DELIVERABLE REPORT

Thermal treatment for radioactive waste minimisation and hazard reduction

Initiative:	EU Horizon 2020 - Euratom Research and training programme
Grant Agreement No:	755480
Start date:	01.06.2017 Duration: 36 Months
Project Coordinator:	VTT Technical Research Centre of Finland Ltd
WP No:	3
Deliverable No:	D3.6
Title:	Hot Isostatic Pressing (HIP) demonstration NNL/USFD
Lead beneficiary:	NNL
Contributors:	USFD, NNL
Dissemination level:	Non-confidential

Due date of deliverable:	31/01/19
Actual submission date:	28/01/19

History Chart			
Type of revision	Document name	Partner	Date
Original version	THERAMIN D3.3.5 Report	USFD/NNL	28.01.2019

Executive Summary

Hot Isostatic Pressing trials for wasteform consolidation were demonstrated at 30 g and 8 L scales at USFD and NNL respectively. All trials resulted in the formation of successful wasteforms with evident volume reduction. Several conceptual formulations were designed to target the immobilisation on magnesium hydroxide sludges and co-mixed wastes, involving materials calcination and canister bake-out prior to consolidation. Both inactive and active (U_3O_8) wasteforms have been produced as a result of this WP. From the initial results of these smaller and larger scale trials HIPing is well suited for batch-to-batch waste processing allowing for variability in heterogeneous waste streams.

Keywords

Thermal treatment, Hot Isostatic Press, Immobilisation, Waste Processing, Radioactive Simulants, Inactive Surrogates, Large Scale

Acknowledgement

This project has received funding from the European Union's Horizon 2020 Euratom research and innovation programme under Grant Agreement No 755480.

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THERAMIN Project Partners

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
GSL	Galson Sciences Limited – UK
FZJ	Forschungszentrum Juelich GmbH – Germany
LEI	Lithuanian Energy Institute – Lithuania
NNL	National Nuclear Laboratory – UK
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
ORANO	Orano – France
SCK•CEN	The Belgian Nuclear Research Centre – Belgium
USFD	University of Sheffield – UK
VTT	Teknologian Tutkimuskeskus VTT Oy (VTT Technical Research Centre of Finland Ltd)
VUJE	VUJE a.s. – Slovakia

THERAMIN End User Group

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
EDF	Electricité de France – France
Fortum	Fortum Oyj – Findland
IGD-TP	Implementing Geological Disposal of Radioactive Waste Technology Platform
Nagra	Die Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle – Switzerland
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
RWM	Radioactive Waste Management Ltd – UK
Sellafield	Sellafield Ltd – UK
TVO	Teollisuuden Voima Oyj – Finland

1. Introduction

1.1 Background

The **Th**ermal treatment for **ra**dioactive waste **min**imisation and hazard reduction (THERAMIN) project is a European Commission (EC) programme of work jointly funded by the Horizon 2020 Euratom research and innovation programme and European nuclear waste management organisations (WMOs). The THERAMIN project is running in the period June 2017 – May 2020. Twelve European WMOs and research and consultancy institutions from seven European countries are participating in THERAMIN.

The overall objective of THERAMIN is to demonstrate the efficacy of thermal treatment in providing improved safe long-term storage and disposal of intermediate-level wastes (ILW) and low-level wastes (LLW). The work programme provides a vehicle for coordinated EU-wide research and technology demonstration designed to provide improved understanding and optimisation of the application of thermal treatment in radioactive waste management programmes across Europe, and will move technologies higher up the Technology Readiness Level (TRL) scale. The THERAMIN project is being carried out in five work packages (WPs). WP1 includes project management and coordination and is being led by VTT. WP2 evaluates the potential for thermal treatment of particular waste streams across Europe, with this WP led by GSL. In WP3, the application of selected thermal treatment technologies to radioactive waste management is demonstrated and evaluated, with this WP led by NNL. In WP4, the disposability of the thermally treated radioactive waste products is assessed, with this WP led by Andra. WP5 concerns synthesis of the project outcomes and their dissemination to other interested organisations.

1.2 Scope - NNL

This document reports the output of the WP3 demonstration trials carried out using Hot Isostatic Pressing (HIP) technology at NNL's Workington facility. The trials take advantage of the large scale HIP unit previously installed and operated in NNL's Workington laboratory for a previous project. Two HIP runs have been carried out on sludge feeds, the immobilisation of which, identified in work package 2, is of interest to the project and appropriate for demonstration using this technology. Magnesium containing sludge typical of those found in the NDA estate has been identified and a surrogate developed and manufactured. In order to demonstrate waste minimisation, co-immobilisation has been demonstrated with clinoptilolite, a good glass forming material which is used in the UK nuclear industry and elsewhere for the clean-up of effluent streams.

1.3 Scope - USFD

This document reports the outputs of demonstrating small scale radioactive hot isostatic pressing at the University of Sheffield (USFD) as part of THERAMIN Work Package 3. USFD are currently the only facility in the UK with capabilities to fabricate and process radioactive HIP wasteforms. This is achieved by using an active furnace isolation chamber (AFIC) developed by American Isostatic Press, GeoRoc Ltd and 8 AMEPT. The AFIC system facilitates the processing of single straight-walled HIP canisters using multiple filters in a lock and seal chamber, which prevents contamination of the HIP in the event of a canister breach during processing. Following the NNL scope (Section 1.2), seven conceptual wasteforms were produced to demonstrate successful HIPing of radioactive materials. The wasteforms were based on the immobilisation of magnesium hydroxide sludges, where five wasteforms used triuranium octoxide (U_3O_8) to simulate waste streams present on the Sellafield Ltd site.

2. Technology Description

HIP technology was developed and patented in the USA by Romp in 1941. Batelle subsequently patented the technology to process diffusion bonded nuclear fuel in 1964. It has subsequently been explored by ANSTO among others for the production of ceramic based wasteforms for the immobilsiation of a range of waste types. In 2002, ANSTO with the then BNFL began the development of the technology for the immobilisiation of plutonium containing residues. This technology is the basis of a current NDA funded programme of work being undertaken by NNL, to develop an immobilisation option for the immobilsiation of PuO_2 stockpile material deemed unsuitable for MOX fuel. The primary thrust of the current phase of the programme is the validation of wasteform chemistry through the installation of a small scale HIP in the NNL Central Lab and the subsequent manufacture and testing of samples containing UK Pu from 2022.

In the context of waste immobilisation, the HIP is used to consolidate a pre-prepared waste feed sealed in a HIP can resulting in a monolithic wasteform produced through the application of pressure and temperature while in the HIP vessel. The product will then be in a form suitable for ongoing storage and ultimate disposal. A schematic is shown in Fig 1. The HIP assembly consists of a monolithic steel pressure vessel surrounded by a water jacket for cooling. Inside the vessel is a molybdenum furnace surrounded by a thermal barrier/heat shield to protect the vessel from the high temperatures required. The workpiece (e.g. canister) is placed inside the furnace and the vessel closed before applying pressure through the use of compressed argon and temperature through power to the molybdenum furnace.

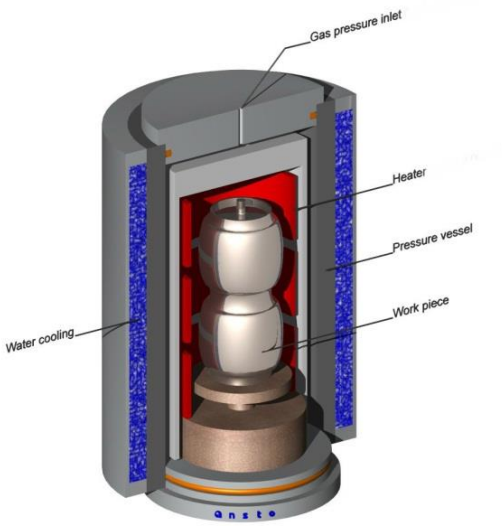

Figure 1. Schematic of HIP (courtesy of ANSTO)

2.1 NNL

The Workington HIP is shown in Fig 2. It is capable of consolidating 8 litre cans containing feeds typically down to 4 litres consolidated volume. Pressures up to 100 MPa can be utilised at temperatures of up to 1320 °C. This HIP is bottom loaded and the vessel is closed through the use of a 4 piece yoke. Preparation of feeds for the HIP generally require the removal of volatile and organic species. This can be carried out through a calcination stage. Following that stage the waste can be mixed with precursors to facilitate the fabrication of a ceramic/glass ceramic wasteform during the consolidation process at temperature and pressure. Feeds once calcined and mixed are loaded into a HIP can which is then evacuated and sealed prior to consolidation.

Figure 2. HIP installed at NNL Workington

2.2 USFD

The hot isostatic press at the Univeristy of Sheffield (Fig. 3) is a small research facility suitable of processing wastreforms up to 1 L, with plug in/plug out furnace options. The molybdenum furnace (suitable for radioactive materials) can operate up to 1300 °C and 200 MPa. In contrast to the NNL HIP, the UFSD HIP is top loading, which allows for easy access and changes to the furnace configuration. The AFIC is prepared in the High Activity Laboratory at USFD, where the main components (filters, o-rings, insulation collar, crucible, and workpiece or canister) are configured to allow a complete seal of the outer chamber. This creates one unit that can be transported to the HIP and directly loaded into the molybdenum furnace, as shown in Fig. 4. The advantage of the AFIC system is that the canister is in the furnace hot zone but the filters are in cold zone, which extends lifetime and minimises potential issues with the filters. Once HIPed, the AFIC is removed from the pressure vessel, monitored for contamination and returned to the High Activity Laboratory for opening under controlled conditions.

Figure 3. Hot Isostatic Press at University of Sheffield

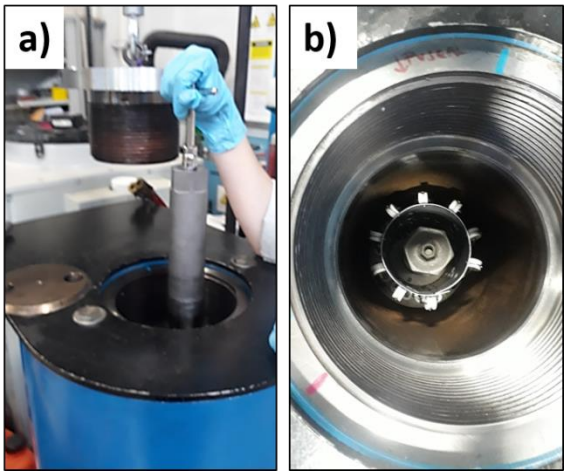

Figure 4. Photographs of a) the sealed AFIC unit being loaded into the pressure vessel and b) the AFIC locked into position within the molybdenum furnace

3. NNL - Description of Experiments/Experimental Conditions

The waste feeds for these trials are surrogates for Magnox sludge and clinoptilolite.

3.1 Feed description

Corroded Magnesium Sludge (CMgS) is a simulant that is prepared by NNL for generic trials in support of Sellafield's mission to decommission the site. In itself it is a surrogate for corroded Magnox sludge having very similar properties to the real materials since Magnox is primarily magnesium metal. In this case, a surrogate produced by NNL for Sellafield Ltd has been used. In order to reduce costs the surrogate is made using magnesium rather than Magnox metal. Magnox is greater than 99% magnesium, which dominates its chemistry and thus proves a good surrogate. The surrogate produced is almost totally reacted and can be considered to be $Mg(OH)_2$.

Clinoptilolite is the ion exchange medium currently used in the site ion exchange effluent plant (SIXEP) and is used to remove active species from effluent streams. Clinoptilolite on the Sellafield site is usually found with 10% sand and associated with sludge material in some cases. It is also a commonly used ion exchanger elsewhere. In this case clinoptilolite alone has been used. The clinoptilolite supplied by a UK supplier originated from Turkey and has a reference formula of $(Na_{0.5}K_{2.5})\ (Ca_{1.0}Mg_{0.5)(}Al_6Si_{30})O_{72}.24H_2O$.

Table 1. Recipe for HIP runs

Component	Theramin HIP 1	Theramin HIP 2
Magnox Sludge	33.3%	44.8%
Clinoptilolite	56.5%	44.8%
Borosilicate Frit	10.2%	-
Borax	-	10.4%
Caesium Oxide	90 g	60 g
Cerium Oxide	10 g	10 g
TOTAL MASS of feeds	8 kg	7.3 kg

The aim of both runs was to produce a wasteform that would be credible for ongoing storage and disposal. The wasteform itself was expected to be a glass ceramic composite. Table 1 shows the recipe used for each of the two trials. In both trials the clinoptiloloite is added as an example of co-immobilisation of waste streams. Note that the percentages shown in the recipe are related to post-calcined materials. Clinoptilolite contains good glass forming elements and thus its use can reduce the requirement for the addition of extra silicate containing species. In the first run a borosilicate frit has been used. This frit is denoted MW ½ Li and is currently used in the vitrification of HLW raffinates on the Sellafield site. Its composition is shown in Table 2. The second run contains borax in place of the frit, in addtion to having a higher percentage of sludge content.

Table 2. Composition of frit used in HIP 1

Component	MW ½ Li frit wt.%
SiO_2	63.4
B_2O_3	22.5
Na_2O	11.4
Li_2O	2.7

The consistency of the raw feeds are illustrated in Figs 5 and 6. The Magnox sludge simulant is typically the consistency of pouring cream but its flow properties can vary. In developing a thermal treatment immobilisation solution, the sludge will need to be dilute enough to enable mobilisation for transfer from the the donor to the receiving immobilisation plant which will subsequently, in the case of HIP, need to remove the water for further processing and consolidation.

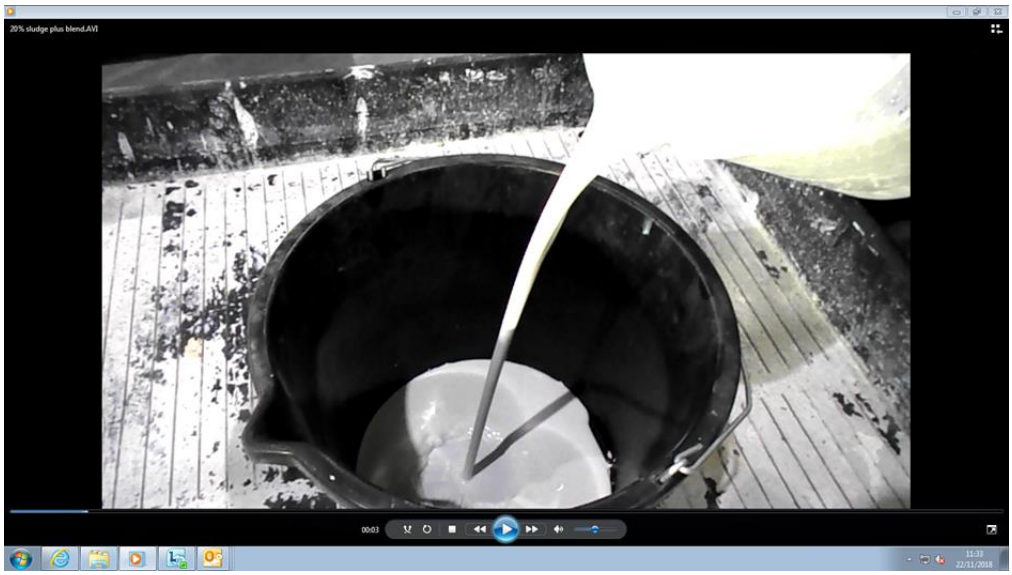

Figure 5. Consistency of sludge demonstrated through pouring

The raw clinoptilolite is shown as a dry powder. Ion exchange operations and mobilisation will mean that the wastes from SIXEP will contain water, which will require removal prior to immobilisation through the HIP process.

Figure 6. Raw clinoptilolite

3.2 Feed preparation

The clinoptilolite was loaded with stable Cs to simulate one of the major radionuclides extracted form the effluent stream. CeO was also then added to the feed to simulate actinide oxides present. While the Cs might be considered to be volatile under the calcination regime, it is considered that the Cs loss is low, potentially due to the absence of borates which can typically exacerbate such volatility in glass melts. The addition of both Cs and Ce have been added to obtain a qualitative assessment of its speciation in the final product rather than to assess any mass balance.

The feed was calcined in batches, largely due restrictions in the capacity of the calciner. Calcination of the major components, sludge and clinoptilolite were carried out separately at 950 °C for 3 hours. The materials were then batched. For run 1, each batch contained 950 g of Cs loaded calcined, 560 g of calcined CMgS andn170 g of MW ½ Li frit with 10 g CeO_2 added as an actinide surrogate. Five batches were prepared with around 8 kg used to fill the 8 L capacity HIP can. A bake out cycle of 600 °C for 6 hours was then applied to remove any moisture that may have been absorbed from the atmosphere post calcination. A mass loss of 0.06 kg was measured. For run 2, each batch contained 650 g Cs loaded calcined clino, 650 g calcined CMgS 150 g Borax and 10 g CeO_2. Five batches were prepared, all 7.3 kg used to fill the 8 L capacity HIP can.

3.3 Trial information – HIP cycle

The HIP can is subject to a simultaneous application of pressure and temperature in a controlled way in order to consolidate the can to an approximate right cyclinder. Failure to do this may result in the can distorting with subsequent stress placed on the welds which may lead to loss of sealing and failure to consolidate. A maximum temperature of 1250 °C was selected for the two trials based on previous fabrication of large cans aimed at forming a glass ceramic composite after consolidation. A 2 hour dwell at peak temperature is considered sufficient to achieve the reaction required between the waste feed and the glass/ceramic forming precursors.

The pressure applied aids in densification of the product. As with the majority of trials carried out on the Workington HIP, 100 MPa is used as peak pressure which is generally maintained for the 2 hour peak temperature dwell period. Due to problems with a fault in the compression system, peak pressure could not be maintained for the total dwell period. However in both runs the pressure was maintained above 70 MPa for that period, a pressure which is known to be sufficient for densification with these materials. Subsequent sectioning of the cans (see Section 3.4) has shown both products to be fully densified on visual inspection.

HIP cycles for each run are shown in Figs. 7-8, which show the parallel increase in pressure and temperature against time, with a total cycle time of around 8-9 hours to the point at which the HIP temperature indicated that the HIP vessel can be opened and the product retrieved. It must be noted that the cycle has not been optimised. Further trials could examine the relationship between

pressure, peak temperature and dwell time to optimise the overall cycle potentially reducing the cycle time.

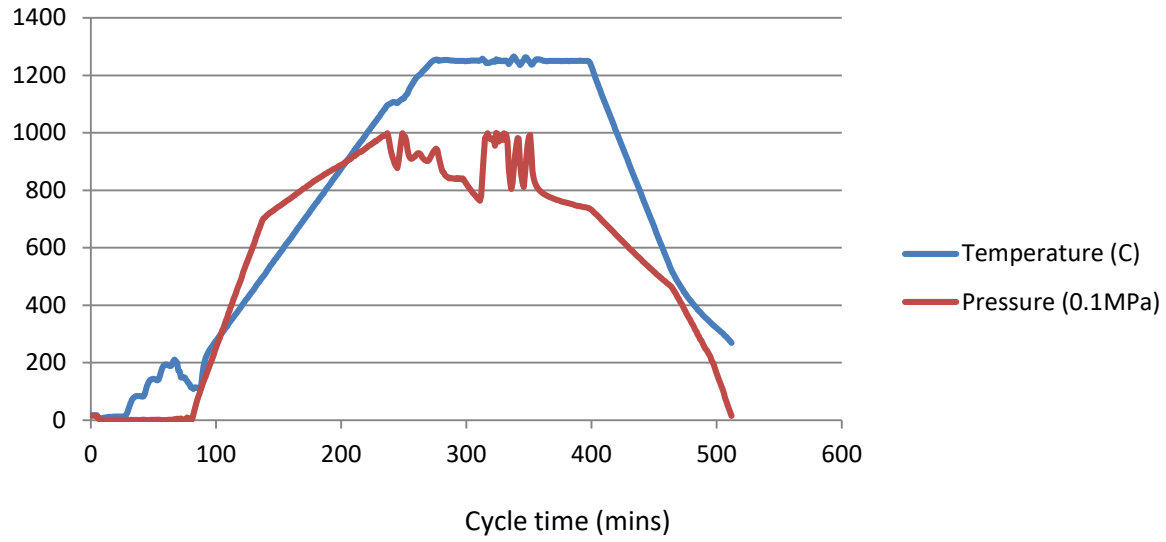

Figure 7. HIP cycle for Theramin HIP 1

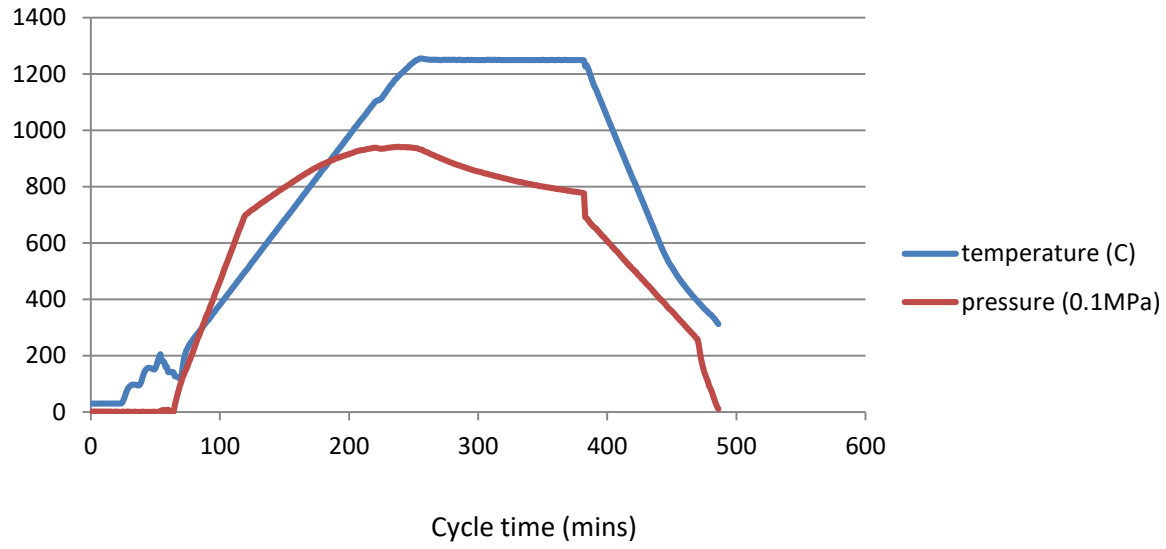

Figure 8. HIP cycle for Theramin HIP 2

3.4 Post-trial activities

Both HIP 1 and HIP 2 were succesfully consolidated, the shrinkage being evidence that the can has retained its seal through out the HIPing process. Following consolidation and cooling down, the product was removed from the HIP and sectioned using a diamond blade and wire saw. Fig 9 illustrates the HIP can before and after consolidation in the HIP. In this case, the can on the left is the THERAMIN HIP 2 sample prepared and ready for consolidation in the HIP. The can on the right is the consolidated THERAMIN HIP 1 can. Note the dumbell shaped contour of the can which is designed to allow a product approximating to a right cylinder to be produced. Without such a design the HIP can is likely to distort making future product handling difficult and potentially causing a rupture in the can or weld, which may result in the can not consolidating and a product not fully densified.

Figure 10 illustrates the comparison between the sizes of the respective HIP 1 and 2 products and shows how the introduction of a higher MgO content has produced a smaller consolidated product as a result of greater shrinkage during consolidation. For reference the cans are also shown against a previous can consolidated for another project. This can (shown partly sectioned) was filled with 100 % clinoptilolite and packed efficiently as a result of the range of particle size of the feed. It thus displayed less shrinkage than the cans produced in this project.

Figure 9. HIP 2 can before (left) and HIP 1 after consolidation (right)

Figure 10. THERAMIN HIP 1 (centre), THERAMIN HIP 2 (right) and previous HIP can (left)

The HIP cans were then sectioned with a "quarter“ removed to enable charactersation to be carried out. The sectioned cans are shown below in Fig 11.

Figure 11. Sectioned cans, HIP 1 (left) and HIP 2 (right)

4. USFD - Description of Experiments/Experimental Conditions

To complement the large scale trials conducted at NNL, the wasteforms under investigation at UFSD were also based on corroded magnesium sludge (CMgS) present on the Sellafield Ltd site. Magnesium hydroxide was used as a surrogate to CMgS, as described in Section 3.1. For ease, each wasteform will be also referred to by the HIP canister identification number with descriptions provided in Section 4.1.

4.1 Wasteform Descriptions

4.1.1 Magnesium sludge/clinoptilolite mixed wasteform

Using material batched at NNL for the THERAMIN HIP 1 trial, a small scale HIP canister (~15 cm^3) was prepared at USFD *(can 17017, NNL-Ce)*. This will allow direct comparison of the microstructure, densification and phase assemblage achieved between the two batch sizes (approx. 8 kg vs 40 g) whilst using CeO_2 as a surrogate for actinide oxides. The NNL-Ce wasteform (*can 17017*) will allow direct comparison between different scales, which is important as the effect of the canister interface/wasteform volume ratio can impact the redox conditions and, potentially the wasteform durability [1]. A second sample was prepared using the source materials from NNL (MgO, glass frit and Cs-exchanged clinoptilolite) and U_3O_8 *(can 17016)*. Equimolar replacement of CeO_2 for U_3O_8 resulted in waste loadings of 0.59 wt. % and 0.97 wt.%, respectively. The alkali borosilicate glass frit used was “MW ½ Li glass frit”, which is currently used in vitrification processes on the Sellafield site, the composition of which is reported in Table 2. The inactive components were pre-calcined at 950 °C for 3 hours by NNL, therefore the U_3O_8 was also calcined at 950 °C for 3 hours prior to batching.

Table 3. Composition of USFD co-mixed wasteforms

Can No.	Sample Name	CMgS* (g)	MW ½ Li (g)	Clino (g)	CeO_2 (g)	U_3O_8 (g)	Waste loading (wt. %)
17016	NNL-U	16.513	5.015	28.012	-	0.481	0.97
17017	NNL-Ce	16.567	5.030	28.120	0.300	-	0.59

*The CMgS provided by NNL was $Mg(OH)_2$ calcined at 950 °C

4.1.2 Magnesium borosilicate glass wasteform

Magnesium borosilicate glasses were prepared using a combination of magnesium metal and magnesium hydroxide to simulate the Magnox sludge waste stream located on the Sellafield site.

Inactive formulations have previously been demonstrated and characterised by PhD candidate Mr Sean Barlow. Using these formulations, wasteforms were prepared using U_3O_8 to simulate the actinide oxides present in the waste, mostly from corroded mechanically decanned Magnox reactor fuel [2, 3]. Due to the heterogeneous nature of the sludge (which can vary from skip to skip), both high and low waste loadings were investigated at 42.22 wt. % (*can 17014*) and 6.76 wt. % (*can 17015*). Any remaining metallic uranium fuel is expected to fully oxidise during the water removal process, which is required during feed preparation, as described earlier. Batching was performed in the High Active Laboratory at USFD, and both wasteforms were pre-calcined at 600 °C for 12 hours in a general muffle furnace (air atmosphere) prior to canister packing.

Table 4. Composition of magnesium borosilicate glass wasteforms

Can No.	Sample Name	$Mg(OH)_2$ (g)	Mg (g)	H_3BO_3 (g)	SiO_2 (g)	U_3O_8 (g)	Waste loading (wt. %)
17014	MBS-U (high)	4.694	2.816	12.208	6.040	18.820	42.22
17015	MBC-U (low)	18.109	1.132	22.200	10.983	3.801	6.76

4.1.3 Alkali borosilicate glass wasteform

The final wasteform investigated was magnesium hydroxide and alkali borosilicate glass (MW ½ Li glass frit, composition in Table 2) batched with and without U_3O_8. The glass frit to $Mg(OH)_2$ ratio was targeted at 18 % percolating volume within the wasteform. To achieve this, $Mg(OH)_2$ was tapped until settled in a 50 mL centrifuge tube until a volume of 25 cm^3 was achieved. The mass of powder was recorded. The MW ½ Li glass frit was size reduced using a planetary ball mill (5 minutes at 500 rpm) until a fine powder. This was tapped into a 15 mL centrifuge tube until a volume 4.5 cm^3 was achieved, the mass was recorded. These measurements formed the baseline inactive $Mg(OH)_2$ and glass frit (18 vol. %) wasteform (*can 17018*). Two active samples were prepared with U_3O_8 at waste loadings 44.43 wt. % (c*an 17019*) and % 6.67 wt. % (*can 17020*), which were similar waste loadings to MBS-U wasteforms discussed in Section 4.1.2. All formulations were pre-calcined at 600 °C for 12 hours in a general muffle furnace (air atmosphere) prior to canister packing.

Table 5. Composition of alkali borosilicate glass wasteforms

Can No.	Sample Name	$Mg(OH)_2$ (g)	MW ½ Li (g)	U_3O_8 (g)	Waste loading (wt. %)
17018	ABS control	32.650	17.350	-	-
17019	ABS-U (high)	17.288	9.187	23.525	44.43
17020	ABS-U (low)	30.507	16.211	3.337	6.67

4.2 HIP canister packing

Following the pre-calcination previously discussed, each wasteform was packed into a straight walled stainless steel HIP canister (15 cm^3 volume) with in-built metal sintered filters. This was performed using a hydraulic press and die plunger in a glovebox to minimise powder distribution/contamination. A hydraulic press was used to maximise the packing density of the wasteform, which also helps to control the canister deformation shape during the HIP process. Once packed, the canister lid was welded into place using a tungsten inert gas (TIG) welding station, which is tailored to handle radioactive materials. The mass of all canisters are reported in Table 6.

Table 6. HIP canister summary

Can No.	Sample Name	Empty can (g)	Packed can (g)	Sample (g)
17014	MBS-U (high)	107.87	141.47	33.61
17015	MBS-U (low)	108.04	127.27	19.23
17016	NNL-U	107.93	127.80	19.87
17017	NNL-Ce	108.14	106.85	18.68
17018	ABS control	107.98	125.66	17.68
17019	ABS-U (high)	107.51	130.82	23.31
17020	ABS-U (low)	107.51	126.51	18.51

Post-welding, all HIP canisters were processed under evacuation and bake-out steps. This involved evacuating the canister at room temperature until a vacuum of <8 Pa was achieved. At this point, the bake-out step commenced, which proceeds until the initial vacuum reading is recovered. The bake-out temperature was set to 600 °C for all wasteforms, the duration varied per sample but this step was typically completed within 4-6 hours. The evacuation tube on the HIP canister was then crimped and welded to produce a hermetically sealed HIP canister ready for HIP processing. These stages are required to remove organic volatiles/excess water from the wasteform and to ensure that the welds are suitable for a high temperature and high pressure environment.

4.3 HIP trials

The target HIP cycle conditions were 1250 °C and 100 MPa with a 2-hour dwell at peak temperature and pressure. These conditions are typical for HIP studies at USFD and correspond with those chosen by NNL (Section 3.3). Following advice for AFIC operations, and to obtain controlled canister consolidation, the temperature was ramped slower than for inactive surrogate wasteforms. The thermal program was completed in several steps, as follows:

- Ramp to 400 °C at 5 °C/min, hold for 30 min
- Ramp to 700 °C at 5 °C/min, hold for 15 min
- Ramp to 1250 °C at 7.5 °C/min, hold for 120 min
- Cool to 100 °C at 10 °C/min

The target pressure was ramped alongside the temperature and held during the dwell periods at 14, 25 and 100 MPa, respectively. However, there is no software function to control the pressure ramp rate at USFD, and, as such, it was manually controlled. The HIP trial data for all wasteforms are shown in Figs. 12-18. During HIP cycles for canisters 17015, 17016, 17017, there was difficulty in achieving the target pressure of 100 MPa. This is evidenced by the pressure data in Figs. 13-15, where the pressure profile decreases and increases throughout the entire dwell segment. The average pressure achieved during the 2-hour dwell for these wasteforms was 77, 70, and 87 MPa, respectively (Table 7).

Upon investigation, the pressurisation issue was identified as due to failed packing in the compressor unit in both the first and second compression stage. Once the packing seals were replaced, a third leak was detected in the high pressure vent valve. The valve had loosened over time, which resulted in the vent valve remaining open during pressurisation and argon escaping from the pressure vessel through the vent network (an internal leak). After the extensive maintenance repairs, it was decided that the target pressure for all remaining canisters should be reduced to 75 MPa. This would put the USFD wasteforms in line with NNL, who also experience compressor issues and achieved pressures >70 MPa for HIP 1 and HIP 2 wasteforms. It is expected that the pressure difference between the target and achieved will have minimal impact on the phase assemblage.

A summary of the bake-out and HIP cycle conditions achieved is provided in Table 7.

Table 7. Summary of bake-out and HIP conditions

Can No.	Sample Name	Bake-out temperature & vacuum achieved (°C, Pa)	HIP conditions (°C, MPa, hrs)	HIPed? (Y/N)
17014	MBS-U (high)	600, <8	1250, 75, 2	**Y**
17015	MBS-U (low)	600, <8	1250, 77*, 2	**Y**
17016	NNL-U	600, <8	1250, 70*, 2	**Y**
17017	NNL-Ce	600, <8	1250, 87*, 2	**Y**
17018	ABS control	600, <8	1250, 75, 2	**Y**
17019	ABS-U (high)	600, <8	1250, 75, 2	**Y**
17020	ABS-U (low)	600, <8	1250, 75, 2	**Y**

* Compressor issue during this trial

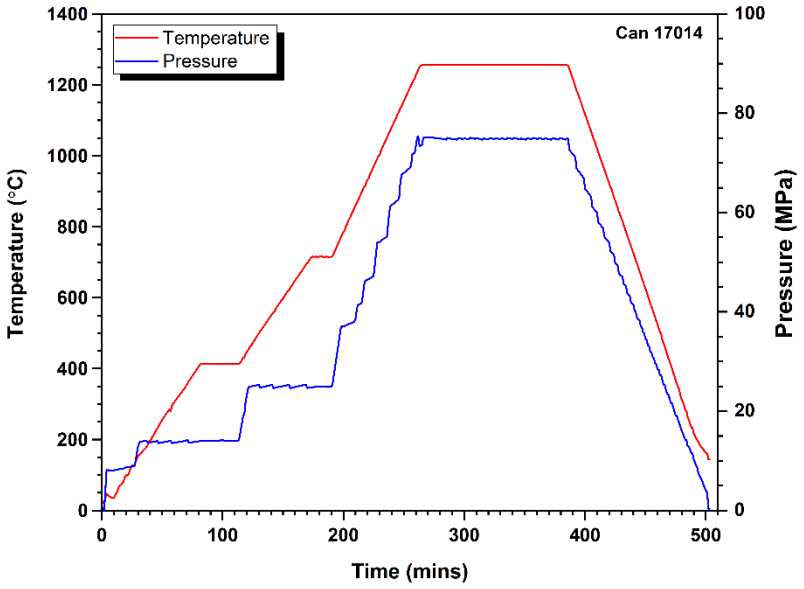

Figure 12. HIP cycle data for Can 17014, sample MBS-U (high)

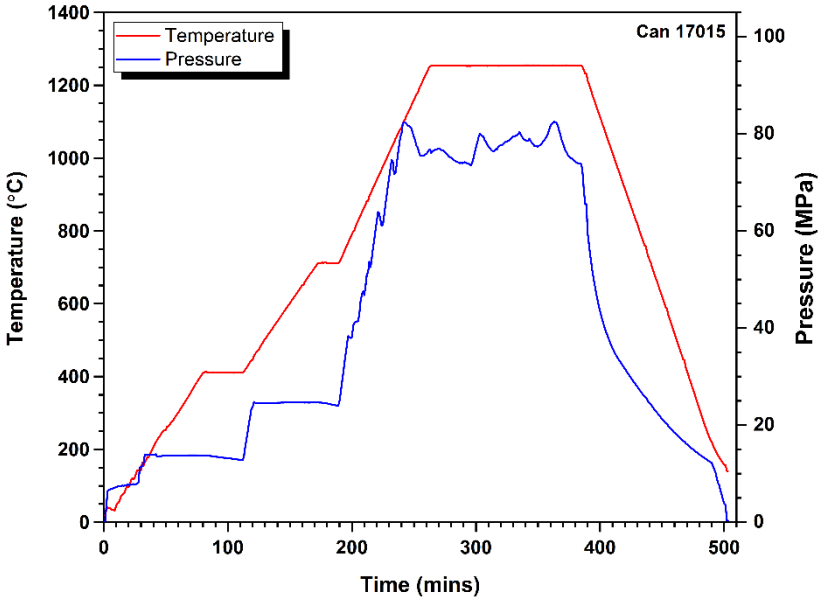

Figure 13. HIP cycle data for Can 17015, sample MBS-U (low)
Note: Compressor issue during this trial.

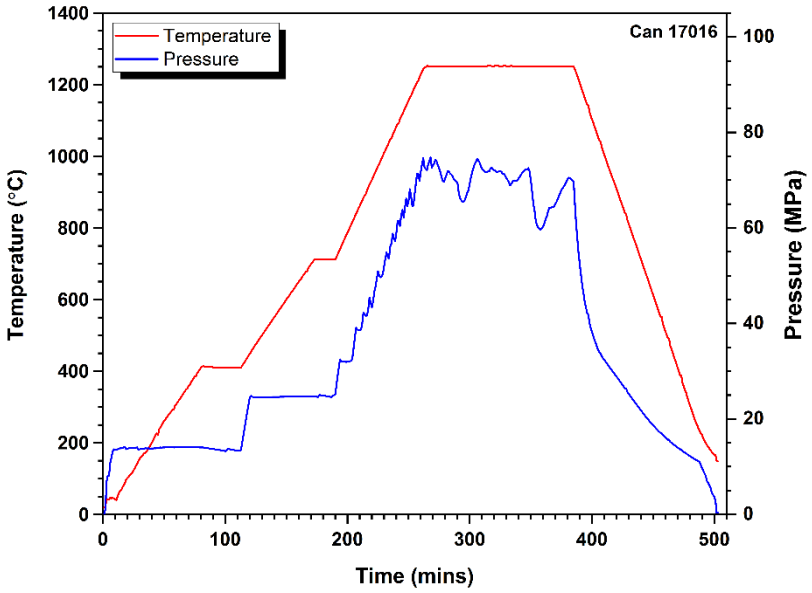

Figure 14. HIP cycle data for Can 17016, sample NNL-U.
Note: Compressor issue during this trial.

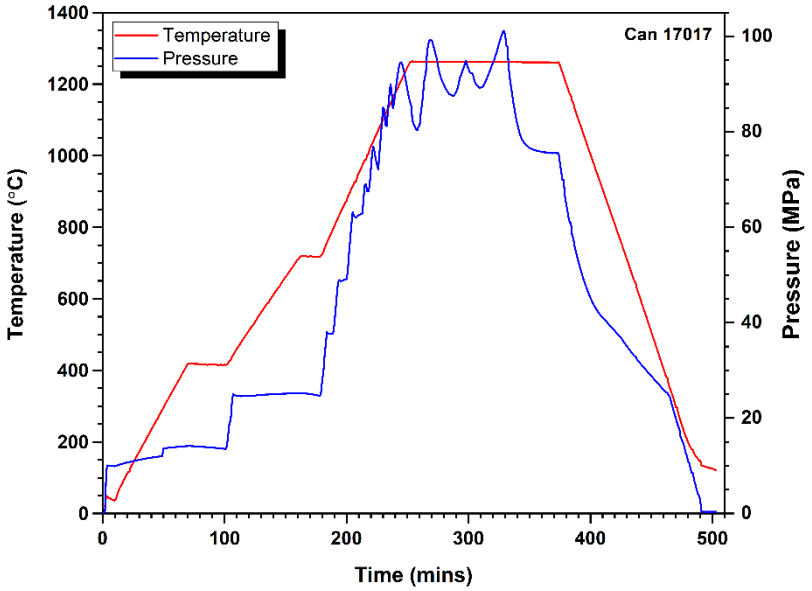

Figure 15. HIP cycle data for Can 17017, sample NNL-Ce
Note: Compressor issue during this trial.

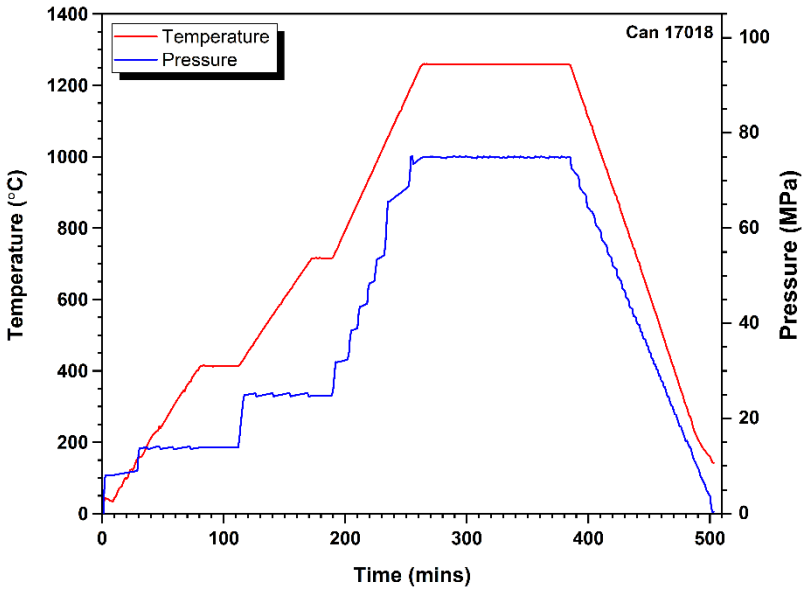

Figure 16. HIP cycle data for Can 17018, sample ABS control

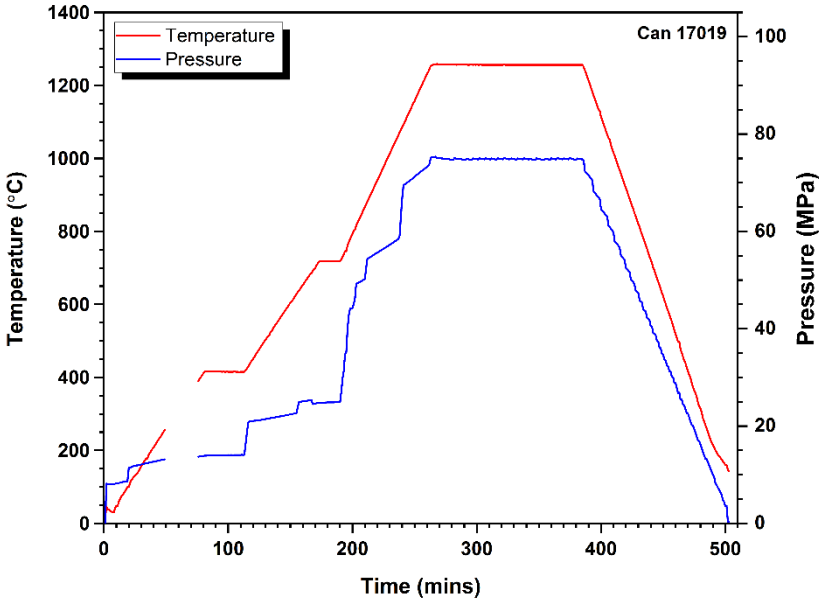

Figure 17. HIP cycle data for Can 17019, sample ABS-U (high)
Note: no data logged between 256-396 °C (28 min).

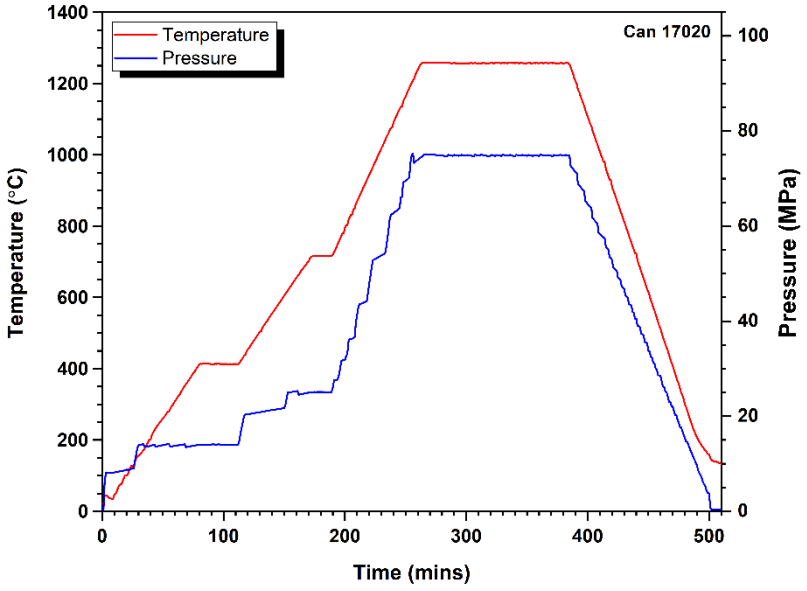

Figure 18. HIP cycle data for Can 17020, sample ABS-U (high)

4.4 Post-trial activities

Photographs taken before and after HIP processing are shown in Figs. 19-24. All canisters were visually confirmed to have been successful. This was denoted by the flattened evacuation tube and reduced diameter of the central body. No loss of containment was observed and the canisters remained hermetically sealed (no weld failure). For the co-mixed immobilisation wasteforms (*cans 17016-17*), and the magnesium borosilicate glass wasteforms (*cans 17014-15*), the deformation observed was very even around the central canister body. However, the alkali borosilicate glass wasteforms (*cans 17018-20*) resulted in a more angular canister, indicative of a lower packing density.

Each canister will be sectioned to generate a central slice of the HIPed wasteform and is expected to take 3 hours per canister. The sectioned wasteform will be characterised under Work Package 4 (task 4.2.2) using the following techniques: X-ray diffraction, scanning electron microscopy with energy dispersion analysis and density measurements. Selected wasteforms will also be prepared for uranium oxidation state by U L_3-edge XANES experiments.

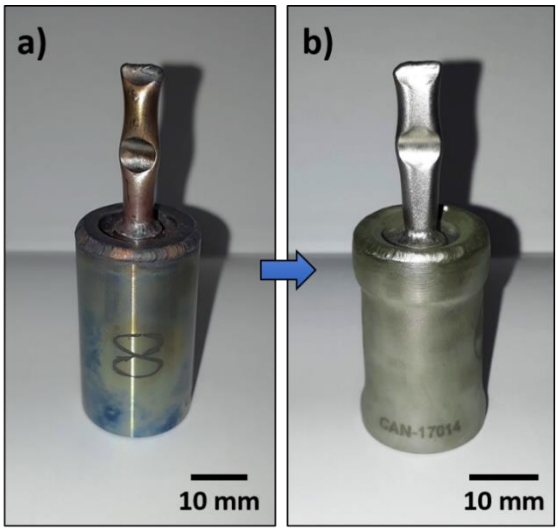

Figure 19. Photographs of Can 17014 a) pre-HIP and b) post-HIP

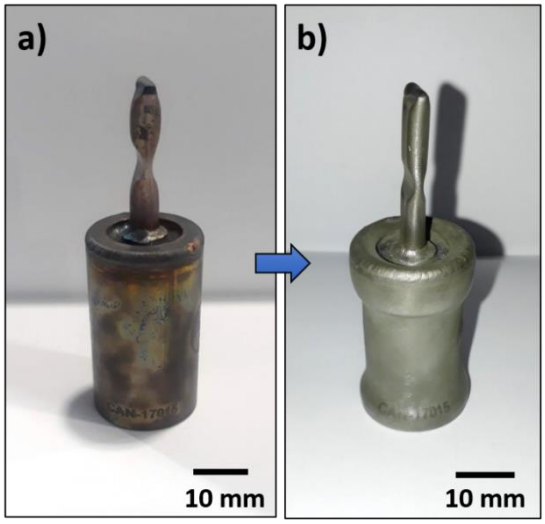

Figure 20. Photographs of Can 17015 a) pre-HIP and b) post-HIP

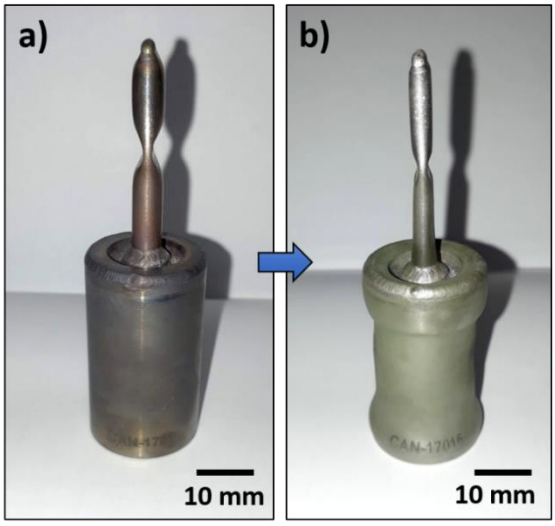

Figure 21. Photographs of Can 17016 a) pre-HIP and b) post-HIP

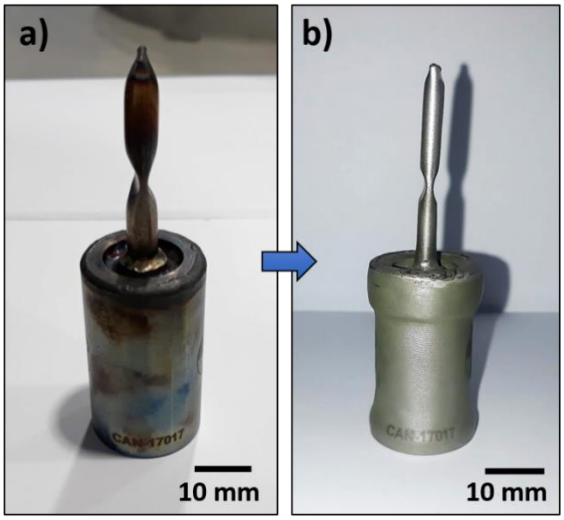

Figure 22. Photographs of Can 17017 a) pre-HIP and b) post-HIP

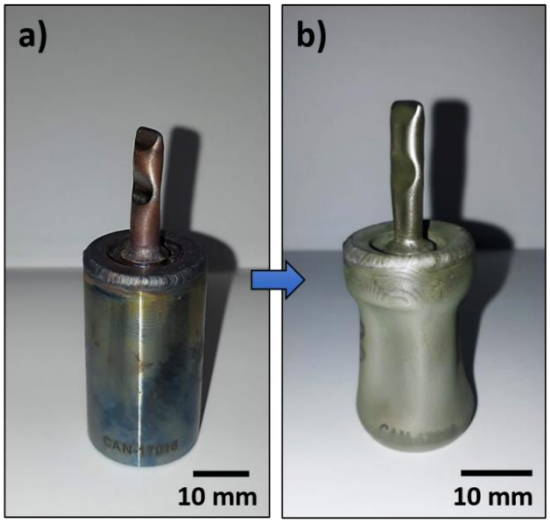

Figure 23. Photographs of Can 17018 a) pre-HIP and b) post-HIP

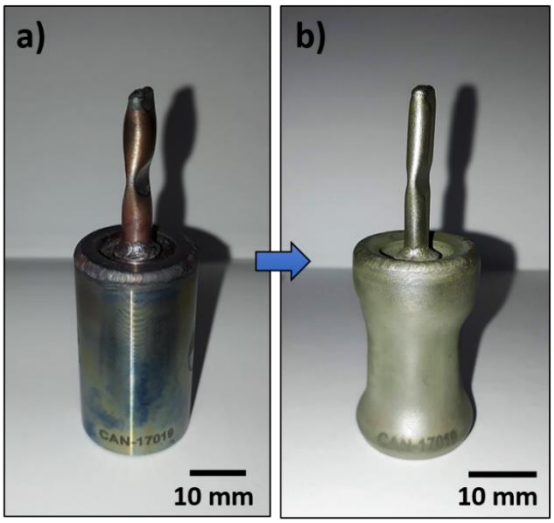

Figure 24. Photographs of Can 17019 a) pre-HIP and b) post-HIP

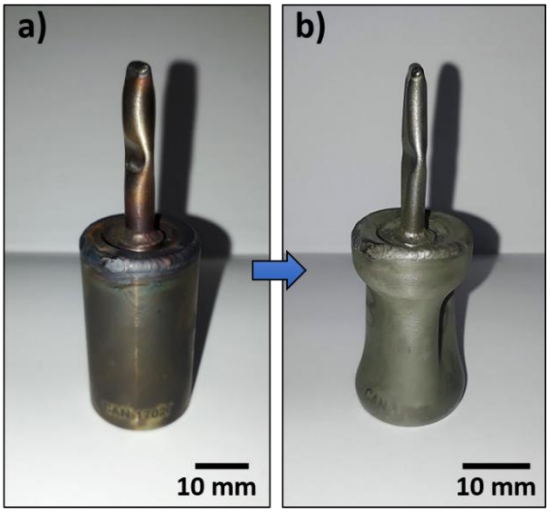

Figure 25. Photographs of Can 17020 a) pre-HIP and b) post-HIP

5. Summary

5.1 NNL

Prior to any characterisation and analysis, some conclusions can be drawn from the observation of the trial. The primary aim was to consolidate the waste feeds into a form that may be suitable for ongoing storage and disposal. As an initial demonstration neither the preparatory steps nor the consolidation step have been optimised. The calcination regime was primarily employed to remove moisture from the feeds and to destroy the tendency for the clinoptilolite to re-absorb moisture. As such, information has not been obtained on the level of Cs that may have been volatilised as a result of calcination, but it is considered that this may be minimal.

From a visual observation the cans consolidated as expected. From this it can be concluded that the pressure temperature cycle was appropriate. On sectioning the product is visibly dense. The texture of the material appears more glassy and less friable on handling on THERAMIN HIP 2, possibly as a result of the higher quantity of flux and lower overall quantity of silica in the feed. This can also be deduced from a comparison with a previous trial (not funded on this project), the product illustrated in Fig 10, where the use of 100 % clinoptilolite consolidated at the same top temperature has yielded a product which is more friable, possibly as a result of the more refractory nature of the total feed and the subsequent reduction in the glassy phase present. The visual observation of the product would suggest that the product of the trials, THERAMIN HIP 1 and HIP 2, would both be suitable for disposal. Producing HIP canisters at a larger scale has been demonstrated in support of the immobilisation of Idaho calcines and it is felt that this technology could be scaled up to produce canisters at 500 litre scale, which would be suitable for diposal in the UK under RWM's GDF concept for ILW.

5.2 USFD

In Work Package 3, seven conceptual wasteforms were successfully prepared and HIPed at USFD. The primary aim was to utilise a unique active furnace isolation chamber (AFIC) system that allows processing of radioactive waste simulants in the HIP without risk of contamination to the processing equipment. This target was achieved with five of the wasteforms produced using U_3O_8 to simulate Magnox sludges located at the Sellafield Ltd site. The pre-calcination, canister packing and bake-out steps were completed with no operational issues. However, the HIP processing of wasteforms MBS-U low (*can 17015*), NNL-U (*can 17016*) and NNL-Ce (*can 17017*) had difficulty achieving and maintaining the target pressure of 100 MPa. Once the HIP repairs were completed, the target pressure for the remaining wasteforms was reduced to 75 MPa in order to have a comparable suite of samples. All wasteforms achieved a pressure >70 MPa during the 2-hour dwell, the lower pressure is not expected to affect the phase assemblage. Characterisation of all wasteforms will proceed in Work Package 4.

References

[1] M.W.A. Stewart, S.A. Moricca, T. Eddowes, Y. Zhang, E.R. Vance, G.R. Lumpkin, M.L. Carter, M. Dowson, M. James, The use of hot-isostatic pressing to process nuclear waste forms, The 12th International Conference on Environmental Remediation and Radioactive Waste ManagementLiverpool, UK, 2009.

[2] Nuclear Decommissioning Authority, Waste stream 2D22: Magnox cladding and miscellaneous solid waste, The 2016 UK radioactive waste inventory, NDA, 2017.

[3] Nuclear Decommissioning Authority, Waste stream 2D24: Magnox cladding and miscellaneous solid waste, The 2016 UK radioactive waste inventory, NDA, 2017.