Vitrification of Sellafield Wastes with High Metallic Magnesium Alloy Content - WM-17495

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ABSTRACT

The Sellafield nuclear complex, located in northwest England, is the largest such site in the United Kingdom. Sellafield Limited, which is the operating contractor for the Nuclear Decommissioning Authority, is evaluating thermal treatment technologies for a potential future facility to process a variety of Intermediate Level Waste sludges and slurries accumulated from historical site operations. In support of that effort, Atkins and the Vitreous State Laboratory (VSL) of The Catholic University of America conducted studies to evaluate the feasibility and implications of installing a joule-heated ceramic melter (JHCM) vitrification system to process a variety of sludge and slurry radioactive wastes at the Sellafield site. These sludges have the potential to contain a significant proportion of reactive metals in localized regions. The metallic fraction derives from unreacted Magnox spent fuel cladding. Thus, an important objective of this work was to investigate the performance of JHCM technology for the treatment of streams with localized regions of high reactive metal contents. The present work was focused on Site Ion Exchange Effluent Plant (SIXEP) Magnox sludges, investigated previously. Suitable waste simulants were developed for the SIXEP Magnox sludge waste stream, which included surrogates for all important radionuclides. High waste-loading, fully compliant glass formulations were designed using a combination of previous experience, extensive waste glass data bases, and small-scale crucible melts. Glasses from the test melts were characterized for properties that are important for processability and product quality. The most viable compositions were then selected for small-scale melter trials to collect information on processing rates and behavior, off-gas and secondary waste compositions, and overall system mass balance. These data were used to support the technology evaluation, which considered such factors as minimization of inactive additions, waste volume reduction, retention of radionuclides, minimization of secondary wastes, and overall process efficiency and effectiveness. The data were also used to develop sizing estimates for the full-scale facility and to estimate treatment durations under various treatment scenarios. A series of tests was then performed with partial replacement of the magnesium hydroxide with a metallic magnesium alloy that is close in composition to Magnox alloy. A commercially available magnesium alloy, Elecktron AZ31B, which has a nominal magnesium content of 95.7%, was used for this purpose. The testing was performed on a DuraMelter 10 (DM10) JHCM system to characterize the melter off-gas, glass product, and the effects of magnesium alloy particle size on feed processing. Data on processing rate and any processing issues, product glass

composition, off-gas composition including hydrogen, and system operating parameters, including flows, temperatures, pressures, etc., were collected and analyzed to evaluate the effects of magnesium alloy on the vitrification process.

INTRODUCTION

The Sellafield nuclear complex, located in northwest England, is the largest such site in the United Kingdom. Sellafield Limited, which is the operating contractor for the Nuclear Decommissioning Authority, is evaluating thermal treatment technologies for a potential future facility to process a variety of Intermediate Level Waste sludges and slurries accumulated from historical site operations. Sellafield Ltd sought bids for proof of concept trials in order to understand the plant and equipment required to thermally process a variety of Sellafield intermediate level waste (ILW) feeds into Radioactive Waste Management Directorate (RWMD) compliant waste package forms [1]. Thermal treatment processes offer a potential alternative approach to the baseline techniques, such as grout encapsulation. The purpose of the trials was to gain confidence in the potential of the technology to treat a range of wastes. These wastes can be categorized radiologically as primarily ILW but also low level waste (LLW). The two physical/ chemical forms of these wastes selected for treatment trials are legacy Magnox sludges and a process waste consisting mostly of zeolite ion exchange media. The trials were intended to provide a scientific evaluation with particular attention to the issues around mass and activity balance and durability of the waste form. Atkins and the Vitreous State Laboratory (VSL) at The Catholic University of America (VSL) in Washington, DC performed thermal treatment trials on the two waste streams, SIXEP Magnox sludge and SIXEP sand/clino, using the Joule Heated Ceramic Melter (JHCM) technology [2, 3].

In previous work for Sellafield Ltd, VSL-Atkins developed and tested glass formulations for SIXEP Magnox sludges [2, 3]. These sludges have the potential to contain a significant proportion of reactive metals in localized regions arising from unreacted Magnox spent fuel cladding. Thus, the principal objective of the present work was to demonstrate and evaluate the performance of JHCM technology for the treatment of streams with high reactive metal contents. Therefore the same waste simulant and glass formulations were employed but with partial replacement of the magnesium hydroxide with a metallic magnesium alloy. A commercially available Mg-Al alloy, Elecktron AZ31B, which has a nominal Mg content of 95.7% (3% Al, 1% Zn, 0.3 Mn), was used for this purpose. The testing was performed on a DuraMelter 10 (DM10) JHCM system to demonstrate processing of a simulated Sellafield waste stream containing a Mg alloy, characterize the melter exhaust, and determine the effects of Mg alloy particle size. This test platform has been extensively used to evaluate glass formulations and processing characteristics for a variety of HLW and LAW simulated waste streams for the U.S. Department of Energy [4-15].

Batches of the waste simulant were prepared with a metal loading equivalent to 15 wt% of the waste solids and combined with the glass forming chemicals required to produce the target product glass composition. The feed was delivered continuously to a DM10 JHCM system, which has a glass production rate of about 40 kg per day depending on the feed and operating conditions. Data on processing rate and any processing difficulties, off-gas composition, and system operating parameters, including flows, temperatures, pressures, etc., were collected. Product glass samples were inspected for the presence of any secondary phases, including metals. Results from tests using the Mg alloy as the primary magnesium source were compared to previous tests conducted with the same glass composition using magnesium hydroxide as the primary magnesium source to investigate the effect of the metallic alloy on the vitrification process.

WASTE COMPOSITION, GLASS FORMULATION, AND MELTER FEED

The composition of the Magnox sludge waste is given in the specification for the Sellafield thermal treatment development programme [1] and shown in Table I. The most abundant waste components are uranium and magnesium with the other component oxides present at less than 5 wt%. Although uranium could be used in small-scale tests for glass formulation development, it needs to be substituted in waste simulants for larger-scale testing in order to reduce costs. Non-radioactive neodymium and zirconium are commonly used as surrogates for uranium. In the present case, since uranium is found at relatively high concentration and in order to simulate the behavior of trivalent and tetravalent oxidation states of uranium, both neodymium and zirconium were used as surrogates in the waste simulant. The substitution was made on a weight basis, with half of the uranium replaced by neodymium (by weight), and the other half by zirconium.

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

Waste Component	Concentration[1] (mg/ml or	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.

Other radionuclides are present typically at sub-microgram levels (per ml of wet sludge) and are consequently negligible on a weight basis. However, in order to demonstrate the effectiveness of vitrification in immobilizing these elements, they need to be included in the simulant to be used in melter tests. For elements that do not have stable isotopes, the following surrogates were used: rhenium for technetium, hafnium for plutonium (cerium is a commonly used surrogate for plutonium but is used presently to replace ^{144}Ce), and europium for americium. Ruthenium was not included for cost reasons. Further, the concentrations of the surrogates are increased in the simulated waste for analysis purpose. Specifically, they are spiked at levels such that they are present in the final glass product at 0.1 wt%, with the assumption that they are completely retained in glass at a waste loading of 50%. The spike levels were adjusted subsequently according to the actual waste loadings. In formulating waste simulants for the melter tests, minor components are omitted to maintain a manageable number of analytes. Components that are present at < 0.5 wt% (oxide basis) in the waste were excluded from the present testing, with the exception of lead, chromium, and nickel — these metals are included so that their immobilization in glass can be evaluated. These three metals are each spiked at a concentration of 1.0 wt% (oxide basis).

A glass was formulated for the Magnox waste stream, UK-Mg-7 [2, 3], with a waste loading of 35 wt%, moderate leach resistance, acceptable processing properties, and acceptable crystallinity. Glass formulation for Sellafield Magnox sludge is limited by crystallization of forsterite (Mg_2SiO_4) and glass durability, as measured by PCT for the present purposes. Glass forming additives that would suppress crystallization from a glass melt tend to degrade the leach resistance of the glass under PCT condition, hence the 35 wt% waste loading. TCLP releases of UK-Mg-7 are acceptable by US EPA regulatory standards; the US TCLP and PCT requirements were used in lieu of RWMD requirements, which have not yet been defined. The viscosity and electrical conductivity at glass melt temperatures are within ranges for JHCM operation. The glass composition was further validated by the production of about 70 kg of this glass through the DM10 with the product being fully characterized and determined to be within acceptable performance parameters [2, 3].

Feed for melter testing was generated by blending the Magnox simulated waste and a magnesium alloy powder as a source for magnesium at a concentration equivalent to 15 wt% of waste solids with glass forming additives targeting the UK-Mg-7 glass composition. The alloy with the highest magnesium content available for testing was Elektron AZ213B with a nominal magnesium content of 95.7 wt%, 3 wt% aluminum, 1 wt% zinc, and 0.3 wt% manganese. This material was available in three size ranges; however, sufficient amounts for sustained melter testing were available only in the 80 to 18 mesh size range (0.18 – 1 mm). Given this availability, a large batch sufficient for producing 20 kg of glass was blended with the 80 to 18 mesh size magnesium alloy for a longer test of at least 8 hours and smaller batches were prepared with the other mesh sizes to evaluate the effect of particle size. The glass forming chemicals used were borax, sodium carbonate, silica, and aluminum hydroxide. Changes made to the feed previously used [2, 3] were: Elecktron Mg alloy used for Mg source in place of $Mg(OH)_2$ at an amount equivalent to 15 wt% of waste solids, all Nd in feed as Nd_2O_3 with no $Nd(NO_3)_3.5H_2O$ in feed, Al_2O_3 omitted from waste, aluminum in Mg metal alloy accounted for, omission of $Eu(NO_3)_3.6H_2O$ from feed, and addition of concentrated nitric acid and water to achieve a pH of 7 prior to the addition of the Mg metal alloy.

Prior to blending the feed batches used for melter testing, several small feed batches of a few hundred grams each were blended to evaluate the potential for hydrogen generation and gross rheological properties. Feed that was not neutralized with nitric acid prior to the addition of the magnesium metal alloy evolved sufficient hydrogen to exceed the flammability limit in the container head space immediately after the addition of the magnesium metal alloy. The feed continued to bubble and evolve hydrogen over the next day until the feed became very viscous. The viscous slurry was similar to that formed from the Magnox sludge with magnesium hydroxide as the primary magnesium source. This indicates that the metal alloy fully converted to magnesium hydroxide shortly after the addition of the magnesium metal alloy. In subsequent small feed batches, the pH was lowered to 7 with the addition of nitric acid prior to the addition of the magnesium alloy. Hydrogen was still generated from these batches but at a much slower rate. Furthermore, the residual reactions did not result in the formation of a viscous slurry after several days. Based on these observations, all feeds prepared for melter tests were neutralized to pH 7 prior to the addition of the magnesium metal alloy, which was added to the batch immediately prior to the start of each test. The addition of nitric acid to the feed has the added benefit of introducing oxidants to the feed to balance the reducing effects of the magnesium metal alloy.

MELTER OPERATIONS

Melter testing was conducted with the DM10 unit, which is 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 was introduced in batches into a feed container that is mounted on a load cell for weight monitoring. The feed was constantly recirculated providing continuous mixing and introduced into the melter by means of a peristaltic pump through a Teflon-lined feed line and water-cooled, vertical feed tube. In each test, the melter was fed to cold-cap-limited conditions while data were collected on feed and glass processing including extensive visual and video observations of the cold cap. Over 41 kg of melter feed containing more than 1 kg of magnesium metal alloy was processed through the melter generating 15.5 kg of glass in these tests.

All tests were conducted targeting the same glass composition at waste loading of 35 wt% on an oxide basis. The tests also employed the same glass former additives, magnesium metal alloy content targeting 15 wt% of waste solids, 1150°C glass temperature, and near complete cold cap coverage. During each test the amounts of feed processed and glass discharged were quantified enabling the calculation of waste processing and glass production rate for each test. A summary of the melter tests that were conducted is provided in Table II. The tests are distinguished below as follows:

- Test 1: 8.8 hour interval processing a simulated SIXEP Magnox waste composition with 18/80 mesh size magnesium alloy. Achieved an average glass production rate of 1374 kg/m^2/day at average bubbling rate of 2.2 lpm. Over 30 kg of feed was processed resulting in the discharge of nearly 10 kg of glass. The feed rate of 3.45 kg/hr was used in most of the subsequent tests. Melter exhaust particulate sample taken for the purpose of calculating elemental mass balances for feed components across the melter.

- Test 2: 1.0 hour interval processing a simulated SIXEP Magnox waste composition with 18/80 mesh size magnesium alloy. Residual feed from Test 1, performed one week earlier, was used to demonstrate the effect of feed aging on processing properties. Achieved an average glass production rate of 1376 kg/m^2/day at average bubbling rate of 0.7 lpm.

- Test 3: 1.0 hour interval processing a simulated SIXEP Magnox waste composition with 80/325 mesh size magnesium alloy. Test conducted to demonstrate the effect of fine grained magnesium metal alloy on processing properties. Achieved an average glass production rate of 1090 kg/m^2/day at average bubbling rate of 0.8 lpm.

- Test 4: 1.0 hour interval processing a simulated SIXEP Magnox waste composition with 18/80 mesh size magnesium alloy. Test conducted for comparison to Tests 2, 3, 5. Achieved an average glass production rate of 1090 kg/m^2/day at average bubbling rate of 0.8 lpm.

- Test 5: 0.9 hour interval processing a simulated SIXEP Magnox waste composition with > 18 mesh size magnesium alloy. Test conducted to demonstrate the effect of coarse grained magnesium metal alloy on processing properties. Achieved an average glass production rate of 1236 kg/m^2/day at average bubbling rate of 0.6 lpm.

An objective of these tests was to demonstrate and evaluate the performance of JHCM technology for the treatment of streams with high metal contents and determine the rate at which a simulated Magnox sludge containing the magnesium metal alloy waste streams can be processed and vitrified. To this end, attempts were made to replicate the melter configuration and operating conditions used for previous tests [4-14]. 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. The feed and glass compositions were processed without significant difficulties during these tests. The most notable observation during processing was the oxidation of the magnesium metal alloy on the glass surface, apparent as flashes of light. This was readily observed in all of the present tests and was not observed in previous tests with same composition with magnesium hydroxide in place of the metal alloy [2, 3]. Another observation during processing was the extensive fuming in the plenum space resulting from water, nitrogen oxides, and particulate release from the cold cap. No obvious differences were observed during tests with various magnesium metal alloy grain size or with the aging of the melter feed.

Table II. Summary of DM10 Tests with Melter Feed Prepared with Simulated Magnox Sludge Containing Magnesium Metal Alloy.

Test		1	2	3	4	5
Slurry Feeding Interval (hr)		8.8	1.0	1.0	1.0	0.9
Feed	Mg Alloy (Elektron)	18/80	18/80	80/325	18/80	> 18
	Feed Used (kg)	30.5	3.46	2.74	3.44	2.86
	Overall Feed Rate	3.45	3.46	2.74	3.44	3.1
	Average Glass Production Rate	1374	1376	1090	1368	1236
Average Bubbling Rate (lpm)		2.2	0.7	0.8	0.7	0.6
Average Temp. (°C)	Glass, 2” from floor	1136	1143	1154	1149	1124
	Glass, 4” from floor	1146	1146	1164	1157	1134
	East Electrode	1106	1088	1114	1124	1118
	West Electrode	1133	1105	1140	1151	1136
	Plenum, thermowell	585	757	724	719	699
	Plenum, exposed	595	755	722	714	695
	Film Cooler Outlet	261	260	258	260	260
Average Electrical	Voltage (V)	29.2	33.0	31.8	33.0	33.4
	Current (amps)	172	154	177	183	180
	Power (kW)	5.2	5.1	5.6	6.1	6.0
	Resistance (ohms)	0.173	0.215	0.180	0.180	0.185
Melter Exhaust Conc.	H_2O (%)	6.1	6.1	5.9	6.0	5.9
	CO (ppmv)	4.9	1.4	2.5	4.4	11.3
	CO_2 (ppmv)	767	714	757	762	803
	HF (ppmv)	5.0	8.9	9.6	11.6	13.7
	NO (ppmv)	1103	1574	1027	822	600
	NO_2 (ppmv)	625	707	740	692	826
	HNO_2 (ppmv)	9.3	19.8	12.9	10.1	6.0
	N_2O (ppmv)	4.2	5.0	2.6	1.9	2.5
	H_2 (ppmv)	68.4	< 1	< 1	< 1	< 1

* – Glass production rates calculated from feed data and target glass conversion ratio

The average feed and glass production rates for the tests are summarized in Table II. The glass production rate obtained for the steady state test was about 1375 kg/m^2/day, which is considerably less than the 2200 kg/m^2/day that was previously achieved with the same Magnox waste feed containing magnesium hydroxide in place of the magnesium metal alloy [2, 3]. The decreased processing rate is attributable to several factors including the decrease in feed solids content (443 g glass per liter feed vs. 800 g glass per liter feed) and the higher nitrate content of the feed in addition to the form of magnesium. The feed rate during the earlier test was only marginally higher (3.9 vs. 3.5 kg/hr), suggesting that the increased feed water content was a major factor in the decreased glass production rate. Despite glass production rates being lower than that in previous tests with the same Magnox waste feed containing magnesium hydroxide in place of the magnesium metal alloy, glass production rates obtained in the present tests were comparable to those for most Hanford HLW waste feeds [8, 11, 13, 14]. Glass production rates determined from short one-hour tests do not represent steady state; however, all but one of the rates obtained were very close to the rate from the longer steady state test.

Target processing conditions, including bubbling rate adjusted to maximize the production rate, a melt pool temperature near 1150°C, and a complete cold cap were achieved throughout the majority of the melter tests. Glass temperatures were within 20°C of the 1150°C throughout the majority of the testing. Contrary to most previously conducted tests on the DM10, glass temperatures closer to the melt pool surface typically average 10°C higher than those lower in the melt pool due perhaps to exothermic reactions occurring on the surface of the melt pool. In keeping with previous DM10 tests, the electrode temperatures were mostly lower than glass pool temperatures by as much as 70°C, depending on which electrode and the time during the test. No temperature increases in the electrodes indicative of heating from reaction associated with the decomposition of the magnesium metal alloy were observed. The plenum temperatures were about 800°C at the start of each melter run series and decreased to 500 - 600°C as the cold cap became established. During the first day of testing, this occurred after about 3 hours of feeding, while this steady state condition was not achieved during the 4.5 hours of the second testing period due to the interruptions in feeding between the tests. The average power usage for the present and previous tests processing the simulated Magnox sludge was about the same (5.2 vs. 5.4 kW); thus, the power required to evaporate the additional water in the present tests was comparable to the amount of power required for the higher rate of glass production.

The glass produced in these tests was discharged from the melter periodically using an airlift system, visually inspected for secondary phases, and sampled for total inorganic analysis. The compositions of glass samples were measured by x-ray fluorescence spectroscopy (XRF). The glass pool composition approached the target concentrations for most oxides by the end of the tests while antimony, cesium, halogens, sulfur, and rhenium were found below target for almost all glasses due to volatilization from the glass pool and cold cap. No secondary phases were observed in any of the glass samples.

OFF-GAS EMISSIONS

Melter emissions were monitored during each melter test for a variety of gaseous components, most notably CO, HF, and NO_x, by Fourier Transform Infra-Red Spectroscopy (FTIR) and H_2 by gas chromatography. Hydrogen was detected in the melter exhaust only during the initial test and after three hours of feed processing. Measured hydrogen concentrations in the melter exhaust stream and measured plenum temperatures are displayed for Test 1 in Figure I. Notice that until the plenum temperature decreases to about 600°C, no hydrogen is detected. Once plenum temperatures reach steady state with the process (between 500 and 600°C), hydrogen concentrations varied over a wide range between 25 and 425 ppmv. Plenum temperatures were mostly greater than 700°C during Tests 2-5 and no hydrogen was detected in the melter exhaust. No hydrogen was detected in previous tests with Magnox sludge but without the magnesium metal alloy even though the plenum temperatures averaged around 550°C indicating that the magnesium metal alloy is responsible for the hydrogen generation. The most abundant nitrogen species monitored was NO for all but Test 5. In a trend opposite to that for hydrogen, the amount of nitrogen monoxide in the exhaust decreases after three hours run time in Test 1. Nitrogen monoxide concentrations mostly ranged between 100 and 300 ppmv while the plenum temperature was above 600°C, and below 100 ppmv when the plenum temperature was below 600°C. The decrease in nitrogen monoxide concentrations was partially compensated for by increases in the nitrogen dioxide concentration. Concentrations of CO, CO_2, and NO_2, were higher and NO was lower during Test 5 than the other tests. As expected, measured concentrations of nitrogen and carbon oxides are considerably greater than those measured during previous tests with the simulated Magnox waste stream as a result of the addition of nitric acid to the feed [2, 3]. No NH_3, HCN, or HCl was detected in any of the tests.

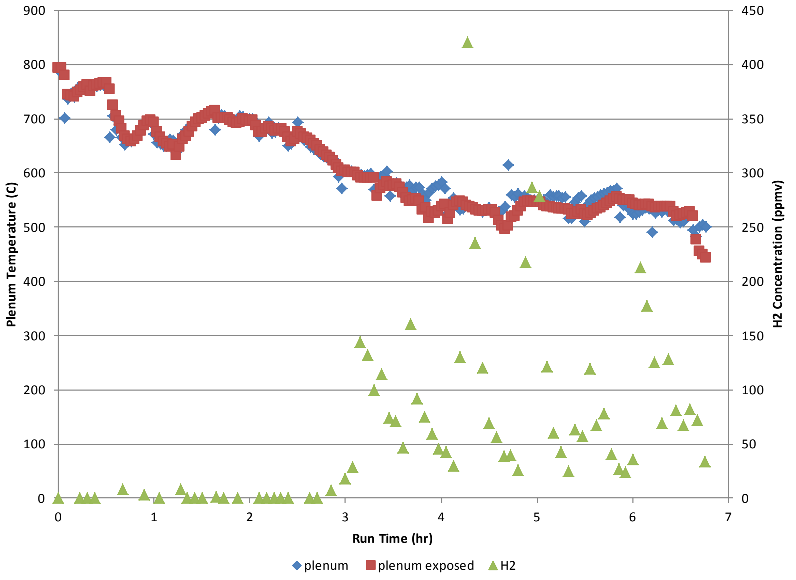

Figure I. Plenum temperatures and hydrogen concentration measured in melter exhaust during Test 1 while processing simulated Magnox waste containing magnesium metal alloy.

The melter exhaust was sampled for metals/particles according to 40-CFR-60 Methods at steady-state operating conditions near the end of the first test; the results are presented in Table III. Particulate emissions from the melter while feeding the Magnox sludge containing the magnesium metal alloy constituted two and a half percent of feed solids, which is over three times higher than in previous tests with magnesium hydroxide [2, 3]. Furthermore, carryover of magnesium is over twenty times greater in the present tests with magnesium metal alloy than in earlier tests with magnesium hydroxide. Almost all elements (except for rhenium and iodine, which were essentially totally lost from the glass during tests with both forms of magnesium) were carried over to the melter exhaust at much higher rates while processing the magnesium metal alloy. The higher percentage of carryover in the present tests with the magnesium metal alloy is attributable to several factors including the magnesium metal alloy itself, which is oxidized in the cold cap creating particulate that is more likely to be entrained into the exhaust stream than magnesium hydroxide. The higher feed water content and nitric acid in the feed also contribute to a more reactive environment in the cold cap as water is volatizing, carrying other feed constituents into the exhaust, and nitrate is reduced to volatile nitrogen oxides. Feed elements emitted at the lowest melter decontamination factor (DF) were iodine and rhenium, which were not retained in the glass in measurable amounts, followed by chlorine, cesium, and sulfur. Higher than typically observed carryover of non-volatile elements such as silicon, aluminum, and iron indicate physical entrainment of particulate feed components.

SUMMARY AND CONCLUSIONS

Thermal treatment trials were conducted with simulated Sellafield ILW feeds demonstrating the potential of thermal treatment technology for a range of wastes including Magnox sludges. Building on previous work [2, 3], the present testing demonstrated the feasibility of directly vitrifying a waste stream containing magnesium metal alloy, the generation of hydrogen associated with reaction of the metal with the alkaline waste or melter feed, the reactions of the magnesium metal alloy in the melter, the consistency of the process over a range of magnesium metal alloy grain sizes, and emissions from the melter while processing the magnesium metal alloy. Oxidation of the magnesium metal alloy on the glass surface was visually evident in these tests. However, no temperature increases in the electrodes, indicative of heating from reactions associated with the decomposition of the magnesium metal alloy, were observed. Power consumption during these tests was similar to that in previous tests without the magnesium metal alloy. Hydrogen generation increased as plenum temperatures fell into the normal operating range but remained in the few hundred ppm range. Particulate emissions from the melter while feeding the Magnox sludge containing the magnesium metal alloy were over three times higher than in previous tests with magnesium hydroxide, which is attributed to increased entrainment resulting from the more vigorous reactions in the cold cap.

Table III. Results from Off-gas Sample Analysis during DM10 Tests with Melter Feed Prepared with Simulated Magnox Sludge Containing Magnesium Metal Alloy.

		Mg Alloy (Elektron 18/80 mesh) 9.28% Moisture, 103% Isokinetic				Mg(OH)$_2$ 7.3% Moisture, 101% Isokinetic [3]			
		Feed (mg/min)	Output (mg/min)	% Emitted	DF	Feed (mg/min)	Output (mg/min)	% Emitted	DF
Particulate	Total	25024	620	2.48	40.4	37808	294.71	0.78	128.7
	Al	164	1.21	0.74	136	263	0.36	0.13	743.8
	B	995	30.4	3.05	32.8	1594	4.76	0.30	345.2
	Ca	160	1.22	0.76	131	257	0.94	0.37	279.6
	Ce	17.1	< 0.10	< 0.50	> 200	27	0.29	1.08	93.7
	Cl	164	123	74.7	1.34	263	NA	NC	NC
	Co	15.7	< 0.10	< 0.64	> 157	32	< 0.10	< 0.31	> 321
	Cr	68.5	3.36	4.91	20.4	110	2.61	2.38	42.2
	Cs	18.9	10.85	57.5	2	30	10.82	35.73	2.8
	Fe	61.6	0.70	1.14	88.0	99	0.26	0.27	399.4
	Hf	17.0	0.13	0.74	134	27	< 0.10	< 0.37	> 272
	I	20.0	<0.10	< 0.50	> 200	32	< 2.0	< 6.25	> 16
	K	120	14.3	11.9	8.38	192	14.94	7.78	13.0
	Mg	1942	91.4	4.71	21.2	3112	7.53	0.24	425.3
	Na	2043	87.4	4.28	23.4	3276	65.16	1.99	50.3
	Nb	14.0	< 0.10	< 0.50	> 200	22	0.13	0.59	170.1
	Nd	1012	0.23	0.02	4451	1622	3.80	0.23	443.0
	Ni	78.6	0.43	0.54	183	126	0.29	0.23	451.8
	Pb	92.9	4.24	4.56	21.9	149	3.51	2.36	42.5
	Re	15.4	11.9	77.4	1.29	25	20.63	83.57	1.2
	S	18.4	13.2	71.6	1.40	30	12.16	41.09	2.4
	Sb	16.7	0.18	1.08	92.8	27	0.27	1.01	101.3
	Si	3278	8.63	0.26	380	5254	4.98	0.10	1082.0
	Sr	16.9	0.10	0.59	168	27	< 0.10	< 0.37	> 272
	Zr	874	2.43	0.28	360	1400	1.46	0.11	1033.3
Gas	B	995	4.35	0.44	229	1594	7.45	0.46	214.3
	Cl	164	< 0.10	< 0.06	> 1641	263	NA	NC	NC
	I	20.0	15.3	76.7	1.30	32	27.95	87.02	1.2
	S	18.4	< 0.10	< 0.54	> 184	30	3.15	10.65	9.4

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REFERENCES

1. “Specification for the Sellafield Thermal Treatment Development Programme - Proof of Concept Phase,” SP/ND-MPG/PROJ/00002, Rev C (2008).
2. K.S. MATLACK, W.K. KOT, H. GAN, I L. PEGG, G. A. DIENER and B. W. BOWAN II, “Sellafield Thermal Treatment Trials Using Advanced Joule Heated Ceramic Melter Technology” WM2010 Conference, March 7-11 2010, Phoenix, AZ
3. K.S. MATLACK, W.K. KOT, N.D. ANGELO and I.L. PEGG, “Sellafield Thermal Treatment Trials Using Advanced Joule Heated Ceramic Melter Technology,” Final Report, VSL-09R1640-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2009).
4. K.S. MATLACK, M. CHAUDHURI, H. GAN, I. S. MULLER, W. GONG, and I.L. PEGG, “Glass Formulation Testing to Increase Sulfate Incorporation,” Final Report, VSL-04R4960-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2005).
5. K.S. MATLACK, W. GONG, and I.L. PEGG, “Small Scale Melter Testing with LAW Simulants to Assess the Impact of Higher Temperature Melter Operations,” Final Report, VSL-04R4980-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2004).
6. K.S. MATLACK, W. GONG, and I.L. PEGG, “Glass Formulation Testing to Increase Sulfate Volatilization from Melter,” Final Report, VSL-04R4970-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2005).
7. K.S. MATLACK, W. GONG, I.S. MULLER, I. JOSEPH, and I.L. PEGG, “LAW Envelope C Glass Formulation Testing to Increase Waste Loading,” Final Report, VSL-05R5900-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2006).
8. K.S. MATLACK, W.K. KOT, W. GONG and I.L. PEGG, “Small Scale Melter Testing of HLW Algorithm Glasses: Matrix 2 Tests,” Final Report, VSL-08R1220-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2008).
9. K.S. MATLACK, S.P. MORGAN, and I.L. PEGG, “Melter Tests with LAW Envelope B Simulants to Support Enhanced Sulfate Incorporation,” Final Report, VSL-00R3501-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2000).
10. K.S. MATLACK, S.P. MORGAN, and I.L. PEGG, “Melter Tests with LAW Envelope A and C Simulants to Support Enhanced Sulfate Incorporation,” Final Report, VSL-01R3501-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2001).

11. K.S. MATLACK, W.K. KOT, H. GAN, and I.L. PEGG, “HLW Enhancement Tests on the DuraMelter™ 10 with Hanford AZ-102 Tank Waste Simulants,” VSL-05R5260-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2005).
12. K.S. MATLACK, H. GAN, and I.L. PEGG, “Glass Formulation and DuraMelter™ 10 Testing with Simulated Idaho HLW Calcine,” VSL-08S1540-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2008).
13. K.S. MATLACK, and I.L. PEGG, “Screening Tests on DuraMelter 10 with C-106/AY-102 Simulant in Support of DuraMelter 1000 Throughput Tests,” VSL-00R2501-2, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2000).
14. K.S. MATLACK, W.K. KOT, F.P. CARDENENAS, and I.L. PEGG, “Screening Tests on DuraMelter 10 with AZ-101 Simulant in Support of DuraMelter 1000 Throughput Tests,” VSL-00R2501-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC (2000).
15. K.S. MATLACK, and I.L. PEGG, “Advances in JHCM HLW Vitrification Technology at VSL through Scaled Melter Testing,” Advances in Materials Science for Environmental and Energy Technologies II: Ceramic Transactions, Vol. 241 (eds J. Matyáš, T. Ohji, X. Liu, M. P. Paranthaman, R. Devanathan, K. Fox, M. Singh and W. Wong-Ng), (2013).