GeoMelt® ICV™ Treatment of Sellafield Pond Solids Waste – 13414

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ABSTRACT

Kurion, Inc., in partnership with AMEC Ltd., is demonstrating its GeoMelt® In-Container Vitrification (ICV)™ Technology to Sellafield Ltd. (SL). SL is evaluating the proposition of directly converting a container (skip/box/drum) of raw solid ILW into an immobilized waste form using thermal treatment, such that the resulting product is suitable for interim storage at Sellafield and subsequent disposal at a future Geological Disposal Facility. Potential SL feed streams include sludges, ion-exchange media, sand, plutonium contaminated material, concrete, uranium, fuel cladding, soils, metals, and decommissioning wastes. The solid wastes have significant proportions of metallic constituents in the form of containers, plant equipment, structural material and swarf arising from the nuclear operations at Sellafield.

GeoMelt's proprietary ICV process was selected for demonstration, with the focus being high and reactive metal wastes arising from solid ILW material. A composite surrogate recipe was used to demonstrate the technology towards treating waste forms of diverse types and shapes, as well as those considered difficult to process; all the while requiring few (if any) pre-treatment activities. Key strategic objectives, along with their success criterion, were established by SL for this testing, namely:

1. Passivate and stabilize the raw waste simulant, as demonstrated by the entire quantity of material being vitrified,
2. Immobilize the radiological and chemotoxic species, as demonstrated via indicative mass balance using elemental analyses from an array of samples,
3. Production of an inert and durable product as evidenced by transformation of reactive metals to their inert oxide forms and satisfactory leachability results using PCT testing

Two tests were performed using the GeoMelt Demonstration Unit located at AMEC's Birchwood Park Facilities in the UK. Post-melt examination of the first test indicated some of the waste simulant had not fully processed, due to insufficient processing time and melt temperature. A second test, incorporating operational experience from the first test, was performed and resulted in all of the 138 kg of feed material being treated. The waste simulant portion, at 41kg, constituted 30wt% of the total feed mass, with over 90% of this being made up

of various reactive and non-reactive metals. The 95 liters of staged material was volume reduced to 41 liters, providing a 57% overall feed to product volume reduction in a fully passivated two-phase glass/metal product.

The GeoMelt equipment operated as designed, vitrifying the entire batch of waste simulant. Post-melt analytical testing verified that 91-99+% of the radiological tracer metals were uniformly distributed within the glass/cast refractory/metal product, and the remaining fraction was captured in the offgas filtration systems. PCT testing of the glass and inner refractory liner showed leachability results that outperform the DOE regulatory limit of $2g/m^2$ for the radiological species of interest (Sr, Ru, Cs, Eu, Re), and by more than an order of magnitude better for standard reference analytes (B, Na, Si).

INTRODUCTION

Feasibility trials were sponsored by the SL Technical Directorate in 2009 to provide data for a technical study into the feasibility and viability of thermal treatment. The technical study was conducted to extend the feasibility, viability and maturity aspects of the technology up the Technology Readiness Level (TRL) scale. SL recognized that thermal treatment provides an alternative approach to the Sellafield Ltd. baseline techniques (e.g., grout encapsulation) and offers a number of benefits, in terms of process and product attributes, including,

1. Passivation and stabilisation of raw waste,
2. Immobilisation of radiological and chemo toxic species,
3. Production of an inert and durable disposal product.

In late 2010/early 2011, SL commissioned GeoMelt to perform a demonstration to support the proposition of directly converting a container (skip/box or drum) of raw solid Intermediate Level Waste (ILW) into an immobilised waste form using its ICV thermal treatment process (1). The wastes of interest included solid wastes with a high metallic content. The immobilised product was to be suitable for disposal in the future Geological Disposal Facility (GDF) in the UK.

The GeoMelt process treats waste combined with glass formers in a refractory-lined ICV container using a proprietary joule-heating vitrification process. The waste/glass mixture is heated to temperatures ranging from 1100 to 1800°C (depending on the glass chemistry and the waste owner's product quality requirements), and in the process 1) organics are destroyed, 2) salts are decomposed, and 3) the materials are fully melted and homogenized. A glass product is produced wherein all radioactive and elemental hazardous constituents are fully immobilized while organic toxic compounds are destroyed

Off-gases produced during processing are safely contained by enclosing the process in a melt vessel that is continuously kept at below-atmospheric pressure. After destruction of 99%+ of organics within the ICV container, the resulting off-gas is drawn through several treatment stages that remove particulates and condensed gases (e.g., water vapor) and non-condensed gases (e.g., NOx, SOx, etc.). The treated off-gas emissions are then released to the atmosphere in compliance with local regulatory requirements. Secondary wastes captured by the off-gas treatment system are either recycled into subsequent ICV treatment runs, or disposed of separately.

OPERATIONAL OVERVIEW

Two tests were performed in April and June 2011, using the 500 liter GeoMelt Demonstration System at AMEC's Birchwood Park facilities in the UK following the Test Plan. For these tests, a 100 liter inner cast refractory vessel provided waste simulant and glass product containment, and was separated from the outer ICV steel vessel by refractory silica sand. Figure 1 provides an external view of the ICV vessel and Figure 2 shows a simplified sketch of the ICV contents.

Figure 1. GeoMelt 500 liter ICV container at Birchwood, UK

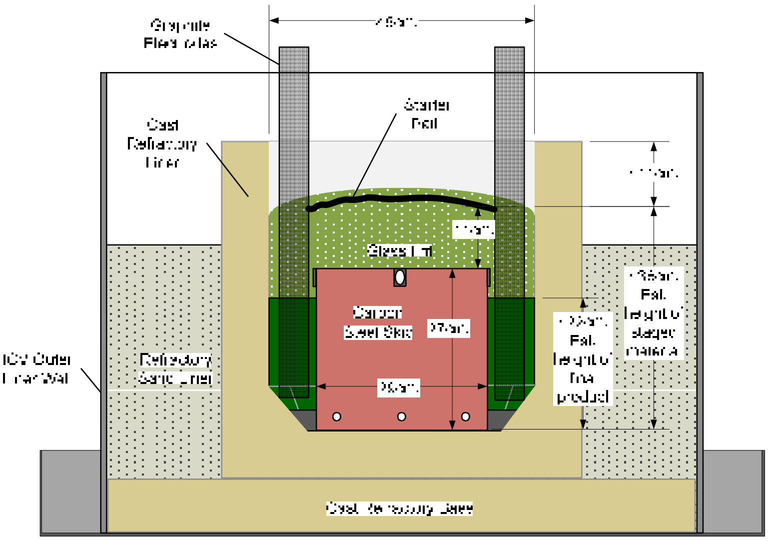

Figure 2. Section sketch of the 500 liter ICV container

Post-melt examination of the first test indicated that some of the waste simulant had not fully processed due to insufficient processing time and melt temperature. A second test was then performed, incorporating operational experience from the first test (2).

Non-radioactive waste simulant was used to 1) replicate the bulk chemistry of the individual waste materials and 2) simulate the trace chemistry of the radiological species found in the wastes. A carbon steel skip, of length, width and height proportional to those of a typical Sellafield pond skip, served to contain the waste simulant and radioactive surrogate tracer metals. Figure 3 shows the carbon steel skip being loaded with various metals and organic materials to be treated. As listed in Table 1, the skip was filled with a range of reactive and non-reactive materials including magnesium rod, misch metal ingots (cerium and lanthanum), stainless steel bar, aluminum rod, MgO, cement and organics (PVC gloves, paper, etc). Table 2 provides a listing of the radioactive tracer surrogates that were added to replicate radiological species found in the SL waste streams.

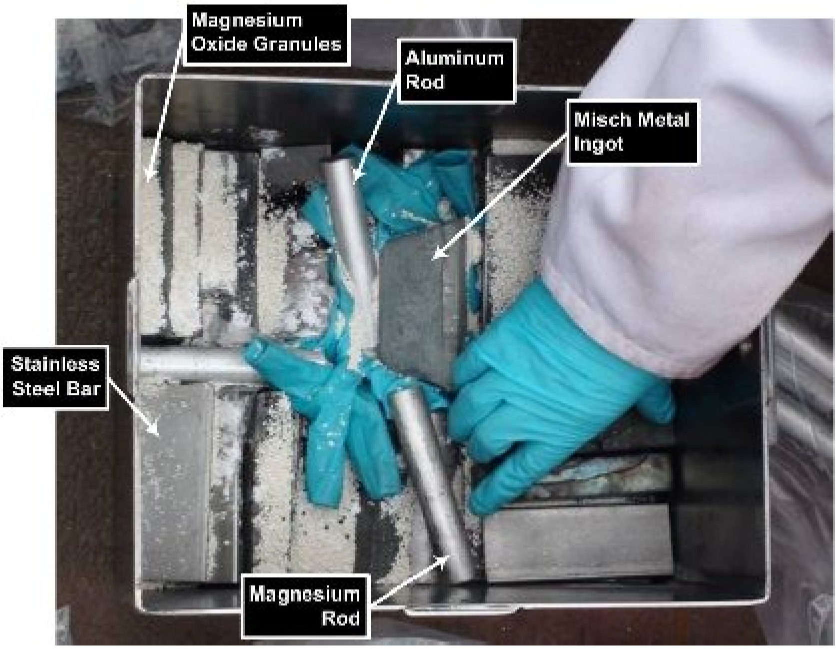

Figure 3. Steel skip partially loaded with waste simulant

Table 1. Inventory of waste simulant materials

Material	**Form**	**Composition (wt %)**	**Mass (kg)**	**Volume (litre)**
Stainless steel	Plate or bars	23.26	9.55	1.19
Mild steel	Skip vessel	25.57	10.50	1.34
Aluminium	Plate or bars	9.26	3.80	1.41
Magnesium	Round bars	4.51	1.85	1.06
Misch Metal (~65% Ce, ~35% La)	Square bars	27.89	11.45	1.75
MgO/Cement/ Organics	Powder/pieces	9.50	3.90	1.40
Total		100	41.05	8.15

Table 2. Tracer metals included with waste simulant

Item	**Radioactive Counterpart**
Eu_2O_3	Plutonium
Cs_2CO_3	Cesium
Re_2O_7	Technicium-99
SrO	Strontium
RuO_2	Ruthenium

Treatment began on the morning of 3 June 2011 and was completed in 16 hours, with power levels ranging from 22 to 28 kW during processing. Other than two short periods when the waste material underwent heightened off-gas production, waste treatment was relatively steady state. The offgas blower maintained a negative atmosphere within the ICV and the offgas components at all times, and each of the various systems operated normally. Table 3 provides a summary of key operational test data.

Table 3. Summary of key operational data

Parameter	Value
Test Location	GeoMelt Facility, Birchwood Park, UK
Start Time (Power to Melt)	3 June, 2011 – 08:42
Stop Time (Melt Power Off)	4 June, 2011 – 01:00
Duration (Melt Power On to Final Off)	16 hours, 18 minutes
Melt Power Rate	22-28 kW after initial power ramp
Feed Type	High Metal Content Simulated SL Waste Stream
Mass of Staged Pre-melt materials	138 kg
Volume of Staged Pre-melt materials	Approx. 95 liters
Average Processing Rate	8.5 kg/hr
Volume of Glass Product Produced	36 liters
Mass of Glass Product Produced	94.2 kg
Volume of Metal Product Produced	4.9 liters
Mass of Metal Product Produced	39 kg

TEST RESULTS

After completion of the test and after the product had sufficiently cooled, the ICV container was disassembled for observation and sampling. All sides of the refractory were inspected and no signs of degradation or structural cracking were found. Additionally, no evidence of erosion at the glass/refractory or metal/refractory interface was apparent. Figure 4 shows the inner treatment vessel being removed from the ICV after the test was completed.

Figure 4. Inner ICV container being removed after test completion

The entire 95 liters of feed material was processed and reduced in volume to 41 liters of a fully passivated two-phase glass/metal product. At 41kg, the waste simulant constituted 30wt% of the total feed mass, with over 90% of this being made up of various reactive and non-reactive metals.

A total of forty three samples were taken from the ICV contents, offgas system piping, and scrubber water. Fifteen samples from various points within the glass and at glass interface surfaces, five samples from the metal phase, and two from the cast refractory vessel were obtained and analyzed for elemental composition using energy-dispersive x-ray spectroscopy (EDX) and laser ablation micro probe (LAMP).

Product Homogeneity

The glass product was shiny with no large voids in the interior. Glass within 25-50 mm below the surface had a more fractured consistency than further below the surface, but had similar color. Some areas had a slightly more opaque grayish mineral-like appearance, as shown in the photo with close-up in Figure 5. Subsequent XRD analyses showed that the major phases in each of the regions consisted of $Ca(Fe,Mg)Si_2O_6$ and $MgLaAlSiO_6$. In addition, smaller amounts of $Ca(Fe,Mg)(CO_3)_2$ was identified in the lower region. These results are consistent with EDX and LAMP analyses and showed no significant different between the upper and lower regions of the glass block. Each region was predominantly amorphous with no large ordered crystal structures and both areas had comparable leach resistance (discussed later).

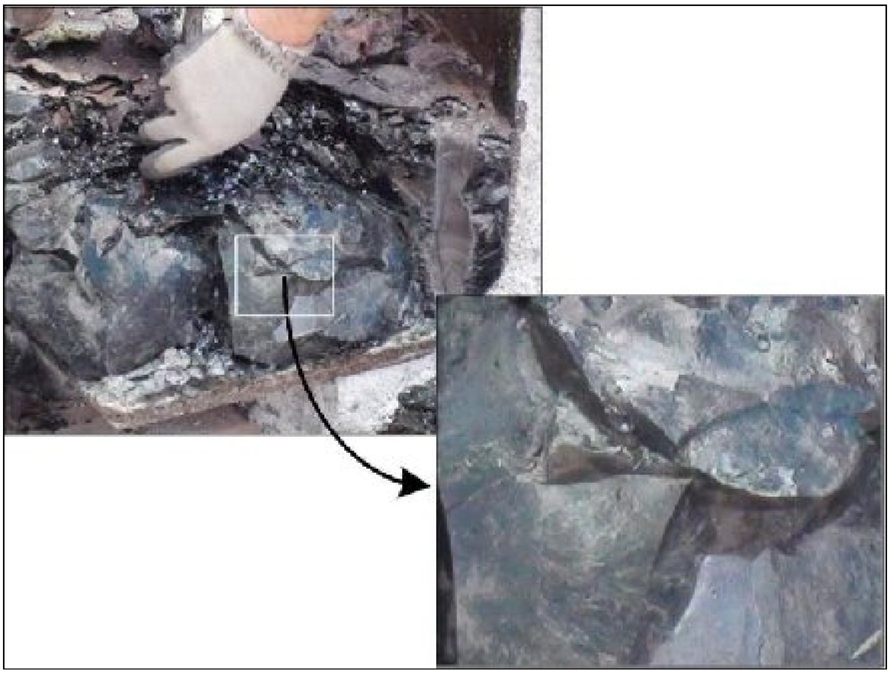

Figure 5 - Glass Block including Close-up View

The metal phase was a solid continuous piece, primarily made up of iron, which had partitioned to the base of the glass product during melting due to its higher density. This piece is shown in Figure 6. Small dark spots were observed in some areas, as shown in Figure 7, but these were later identified via SEM analyses to be specks of glass that had likely been deposited into the metal phase by convective melt currents, and were trapped in place during cooling.

The metal ingot was primarily composed of iron (75%) and silicon (8%). Other major elements included the waste surrogate aluminum (4.5%), chromium (5%) and nickel (2.3%). Very small quantities of magnesium, lanthanum and cerium were present in the metal ingot indicating the majority of these surrogates were oxidized into the glass. For the tracers, a significant fraction of Re and Ru remained in the ingot, while the other tracers predominantly partitioned into the glass. The elemental analysis showed a consistent elemental distribution within the metal ingot.

Figure 6 - Topside of Metal Phase with Two Glass Pieces Attached

Figure 7 – Portion of metal phase showing dark spots

Tracer Metal Distribution

The mass balance distribution of surrogates and other metals of interest within the system, presented as a normalized distribution of the amount recovered, are shown in Table 2. The product showed a very high incorporation of the waste surrogates into the glass, the exceptions being iron (at 8%), which as expected formed the bulk of the reduced metal phase. Of the amount recovered, 91.4 to 99.9% of the tracer metals were retained within the ICV glass/metal product. Strontium, cesium, cerium, lanthanum, and europium were primarily retained in the glass, while ruthenium and rhenium were primarily retained in the metal phase.

Table 4. Indicative mass balance of tracer metals shown as normalized percentage

Element	Normalized Distribution of Surrogate/Tracer Metals (%)									
	Glass	Metal	CRB	***Product Subtotal***	ICV Hood	Pre HEPA Piping	HEPA Housing	Scrubber Water	***Off-gas System Subtotal***	**Total**
Sr	92.0	1.7	3.0	96.7	0.6	0.1	2.6	0.0	3.3	100.0
Ru	0.2	99.7	0.0	99.9	0.1	0.0	0.0	0.0	0.1	100.0
Cs	89.2	0.2	0.0	89.4	7.1	0.2	2.0	1.3	10.6	100.0
Eu	98.8	0.1	0.1	99.0	0.7	0.1	0.1	0.0	1.0	100.0
Re	0.3	91.1	0.0	91.4	5.1	1.2	1.7	0.7	8.6	100.0
Fe	20.7	79.3	0.0	100.0	0.0	0.0	0.0	0.0	0.0	100.0
Al	67.4	29.4	3.1	100.0	0.0	0.0	0.0	0.0	0.0	100.0
Mg	99.2	0.8	0.0	100.0	0.0	0.0	0.0	0.0	0.0	100.0
La	98.7	1.3	0.0	100.0	0.0	0.0	0.0	0.0	0.0	100.0
Ce	99.0	1.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	100.0

Product Leach Resistance

Although a UK regulatory specification for ILW glass leach resistance does not exist, the US Department of Energy uses a standardized Product Consistency Test (PCT) to determine durability of radioactive, hazardous, and mixed waste glasses (3). DOE sets a regulatory limit of 2g/m^2, cumulative, which is also applied here for comparison. PCT leach testing was performed on glass and CRB samples. Results demonstrated that the glass was homogeneous and both it and the CRB had good leach resistance with test results of 0.078 to 0.216 g/m^2 (Si), 0.062 to 0.235 g/m^2 (Na), and 0.118 to 0.753 g/m^2 (B) - an order of magnitude or more below the DOE limit. In addition, leachate analyses for the tracer metals (Sr, Ru, Cs, Eu, Re) from each of sixteen glass and CRB samples showed results below the 2 g/m^{2}DOE limit. This is noteworthy given that the glass formula incorporated a relatively high weight fraction of metal waste surrogate, and no bench-scale (laboratory) glass optimization work has yet been performed for this waste stream. Leach testing was not performed on the metal phase.

Off-gas Analyses

Offgas samples were captured hourly and analyzed using gas chromatography for hydrogen, methane and carbon dioxide. The analytical data, as shown in Figure 8, demonstrates that only trace amounts of H_2 were detected in the stack gas over the course of the Test, never exceeding 0.24%, well below the lower flammability limit of H_2 in air, which is 4.0% v/v[2]. These results indicate that over 99% of the organic waste component was destroyed throughout the test. These results are consistent with typical GeoMelt operations wherein greater than 99% destruction of organics occurs within the ICV. This destruction and removal efficiency (DRE), along with dilution air injected immediately upstream and downstream of the ICV, ensure that flammable gas concentrations are not attained within the off-gas system, regardless of the scale of the melter.

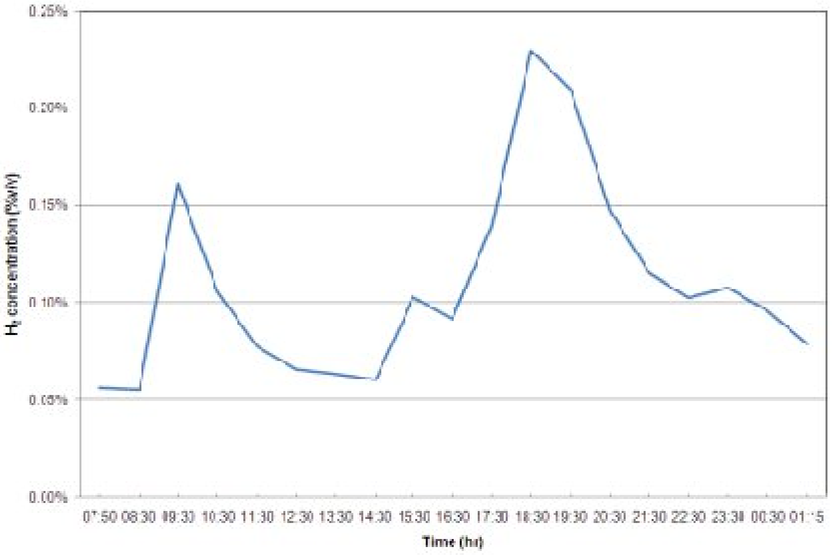

Figure 8. Hydrogen percent measured in the stack gas during processing

CONCLUSION

Key strategic objectives, along with their success criterion, were established by SL for this testing, namely:

1. Passivate and stabilize the raw waste simulant, as demonstrated by the entire quantity of material being vitrified,
2. Immobilize the radiological and destroy the chemotoxic species, as demonstrated via indicative mass balance using elemental analyses from an array of samples,
3. Production of an inert and durable product as evidenced by transformation of reactive metals to their inert oxide forms and satisfactory leachability results using PCT testing.

As shown in this report, each of these objectives were met, demonstrating the ability of the GeoMelt process to treat problematic waste streams currently stored at the Sellafield Site.

REFERENCES

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(3) ASTM C1285-97; "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT), (1997).