	Not Measured	<0.130 ± 0.003	14.0	
Cl	μg/s	Not Measured	<15.4 ± 0.3	None	
HCl	μg/s	Not Measured	24.4 ± 2.7	16600	
HF	μg/s	Not Measured	<60.6 ± 4.8	None	
Particulate	mg/s	192 ± 31	0.529 ± 0.551	None	99.72
Particulate @ 7% O ₂	mg/m ³ (dry)	4915 ± 380	9.00 ± 9.67	45.8	

Several glass samples from the end of the demonstration were combined and analyzed by the Toxic Characteristic Leaching Procedure. Table V shows that the glass was well below the Universal Treatment Standard (UTS)¹² limits for all species. The concentration ranges in the feeds and in the glass are also shown for comparison. Mercury was not expected to be found in the glass due to its volatility.

Table V. TCLP Results for Composite Glass Sample

Element	Feed Range (mg/kg)	Glass ^a (mg/kg)	TCLP Results (mg/L)	UTS Limits (mg/L)
Ag	3.3-5.0	not measured	<0.04	0.30
As	<4.9-21	<307	<0.4	5.0
Ba	59-91	319	<1	7.6
Cd	2.8-5.0	<18	<0.02	0.19
Cr	63-82	273	<0.04	0.86
Hg	0.18-21	not measured	<0.0002	0.025
Se	<4.8	not measured	<0.005	0.16
Pb	110-258	<325	<0.2	0.37

^a Average analyses of samples used for TCLP composite.

CONCLUSIONS

The TVS mixed waste demonstration showed that a mixture of sludge wastes of variable compositions could be successfully vitrified to produce a glass product that met the Universal Treatment Standards. Although the amount of waste treated was less than the original goal due to funding limitations, the demonstration showed that the TVS could be used to treat larger quantities of waste. A number of problems were encountered prior to and during the demonstration. Many of these problems were equipment problems that could occur in any process, and some were specific to the TVS system. All were successfully overcome, but a few additional improvements could be made to improve the reliability of the TVS for future operations.

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