Sellafield Thermal Treatment Trials Using
Advanced Joule Heated Ceramic Melter Technology - WM-10110

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ABSTRACT

The viability of thermal treatment using vitrification to immobilize two types of Sellafield intermediate level wastes (ILW) has been successfully demonstrated in proof-of-concept trials. The testing employed a type of Joule Heated Ceramic Melter (JHCM) technology that incorporates active mixing of the melt pool. Melt pool mixing improves heat and mass transport, increases waste processing rates, thereby reducing systems size and/or operating duration, and therefore overall treatment costs. Simulants for two Sellafield ILW streams—a Magnox sludge and a sand/clinoptilolite ion exchange waste slurry—were developed for testing in this work. Glass formulations were developed and tested for each of the two ILW streams. Acceptable glass formulations that met all processability and product quality constraints were selected for testing on a small-scale continuously-fed vitrification system. Two tests of nominally 50-hour duration were completed. Data were collected to characterize operating conditions, processing rates, and glass and off-gas compositions for mass balance. Key performance objectives included minimum non-active additives; maximum volume reduction for the wastes; maximum retention of radionuclide and chemotoxic elements; minimal secondary wastes that require other processing; maximum passivation and stabilization of wastes; and meeting product compliance requirements. Test results demonstrate that vitrification using JHCM technology is well suited to immobilize the two Sellafield waste streams tested. The required system size and operating duration are well within the realm of prior experience of this technology. The technology offers the potential to significantly reduce lifecycle cost because the high volume reductions minimize the volume of treated wastes to be disposed, while the glass waste form offers superior waste form performance compared to almost all alternatives.

INTRODUCTION

Sellafield Ltd sought bids for proof-of-concept trials in order to understand the plant and equipment required to thermally process a variety of intermediate level waste (ILW) feeds into Radioactive Waste Management Directorate (RWMD) compliant waste package forms [1]. The trials were intended to provide a technical and scientific evaluation with particular attention to the issues around mass and activity balance and durability of the waste form. Energy*Solutions* and the Vitreous State Laboratory (VSL) at The Catholic University of America (CUA) have extensive experience in various aspects of radioactive waste vitrification using the Joule Heated Ceramic Melter (JHCM) technology and were selected to perform this study.

In joule heated ceramic melters (JHCMs), waste and glass forming chemicals or glass frit are fed onto the surface of the molten glass pool to form a "cold cap." The rate controlling feed-to-glass conversion reactions occur in this region. The essential melt-rate limiting processes are the transport of heat to this region to fuel the conversion reactions and the mass transport of the reaction products away from this region. In traditional JHCMs, the electrical energy supplied to the molten glass pool by joule heating is transported to the cold cap region by natural thermal convection, which is relatively inefficient in the viscous glass melt. Mass transport is similarly limited. In advancing the JHCM technology, Energy*Solutions* and VSL have demonstrated on very large scale melters that active mixing of the glass pool using Energy*Solutions*' patented bubbler technology significantly increases the glass production rate by 300% - 400% or more. This is a significant advance for radioactive waste treatment as the size of the

melter can be dramatically reduced over a non-agitated melter and the radioactive waste can be treated in less time than with a non-agitated melter. As a result, the overall cost for using the JHCM technology for treating radioactive waste is significantly reduced as smaller melters can be utilized (which requires smaller shielded cells and smaller support equipment) and the waste is processed more quickly (which reduces the overall life cycle cost to treat the waste).

In the present work, a DuraMelter 10 (DM10) melter system was used to demonstrate processing of the two simulated Sellafield waste streams, mass balance of waste components, and product quality. This test platform was used previously to evaluate glass formulations and processing characteristics for a variety of HLW and LAW simulated waste streams for the U.S. Department of Energy [2-6]. Prior to melter testing, appropriate waste simulants were developed and suitable glass formulations were designed based on a series of crucible melts and subsequent characterization of the crucible glasses. The present work on glass formulation and melter testing builds on extensive previous work performed at VSL to achieve high waste loadings and processing rates for a variety of waste streams of diverse compositions.

The principal objective of the work described in this report was to develop suitable glass formulations for the two Sellafield waste streams and to demonstrate the processing of the simulated wastes with glass forming chemicals on the DM10 system. The key objectives stated in the "Specification of the Sellafield Thermal Treatment Development Programme – Proof of Concept Phase" [1] for the technology are:

- Minimum non-active additives;
- Maximum volume reduction for the waste solids;
- Maximum retention of radionuclide & chemotoxic elements;
- Minimal secondary wastes that require other processing;
- Maximum passivation & stabilization of waste;
- Meet the RWMD product compliance requirements.

WASTE COMPOSITIONS AND FORMULATION OF GLASSES

Two separate waste streams were tested: Magnox sludge and a slurry consisting of sand/clinoptilolite loaded with radioactive species from the Site Ion Exchange Effluent Plant (SIXEP) at Sellafield. Tables I and II summarize the compositions of the two wastes, respectively. The following describes how the wastes were simulated in glass formulation development and melter tests.

As seen in Table I, the most abundant components in the Magnox sludge are uranium and magnesium, with the other components present at < 5 wt% on an oxide basis. Although radioactive uranium could be used in small scale tests during glass formulation development, it needed to be substituted in waste simulants in larger scale testing in order to reduce costs. Non-radioactive neodymium and zirconium were used as surrogates for uranium; the substitution was made on a weight basis, with half of the uranium replaced by neodymium and the other half by zirconium (by weight). Other radionuclides were present in the Magnox sludge at levels of < μg/ml (wet sludge) and are negligible on a weight basis. However, in order to demonstrate the effectiveness of vitrification in immobilizing these elements, surrogates for these components were included in the simulant. Table I lists the surrogates used in the formulation of the simulant. Surrogates were spiked at elevated levels for analytical purposes; if completely retained, they would be present in the final glass product at 0.1 wt% (oxide basis). Components that were present at < 0.5 wt% (oxide basis) were excluded from testing, with the exception of lead, chromium, and nickel—these metals were included so that their immobilization in glass could be evaluated. These three metals were each spiked at a concentration equivalent to 0.5 wt% in the final glass product (oxide basis).

Table I. Compositions of the Sellafield Magnox Sludge and Surrogates Identified for the Radioactive Components.

Waste Component	Concentration[1] (mg/ml or Bq/ml)	Oxide	Oxide wt%	Component/Surrogate in Simulant
U	1.00E+02	U_3O_8	35.81%	Nd and Zr
Mg	9.70E+01	MgO	48.84%	Mg
Cl	8.20E+00	Cl	2.49%	Cl
Ca	8.00E+00	CaO	3.40%	Ca
K	6.00E+00	K_2O	2.19%	K
Na	5.60E+00	Na_2O	2.29%	Na
Fe	3.10E+00	Fe_2O_3	1.35%	Fe
Al	2.90E+00	Al_2O_3	1.66%	Al
S	9.40E-01	SO_3	0.71%	S
Pb	6.20E-01	PbO	0.20%	Pb
Zn	5.20E-01	ZnO	0.20%	Zn
Cu	3.50E-01	CuO	0.13%	Cu
P	3.40E-01	P_2O_5	0.24%	P
Ba	3.20E-01	BaO	0.11%	Ba
Pu	2.90E-01	PuO_2	0.10%	See Below
Cr	2.50E-01	Cr_2O_3	0.11%	Cr
Ti	2.00E-01	TiO_2	0.10%	Ti
Ni	1.40E-01	NiO	0.05%	Ni
^{60}Co	1.60E+04	^{60}CoO	Negligible	Stable Co
^{90}Sr	3.00E+07	^{90}SrO	Negligible	Stable Sr
$^{95}Zr/^{95}Nb$	3.20E+04	$^{95}ZrO_2/^{95}Nb_2O_5$	Negligible	Stable Nb
^{99}Tc	6.30E+03	$^{99}Tc_2O_7$	Negligible	Stable Re
^{106}Ru	2.10E+05	$^{106}RuO_2$	Negligible	Not used
^{125}Sb	8.60E+04	$^{125}Sb_2O_3$	Negligible	Stable Sb
^{129}I	1.90E+01	^{129}I	Negligible	Stable I
^{134}Cs	1.20E+05	$^{134}Cs_2O$	Negligible	Stable Cs
^{137}Cs	7.10E+06	$^{137}Cs_2O$	Negligible	Stable Cs
^{144}Ce	1.50E+05	$^{144}Ce_2O_3$	Negligible	Stable Ce
^{241}Pu	2.70E+07	$^{241}PuO_2$	Negligible	Stable Hf
^{241}Am	1.20E+06	$^{241}Am_2O_3$	Negligible	Stable Eu

[1] Concentration unit for major components = mg/ml wet sludge, for negligible (by weight) radionuclides = Bq/ml wet sludge.

Simulation of the SIXEP sand/clinoptilolite waste stream followed a similar approach. A theoretical chemical formula of $Na_6Al_6Si_{30}O_{72} \cdot 24H_2O$ was assumed for the clinoptilolite, while the relative proportion of clinoptilolite to (silica) sand was 10 to 1. Formulation of the simulant started with a 63 wt%-slurry of the sand/clinoptilolite mixture in water. Other non-volatile elements were also present in the waste, but the total concentration amounted to < 0.36 g/ml wet sludge. Further, the most abundant elements were determined to be sodium and aluminum, both of which were already found in clinoptilolite at higher levels. Formulation of the simulant therefore omitted these minor components, but retained the surrogates for radionuclides and spikes of toxic metals (i.e., lead, nickel, and chromium). Surrogates identified in the formulation of the Magnox sludge simulant were also used in this case to replace the

radioactive components. The spike levels for the surrogates and toxic metals were the same as those found in the Magnox simulant.

Table II. Compositions of the Sellafield Sand/Clinoptilolite Slurry and Surrogates Identified for the Radioactive Components.

Waste Component	Proportion/ Concentration[1]	Oxide	Oxide wt%[2]	Component/Surrogate in Simulant
Clinoptilolite[3]	10	NaO	7.18%	Zeolite (ZeoSand®)
Sand (Silica)	1	Al_2O_3	11.80%	Silica Sand
		SiO_2	81.02%	
Pb	2.30E+01	PbO	4.87%	Pb
Ni	8.50E+00	NiO	2.13%	Ni
Cr	6.50E+00	Cr_2O_3	1.87%	Cr
U	1.10E+00	U_3O_8	0.25%	Nd and Zr
Pu	2.50E-01	PuO_2	0.06%	See below
^{60}Co	1.50E+04	^{60}CoO	Negligible	Stable Co
^{90}Sr	6.30E+06	^{90}SrO	Negligible	Stable Sr
$^{95}Zr/^{95}Nb$	8.70E+04	$^{95}ZrO_2/^{95}Nb_2O_5$	Negligible	Stable Nb
^{99}Tc	5.90E+02	$^{99}Tc_2O_7$	Negligible	Stable Re
^{106}Ru	6.00E+05	$^{106}RuO_2$	Negligible	Not used
^{125}Sb	4.80E+05	$^{125}Sb_2O_3$	Negligible	Stable Sb
^{129}I	1.70E-01	^{129}I	Negligible	Stable I
^{134}Cs	7.30E+05	$^{134}Cs_2O$	Negligible	Stable Cs
^{137}Cs	6.10E+07	$^{137}Cs_2O$	Negligible	Stable Cs
^{144}Ce	3.30E+05	$^{144}Ce_2O_3$	Negligible	Stable Ce
^{241}Pu	3.30E+05	$^{241}PuO_2$	Negligible	Stable Hf
^{241}Am	4.80E+04	$^{241}Am_2O_3$	Negligible	Stable Eu

[1] Concentration unit for major components = mg/ml wet sludge, for negligible (by weight) radionuclides = Bq/ml wet sludge; Relative proportion by weight is given for clinoptilolite and sand.
[2] Wt% of Al_2O_3, Na_2O, and SiO_2 given for the sand/clinoptilolite mixture, while wt% for all other oxides are based on remainder of the waste.
[3] Chemical formula used for Clinoptilolite = $Na_6Al_6Si_{30}O_{72}\cdot24H_2O$.

After compositions of the waste simulants were defined, suitable glass formulations were developed for each of the two waste streams using past experience and waste glass databases at VSL. Glasses were prepared at crucible scale (about 400 g) with reagent grade chemicals, which were melted in a platinum/gold crucible at about 1150°C for 2 hours. The prepared glasses were then characterized with respect to chemical compositions and properties important to processability and product quality. Table III summarizes the properties characterized and the associated requirements. Characterization data obtained were fed back for use in the formulation of the next set of glasses. The iterative process was repeated not only to ensure the formulated glasses meet all processing and product quality requirements, but also to optimize the waste loadings.

Table III. Glass Processing and Product Quality Requirements.

Property	Requirement(s)
Volume % Crystals (Processing)	< 1 Volume % at 950°C Preferred, but higher levels may be tolerable
Viscosity (P) at 1100°C (Processing)	10 to 150
Electrical Conductivity (S/cm) at 1100°C (Processing)	0.2 to 0.7
* Product Consistency Test (PCT) per ASTM C1285 Test conducted at glass to water ratio of 1 gram of glass (-100 +200 mesh) per 10 ml of water (90°C) (Product Quality)	B < 16.695 g/l Na < 13.346 g/l Li < 9.565 g/l Normalized mass loss less than that of DWPF-EA reference glass
* Toxicity Characteristics Leaching Procedure (TCLP) per EPA Method SW-846-1311 [7] (Product Quality)	Ag < 5 mg/l; As < 5 mg/l; Ba < 100 mg/l; Cd < 1 mg/l; Cr < 5 mg/l; Hg < 0.2 mg/l; Pb < 5 mg/l; Se < 1 mg/l

* Used in lieu of RWMD requirements, which have not yet been defined.

For the Magnox waste, a total of 11 glasses were formulated and characterized, with waste loadings (oxide basis) ranging from 30 wt% to 40 wt%. Glass-forming additives, which provided Al_2O_3, B_2O_3, Na_2O, and SiO_2, were added in various combinations and proportions to result in the glass formulations. The primary constraints in developing glass formulations for the Sellafield Magnox sludge was the formation of crystals (forsterite, Mg_2SiO_4) in the glass melt and durability of the glass product. In spite of these challenges, glass formulations suitable for immobilizing the Magnox waste were successfully developed and a formulation with 35 wt% waste loading was identified for melter testing.

Glass formulation efforts for the sand/clinoptilolite waste were relatively straightforward because the major components in the waste simulant (i.e., SiO_2 and Al_2O_3) are highly compatible with typical silicate-based waste glasses. Formulations with considerably higher waste loadings of 75 wt% to 80 wt% were developed and tested, with the addition of B_2O_3, Li_2O, and Na_2O. In addition to meeting all processing requirements, the formulated glasses performed significantly better in leach tests than the corresponding limits for the US HLW repository (PCT) and US hazardous waste disposal (TCLP); these criteria were employed in place of those specified by the RWMD since they have not yet been defined. A confirmatory melt was performed with a commercially available clinoptilolite zeolite (ZeoSand®) to ensure it could be melted to form a borosilicate glass at 1150°C. Although the analyzed composition of ZeoSand® differed from the assumed chemical formula of $Na_6Al_6Si_{30}O_{72} \cdot 24H_2O$—part of the sodium in the theoretical formula was replaced by potassium, calcium, and magnesium—melting of the zeolite to give a borosilicate glass proceeded without any difficulty. The substitution of other alkali and alkaline earth metals for sodium had little impact on the glass formulation or properties. The glass formulation selected for melter testing has a waste loading of 75 wt%. The glass was selected because of its lower viscosity, which is more favorable for melter processing. Some of the properties characterized of the selected glass are given in Table IV.

Table IV. Selected Characterization Data for the Crucible Glass (75% Waste Loading) Prepared for the Sand/Clinoptilolite Waste.

Crystals after Heat-Treatment at 950°C for 70 hours	None
Melt Viscosity (P) at 1100°C	121.0
Electrical Conductivity (S/cm) at 1100°C	0.314
Normalized PCT Boron Release (g/l)	2.310
Normalized PCT Lithium Release (g/l)	1.970
Normalized PCT Sodium Release (g/l)	1.472
TCLP Chromium (mg/l)	0.07
TCLP Lead (mg/l)	0.16

MELTER OPERATIONS

Glass formulations developed to meet all processability and product performance requirements for the two Sellafield waste streams were processed as simulated wastes and glass forming chemicals on the DuraMelter 10 (DM10) vitrification system at VSL. The simulated wastes were prepared at VSL using reagent grade chemicals and commercially available zeolite (ZeoSand®) and silica sand. Glass forming chemicals provided the sources for B_2O_3, Li_2O, Na_2O, and SiO_2 in Test 1 (sand/clinoptilolite waste), and for Al_2O_3, B_2O_3, Na_2O, and SiO_2 in Test 2 (Magnox sludge).

The DM10 vitrification system consists of a ceramic refractory-lined melter fitted with two Inconel 690 plate electrodes that are used for joule-heating of the glass pool and a bubbler for stirring the melt. The glass product was removed from the melter by means of an air-lift discharge system. The DM10 unit has a melt surface area of 0.021 m^2 and a glass inventory of about 8 kg. The melter feed is introduced into the melter as an aqueous slurry through recirculation loop to a peristaltic pump.

An objective of these tests was to determine the rate at which two Sellafield waste streams can be processed and vitrified. In general, the melter configuration and operating conditions replicated those used for previous tests [3-5]. These conditions include a near complete cold cap, which is between 80%-95% melt surface coverage for the DM10 since a 100% cold cap tends to lead to "bridging" in smaller melters. The bubbling rate was optimized to achieve the maximum production rate throughout testing. Average feed, glass production, and waste processing rates are summarized in Table V.

As seen in Table V, the glass production rate for the Magnox waste (Test 2) is significantly faster than that for the sand/clinoptilolite waste (Test 1). The difference in glass production rate between the two Sellafield waste feeds can be attributed to the glass composition and property differences. Previous tests have demonstrated that glass compositions higher in silica and alumina that are more viscous tend to process more slowly than glass compositions that are higher in boron and less viscous [6, 8]. The sand/clinoptilolite waste glass is higher in silica and alumina; it has a higher viscosity than that of the Magnox waste glass and therefore processed more slowly, as expected. The processing rate could likely be increased by glass compositional adjustments but possibly at the expense of waste loading. The *waste*

processing rate, however, is higher for the sand/clinoptilolite waste as result of the much higher waste loading for the sand/clinoptilolite waste (75% vs. 35% on an oxide basis)

Table V. Summary of Sellafield Melter Test Conditions and Results.

Test			1	2
Test Duration (hr)			60.1	37.25
Feeding Interruptions (hr)			5.4	0.65
Net Slurry Feeding (hr)			54.7	36.6
Feed		Waste	Sand/Clinoptilolite	Magnox Sludge
		Oxide Waste Loading	75%	35%
		kg glass/kg feed	0.30	0.49
		Feed Used (kg)	227.8	143.8
		Overall Feed Rate (kg/hr)	3.79	3.86
		Net Feed Rate (kg/hr)	4.16	3.93
Overall Average Glass Production Rate (kg/m^2/day)[1]			1299	2162
Net Average Glass Production Rate (kg/m^2/day)[1]			1428	2200
Overall Average Waste Oxide Processing Rate (kg/m^2/day)[1]			974	757
Average Bubbling Rate (lpm)			3.3	1.9
Average Temperatures (°C)		Glass, 2" from floor	1163	1146
		Glass, 4" from floor	1160	1139
		Electrode	1090	1110
		Plenum, thermowell	474	551
		Plenum, exposed	433	530
Average Electrical		Voltage (V)	40	38
		Current (amps)	132	143
		Power (kW)	5.3	5.4

[1] Glass production rates calculated from feed data.

Target processing conditions were achieved throughout the majority of the melter tests and included bubbling rate adjusted to maximize the production rate, a melt pool temperature near 1150°C, and a complete cold cap. Table V lists some of the average parameters measured during the two tests. The sand/clinoptilolite waste used in Test 1 formed a thicker, more refractory cold cap than did the Magnox waste feed, which formed a thinner more regular cap across the melt surface. The measured plenum temperatures largely ranged between 500 and 600°C during Test 2, in contrast to the lower plenum temperatures measured during Test 1. For comparison, glass temperatures were about 20°C higher during Test 1 with the sand/clinoptilolite waste, fluctuating mostly between 1150°C - 1175°C, than during Test 2 with the Magnox waste, which fluctuated mostly between 1130°C - 1155°C. Bubbling of the melt pool was almost twice as high and more variable during Test 1 than Test 2 as a result of the thicker less uniform cold cap formed by the sand/clinoptilolite and waste feed.

The feed and glass compositions were processed without significant difficulties during these tests, with two minor exceptions during Test 1. At the onset of Test 1, some foaming on the glass surface was observed that contributed to poor cold cap conditions and therefore difficulties in optimizing the feed rate.

Review of the feed recipe suggested that the nitrates used to introduce various spike and surrogate compounds to the feed led to foaming in the viscous glass. Small amounts of sucrose were then added to the feed (3.9 g per kg feed) in proportion to nitrates using an algorithm developed and routinely used for high nitrate feeds [4-5, 9]. Cold cap conditions subsequently improved. However, the sand/clinoptilolite waste feed was never as fluid and evenly spreading over the melt surface as was the Magnox waste feed used during Test 2. Another difficulty with the sand/clinoptilolite waste feed arose while mixing the last feed batch. After approximately two hours of blending the feed batch, the feed thickened significantly to form a viscous paste. Although the feed was successfully fed into the melter to complete the test, this is an issue that warrants further evaluation prior to scale up.

Feed samples from each test were analyzed to confirm physical properties and chemical compositions. Samples were taken during melter testing from an inline sampling port. All samples were measured for density, pH, water content, glass conversion ratio, and oxide composition by x-ray fluorescence (XRF) spectroscopy.

About 140 kg of glass was produced during the melter tests. The glass was discharged from the melter periodically using an airlift system. The discharged product glass was sampled at the end of each test by removing sufficient glass for the various analyses. Compositions of glass samples were analyzed by XRF. The vast majority of the glass samples after the glass pool reached steady state showed compositions that compared very well to their corresponding target values and feed sample analyses. Halogens, sulfur, and rhenium were found below target for almost all glasses due to volatilization from the glass pool and cold cap. Glass samples also underwent leach testing using the PCT and TCLP. All results are consistent with the data obtained for the crucible glasses, demonstrating the good chemical durability of the glass products. In spite of their relatively high spike concentrations, TCLP metals were released from the glasses at levels considerably beneath their regulatory limits (Table IV).

OFF-GAS EMISSIONS AND MASS BALANCE

Melter emissions were monitored during each melter test for a variety of gaseous components, most notably CO, NH_3, SO_2, and NO_x, by Fourier Transform Infra Red Spectroscopy (FTIR). The off-gas system temperature is maintained well above 100°C beyond the sampling port downstream of the high efficiency particulate air (HEPA) filter in order to prevent analyte loss due to condensation prior to monitoring. No SO_2 or HCl was detected in either of the tests and no CO and NH_3 were detected during Test 2. Byproducts of incomplete organic combustion were only detected during Test 1 as a result of the addition of small amounts of sugar to mitigate foaming during that test. The most abundant nitrogen species monitored was NO, which is consistent with previous tests [3-5, 9] in which nitrates and nitrites were included in the feed. The measured concentrations of most monitored components increase with increasing feed nitrogen oxide content and feed rates.

The melter exhaust was sampled in triplicate for metals/particles according to 40-CFR-60 Methods at steady-state operating conditions during tests with each feed composition. Particulate emissions from the melter constituted on average 0.57 and 0.78 percent of feed solids for Tests 1 and 2, respectively. This level of carryover is well within the range observed during earlier melter tests [10]. The higher percentage of carryover during Test 2 is probably attributable to the presence of the volatile species chlorine and sulfur in the Magnox waste stream. Particulate carryover did not increase with increased bubbling rate and glass temperature as observed in several previous melter tests [3, 10-11], due presumably to the small magnitude of the bubbling and glass temperature changes as compared to the higher concentration of volatiles in the Magnox waste stream.

The measured volatility of feed components was consistent with extensive testing previously performed with high-level waste (HLW) and low-activity waste (LAW) feeds [3-6, 8-11]. As expected, the feed

elements emitted at the lowest melter DF were halogens, rhenium, and sulfur. Other elements exhibiting volatile behavior in some of the tests include boron and alkali metals. Iodine was exclusively detected as a gaseous species, also consistent with previous observations.

An elemental mass balance was calculated for all feed constituents except for hydrogen, carbon, nitrogen, and oxygen. The results presented in Table VI show excellent mass balance closure for the vast majority of the elements. All elements except for rhenium and iodine in Test 1 and chlorine, cesium, sulfur, rhenium, and iodine in Test 2 are represented in the glass at 90% of the feed or greater. Virtually all of the iodine is emitted from the melter, consistent with previous tests [10]. The percentages of cesium and rhenium retained in the glass are consistent with testing conducted at similar molar ratios of the two elements for HLW glasses for the sand/clinoptilolite wastes and for LAW glasses for Hanford wastes [12]. Increasing the ratio of rhenium to cesium would result in higher loss of cesium from the glass. High total recoveries were measured for chromium due to corrosion of melter bricks and hafnium due to its presence as a contaminant in zirconium.

Table VI. Elemental Mass Balances across the DM10 Vitrification System.

Ele-ment	Test 1			Test 2		
	%			%		
	Glass	Emissions	Total	Glass	Emissions	Total
Al	101	0.2	101	102	0.1	102
B	100	2.5	102	100	0.8	101
Ca	100	0.3	100	115	0.4	116
Ce	100	1.3	101	100	1.1	101
Cl	—	—	—	43	NA[1]	NA
Co	110	0.6	111	100	< 0.4	100
Cr	114	2.0	116	118	2.4	120
Cs	90	9.5	100	80	35.7	116
Eu	110	0.7	111	100	< 0.4	100
Fe	103	0.3	103	164	0.3	164
Hf	110	0.8	111	310	0.4	310
I	< 10	102.1	102	< 10	87	87
K	91	1.3	92	90	7.8	98
Mg	96	0.2	96	99	0.2	99
Na	106	0.9	107	95	2.0	97
Nb	90	1.8	92	100	0.6	101
Nd	100	0.7	101	105	0.2	105
Ni	110	0.8	111	120	0.2	120
Pb	98	1.0	99	108	2.4	110
Re	40	83.1	123	20	83.6	104
Sb	110	3.0	113	90	1.0	91
Si	99	0.2	99	100	0.1	100
S	—	—	—	70	51.7	121
Sr	110	0.8	111	110	0.4	110
Zr	111	0.3	111	108	0.1	108

[1]NA = Not Available.

PRELIMINARY JHCM SIZING AND WASTE VOLUME REDUCTION

Information obtained from the glass formulation work as well as the small scale melter testing can be used to calculate the size of a joule heater ceramic melter needed to process the sand/clinoptilolite and the Magnox waste streams. From the results of the glass formulation work and the demonstrated waste loadings that were achieved, the mass of glass produced per mass of dry waste was determined to be 1.083 kg glass/kg of dry waste and 2.039 kg glass/kg of dry waste for the sand/clinoptilolite and Magnox wastes, respectively. Therefore, the total mass of glass to be produced for the two waste streams would be 3,234 metric tons. These figures are based on the waste quantities (1200 m^3 of each waste type) and waste densities (890 and 849 kg dry waste/m^3 of wet waste for sand/clinoptilolite and Magnox, respectively) as reported in the Sellafield, Ltd specification [1].

Once the total volume of glass to be produced is determined, the melter glass pool can be sized so that processing can be completed in the desired time frame. Table VII provides the size of the melter over a range of durations and glass production rates. Table VII assumes an average facility reliability, availability, and maintainability (RAM) of 80%, which is based on actual operating experience from the West Valley Demonstration Project and Energy*Solutions* experience from operating the M-Area vitrification facility at the Savannah River Site. Table VII shows that at an average processing rate of 1500 kg of glass per square meter of glass pool surface per day over a six-year period would result in a melter with a glass pool surface area of 1.23 square meters. This size is attractive since it corresponds to an operating duration that is within the demonstrated lifetime of typical joule heated ceramic melters. This melter would have essentially the same surface area as the DM1200 melter (1.20 m^2) that is currently operating at the VSL. The average overall production rate determined for the Magnox waste is 2162 kg/m^2/day (Table V), considerably faster than 1500 kg/m^2/day. Using the specific processing rates determined for the two wastes in the DM10 tests, it can be calculated that a 1.0 m^2 melter will be sufficient to process the two waste streams within six years. It is therefore concluded that a melter with a glass pool surface area of 1.00 m^2 – 1.25 m^2 would be needed to process all of the sand/clinoptilolite and Magnox waste at Sellafield within the typical lifetime of a joule heated ceramic melter, thereby precluding the need for melter change-out.

Table VII. JHCM Sizing (Melt Pool Surface Area in m^2) for Various Glass Production Rates and Processing Durations.

Processing Duration, yrs	Melter Glass Production Rate, kg/m^2/day		
	1000	1500	2000
3	3.69	2.46	1.85
4	2.77	1.85	1.38
5	2.21	1.48	1.11
6	1.85	1.23	0.92
7	1.58	1.05	0.79
8	1.38	0.92	0.69

Blending the two waste streams has the potential to significantly reduce the total amount of glass that is produced, because of the compatible nature of the waste chemistries from a glass formulation perspective. The loading of the sand/clinoptilolite waste stream is limited by melt viscosity due to the high silicon and aluminum content. Conversely, the Magnox loading is limited by crystallization (and durability) due to the high magnesium content. Blending the two wastes reduces the concentrations of all of these species. From another perspective, a significant amount of silica must be added to form the Magnox waste glass,

whereas that additive is provided by the sand/clinoptilolite waste stream in the blended waste approach. Although the extent of the benefit of blending was not explicitly tested, it is possible to make some rough projections based on the data that were collected.

When the two streams are treated separately, the average overall waste oxide loading is 49 wt%. Considering magnesium as the most limiting constituent in the blended waste, a waste loading of ~75 wt% could be achieved for the same magnesium concentration in the final glass as was tested for the Magnox waste alone (~16 wt%). Allowing some margin for incorporation of other waste constituents, a waste loading of ~65 wt% would appear to be quite possible for the blended stream. This would produce 2453 metric tons of glass, which is about 24% less than that obtained by treating the two streams separately. For the same assumed treatment duration of six years, this would provide a corresponding reduction in the size of the melter and support equipment that would be needed. A further benefit would be that the product durability would likely be significantly better than that of the glass produced from the Magnox stream alone at the presently assumed loading.

Volume reduction of the two waste streams treated separately can be calculated using the estimated mass of glass to be produced from each waste, the density values measured on the glass samples taken from the melter tests, and the stated volume of 1200 m^3 for each waste stream [1]. The glass samples recovered from the sand/clinoptilolite test had a measured density of 2.415 g/ml, while samples from the Magnox test had a higher density of 2.760 g/ml. The volumes of glass corresponding to 1157 and 2077 metric tons of glass produced from the sand/clinoptilolite and Magnox wastes are calculated to be 479 m^3 and 753m^3, respectively. The volume reduction factors for each of the 1200 m^3 waste streams are therefore 2.5 for the sand/clinoptilolite waste and 1.6 for Magnox waste; the overall volume reduction factor for both streams is about 1.95. The higher volume reduction of the sand/clinoptilolite waste stream is attributable to the higher waste loading. However, if the two waste streams are blended before treatment, the overall volume reduction may be increased further. For example, assuming a waste loading of 65 wt% and a glass density of 2.59 g/ml would lead to a volume reduction factor of 2.5.

SUMMARY AND CONCLUSIONS

Energy*Solutions* and the VSL at The Catholic University of America performed thermal treatment trials with simulated Sellafield ILW feeds to demonstrate the potential of JHCM technology for a range of wastes. The two wastes selected for treatment trials were legacy Magnox sludge and a process waste consisting mostly of zeolite and silica sand. The results of these tests provided the basis for determining the size of the melter and the time required to treat the Sellafield waste streams, the quality of the vitrified waste form, the nature of the vitrification exhaust from treating Sellafield wastes, the retention of radionuclides and toxic elements in the vitrified product, and the potential volume reduction of the Sellafield waste streams.

Compositions of simulants were defined for the two Sellafield waste streams, followed by development of glass formulations. The formulated glasses were prepared at crucible scale and characterized to ensure processability (minimum secondary phase, melt viscosity and electrical conductivity) and product quality as determined by PCT and TCLP. Acceptable glass formulations achieved waste loadings of 35% and 75%, on an oxide basis, for the Magnox and sand/clinoptilolite waste streams, respectively. The selected glass formulations were processed as simulated waste and glass-forming chemicals on the DM10 vitrification system. Over 370 kg of feed was processed to produce nearly 140 kg of glass in these tests. The two tests are summarized below in the order in which they were conducted:

- Test 1: 60-hour test processed a simulated sand/clinoptilolite waste. Achieved an average glass production rate of 1299 kg/m^2/day with an average bubbling rate of 3.3 lpm and an average glass temperature of 1163°C.

- Test 2: 37-hour test processed a simulated Magnox waste sludge. Achieved an average glass production rate of 2177 kg/m^2/day with an average bubbling rate of 1.9 lpm and an average glass temperature of 1146°C.

To demonstrate the effectiveness of JHCM technology in treating the selected Sellafield waste streams, performance against the key objectives stated in the "Specification of the Sellafield Thermal Treatment Development Programme – Proof of Concept Phase" [1] is summarized below:

- Minimum non-active additives
  - Waste loadings of 35 wt% and 75 wt% (waste oxide basis) were obtained for the Magnox and sand/clinoptilolite streams, respectively.
- Maximum volume reduction for the waste solids
  - Volume reduction factors of 1.6 and 2.5 (ratio of waste volume to glass volume) were obtained for the Magnox and sand/clinoptilolite streams, respectively. The overall volume reduction factor for both streams is about 1.95. However, if the waste streams were blended, the estimated volume reduction factor would be even higher (about 2.5).
- Maximum retention of radionuclide and chemotoxic elements
  - With a few exceptions of the volatile components, all elements are retained at 90% of the feed or greater. Glass samples from the crucible and melter tests were subjected to leach tests (PCT and TCLP) to evaluate product quality. All glass products satisfied both test method criteria, demonstrating the integrity of the glass matrix and the retention of toxic metals upon exposure to aqueous solutions. Glasses performed better than the DWPF-EA benchmark glass in the PCT tests and exhibited TCLP leachate concentrations well below the US EPA regulatory limits.
- Minimal secondary wastes that require other processing
  - Wastes from the off-gas treatment system can be recycled to the melter feed.
- Maximum passivation and stabilization of waste
  - Glass is a highly stable inert material that is resistant to phenomena such as radiation damage, hydrogen generation, and alteration in the environment. It is the internationally preferred material for immobilization of high level nuclear waste.
- Meet the RWMD product compliance requirements
  - Since specific requirements were not available for this work, selected US requirements were used (PCT and TCLP). All glass products easily met both requirements.

In conclusion, based on these results, vitrification using JHCM technology is well suited to immobilize the two Sellafield ILW streams tested. The required system size and operating duration are well within the realm of prior experience with this technology. The high volume reductions offer the potential to significantly reduce lifecycle costs due to the reduced volume of treated waste to be disposed while the glass waste form offers superior waste form performance compared to almost all other alternatives.

AKNOWLEDGEMENTS

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