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Hot isostatic pressing: thermal treatment trials of inactive and radioactive simulant UK intermediate level waste

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Hot isostatic pressing: thermal treatment trials of inactive and radioactive simulant UK intermediate level waste

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Abstract. Hot Isostatic Pressing (HIPing) is a batch process thermal treatment technology where wastes are heated and compressed within a sealed stainless steel canister; typically resulting in durable, high density ceramics or glasses with minimal loss of volatile elements, and accountability of active inventories. The University of Sheffield has a small-scale research HIP with capability to process simulant wasteforms containing radioactive materials, to help underpin larger-scale industrial applications of this technology. It was under this remit that a series of trials were undertaken, to produce small simulant radioactive wasteforms incorporating problematic UK waste streams such as Magnox sludges and clinoptilolite ion-exchange material. Each trial was successfully batched, sealed, and HIPed at 1250 °C, resulting in solidified products entirely contained within the steel HIP canisters. The ability to safely produce active wasteforms within the same facility validates the active furnace isolation chamber (AFIC) system. Overall the success of these trials demonstrate the ability of smaller research HIP facilities to build up the scientific and technical case for further implementation of HIP technology as a viable waste treatment option.

1. Introduction

Hot isostatic pressing (HIPing) is a batch thermal treatment technology, which could be utilized to consolidate a wide range of wastes from sludges and spent ion exchange materials, to co-mixed waste streams and for plutonium immobilization, as an alternative to cementation and vitrification technology. The resultant wasteform is typically a durable ceramic or glass-ceramic with hazardous/radioactive elements immobilized within the bulk matrix or bound in tailored crystalline phases. The advantages of HIPing include: batch to batch processing allowing for inventory accountancy, relatively lower processing temperature, high waste loadings, zero off-gas, volume reductions, minimal secondary wastes, and tailorable processing conditions [1]. HIPing for nuclear waste immobilization has largely been limited to inactive surrogates due to the risks associated with handling radioactive compounds and equipment contamination. The Australian Nuclear Science and Technology Organisation (ANSTO) have developed a fully automated HIP process plant for the immobilization of wastes generated from Mo-99 production, due to be completed in 2020 [2]. This will be the first commercial facility available for the processing of radioactive wasteforms via HIPing. Within the UK, the University of Sheffield have the capacity to HIP both inactive and radioactive wasteforms on a prototype scale (~20-50g) using an active furnace isolation chamber (AFIC), which is designed to allow safe use of radioactive materials within a conventional HIP setup, providing a unique opportunity to produce and characterize high waste loaded radioactive simulant wasteforms.

The EC THERAMIN project (Thermal Treatment for Radioactive Waste Minimization and Hazard Reduction) enabled feasibility demonstration of radiological HIPing with regards to simulant intermediate level wastes. For UK wastes, the scope was limited to magnesium-rich wastes, typically corroded Magnox sludge in addition to clinoptilolite in co-mixed wasteforms. This research program contributed towards the understanding, experience and knowledge gained of radiological HIPing, which could be transferred to large commercial facilities if technology uptake was reached.

2. Methodology

2.1. Wasteform composition

Within THERAMIN Work Package 3, three trials were undertaken, utilizing different wastes and targeted chemistries relevant to UK radioactive waste streams. Trial 1, in collaboration with the National Nuclear Laboratory, was a co-mixed product consisting of calcined Magnox sludge (Mg-rich), clinoptilolite, and glass frit, with both CeO_2 as a simulant and U_3O_8. Trial 2 targeted the formation of a magnesium borosilicate glass, using simulant Magnox wastes, boric acid, quartz and U_3O_8; whilst in Trial 3, a simplified composition was targeted, consisting of $Mg(OH)_2$, glass frit and, U_3O_8.

In this study, details are provided for the result of Trial 2 magnesium borosilicate glass wasteforms (MBS-U high and MBS-U low). These glasses were prepared using a combination of magnesium metal and magnesium hydroxide to simulate Magnox sludge – a problematic higher volume intermediate level waste which requires a conditioning route for disposal. Wasteforms were prepared using U_3O_8 to simulate the uranium oxides present in the waste, mostly from corroded mechanically decanned Magnox reactor fuel [3]. Due to the heterogeneous nature of the sludge (which can vary from skip to skip), high and low uranium contents were chosen (42.22 and 6.76 wt. %) to investigate the impact of a varying composition. Any remaining metallic uranium fuel is expected to fully oxidize during the water removal process, which is required during feed preparation. The overall waste loading with respect to magnesium sources and uranium oxide were 59.06 and 40.98 wt. %, respectively. Batching was performed in a controlled laboratory, both wasteforms were pre-calcined in alumina crucibles at 600 °C for 12 hours in a general muffle furnace (air atmosphere) prior to canister packing (discussed in Section 3).

Table 1. Composition of radioactive HIP wasteforms based on a 50g batch

Can No.	Sample Name	$Mg(OH)_2$ (g)	Mg (g)	H_2BO_3 (g)	SiO_2 (g)	U_3O_8 (g)	Waste loading* (wt. %)
17014	MBS-U (high)	5.26	3.16	13.69	6.77	21.11	59.06
17015	MBS-U (low)	16.10	1.01	19.74	9.77	3.38	40.98

*where waste loading refers to $Mg(OH)_2$, Mg and U_3O_8 content

2.2. Analytical methods

HIPed canisters were photographed and then sectioned using a Buehler Isomet 1000 precision saw. Powder X-ray diffraction patterns were collected between $5° < 2\theta < 70°$ using a Bruker D2 Phaser diffractometer with a Lynxeye detector and a Ni filtered Cu K_α radiation (1.5418 Å) using a step size of 0.02° 2θ and a count time of 3 s per step. Micrographs were collected using a low vacuum Hitachi TM3030 analytical benchtop SEM with an integrated Bruker EDX system (Quantax 70) at 15 kV and a 7.0 mm working distance on polished (1 μm finish) and carbon coated specimens.

3. Hot isostatic pressing

3.1. Canister preparation

Each sample was packed into a straight walled 304 stainless steel HIP canister (*h;* 45 mm, ø; 22 mm) with in-built metal sintered filters. Canister packing was performed using a hydraulic press and die

plunger, U_3O_8 samples were prepared in a glovebox to minimize powder distribution/contamination. A hydraulic press was used to maximize the packing density of the wasteform, which also helps to control the canister deformation (i.e. final shape) during the HIP process. Once packed, the canister lid was welded into place using a tungsten inert gas (TIG) welding station. Following this, all canisters were prepared for HIPing by evacuation and bake-out steps. This involved evacuating the canister at room temperature until a vacuum of <8 Pa was achieved after which, the process was repeated at temperature (600 °C) until the initial vacuum recovered. The evacuation tube on the canister was then crimped and welded to produce a hermetically sealed canister ready for processing. These stages are required to remove volatiles/excess water from the wasteform that could affect densification and generate porosity in the final wasteform [4, 5].

3.2. Active furnace isolation chamber

The active furnace isolation chamber (AFIC) is a plug-in component for existing hot isostatic press facilities. The University of Sheffield is uniquely equipped to utilise this containment design, which enables the passively safe processing of uranium-containing wasteforms. The AFIC is engineered to process one canister per HIP cycle, whilst maintaining multiple layers of containment to prevent contamination to the HIP and surrounding work environment in the event of a canister failure, where radioactive powder could be distributed as a result. Other AFIC design features include; a two-way pressure differential, verifiable and changeable filters and seals and, compatibility with glovebox handling operations. Figure 1 showcases the AFIC design, which is protected under patent number WO 2018/009782 A1 [6]. The AFIC was designed for repeated operation without component fatigue beyond typical wear and tear but importantly, the modular design allows for frequent examination and replacement of components without significant cost. Prior to each HIP cycle, the canister is placed in the AFIC and sealed within a controlled laboratory environment before placing into the HIP pressure vessel for processing.

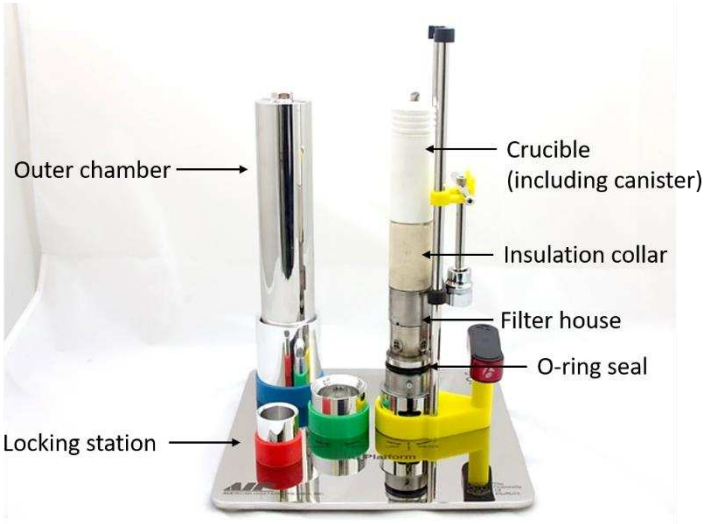

Figure 1. Active furnace isolation chamber (AFIC) components

3.3. HIP process conditions

Hot isostatic pressing was undertaken using an AIP-630H research HIP facility at The University of Sheffield, using argon gas as the pressurizing media. The HIP cycle data are shown in Figure 2 for the magnesium borosilicate glasses, MBS-U high and MBS-U low. The canisters were processed in consecutive stages to protect the welds and control canister deformation to minimise the risk of weld failure. After purging the pressure vessel with argon, the temperature and pressure were ramped to 400 °C and 15 MPa at 5 °C min^{-1} and held for 30 min, followed by a second ramp to 700 °C and 25 MPa

at 5 °C min^{-1} and held for 15 min, the final ramp was to 1250 °C and 70 MPa at 7.5 °C min^{-1} and held for 2 hours. The cooling rate was 10 °C min^{-1} and the depressurization rate was -0.6 MPa min^{-1}.

In Figure 2b, it is evident there was an issue maintaining pressure for the MBS-U low wasteform (pressure target was 100 MPa). This was the result of failed compressor packing, which was replaced prior to processing the MBS-U high wasteform, where a controlled pressure ramp and dwell process was achieved. The average pressure during the dwell for the affected wasteform was 77.3 MPa, as such, the target pressure was reduced to 70 MPa for all remaining wasteforms in the work package. Typically, HIP research undertaken at the University of Sheffield targets 100 MPa but the HIP compressor issue limited the maximum controllable pressure to 70 MPa. The difference in pressure is not expected to affect the phase assemblage, which is driven by the temperature and was maintained at target throughout all HIP runs.

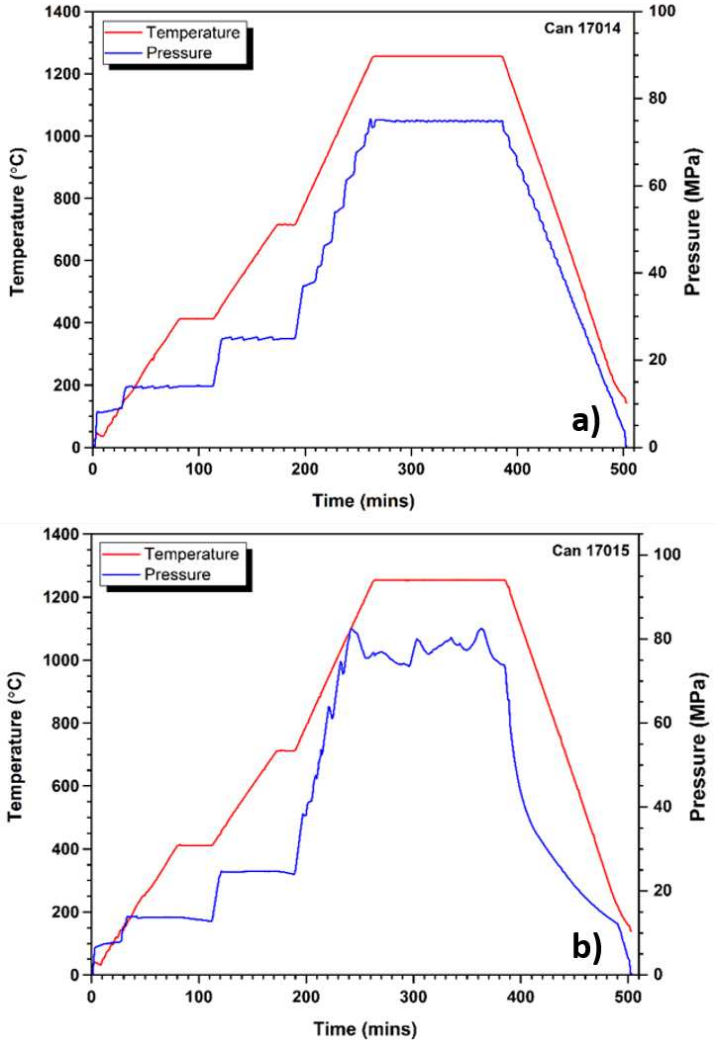

Figure 2. Active HIP process data for canisters 17014 (MBS-U high) and 17015 (MBS-U low)

3.4. Post-HIP observation

The typical appearance of the canisters before and after HIP processing is shown in Figure 3. All canisters in this study were successfully HIPed, this was denoted by the flattened evacuation tube and reduced diameter of the central body and, the canisters remained hermetically sealed (no weld failure). Each canister was sectioned to generate a central slice of the HIPed wasteform (Fig. 3c-d) for characterisation. The sliced sections reveal that both wasteforms formed heterogeneous dense glass/ceramics, with little visible porosity. For MBS-U high (Fig. 3c), the wasteform was largely

red/brown in colour with bright white particles distributed throughout, whilst the MBS-U low (Fig. 3d) bulk wasteform was grey in colour with dark grey and bright white particles visible.

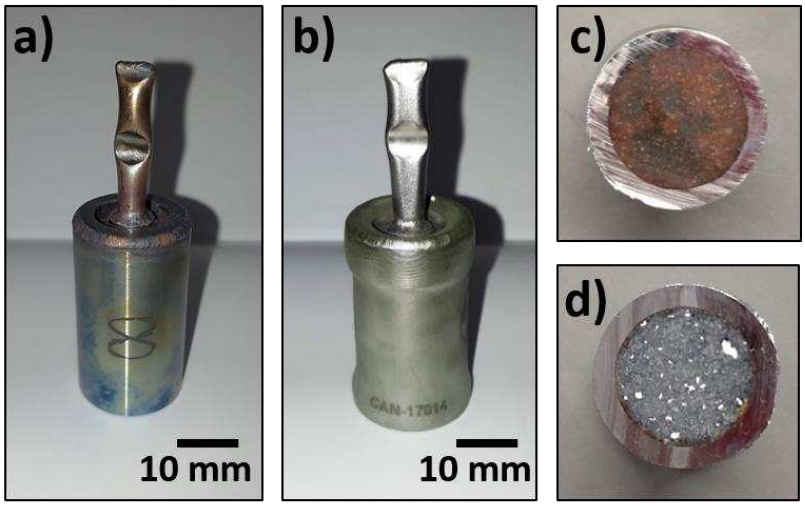

Figure 3. Photographs of a HIP canister a) pre-HIP and b) post-HIP and photographs of sectioned HIPed canisters c) MBS-U high and, d) MBS-U low.

3.5. Wasteform characterisation

The phase assemblage for MBS-U high and MBS-U low are reported in Figure 4. For the former, the reflections present were indicative of uranium oxide (likely UO_{2+x}), implying U_3O_8 was reduced by Mg metal during the HIP process. In addition to UO_{2+x}, reflections were assigned to quartz (precursor) and suanite, which is a magnesium borate mineral, $Mg_2B_2O_7$. The lack of intense MgO reflections suggests that both added $Mg(OH)_2$ and Mg metal have reacted, and the targeted magnesium borosilicate glass was formed, with some Mg bound in the suanite phase. For MBS-U low, the phase assemblage was similar, with reflections assigned to UO_{2+x}, quartz and suanite. However, reflections associated with U_3O_8 were also present, indicative of an incomplete uranium reduction compared to MBS-U high. Further data collection is underway to identify the exact uranium oxidation states present in both wasteforms.

The micrographs in Figure 5 highlight the heterogeneous nature of these wasteforms. The large grey particles represent unreacted quartz. This indicates that a more reactive source of silica (e.g. using a simple glass frit) might be more suitable to ensure that the full SiO_2 content was available for glass formation. The bulk matrix is rich in Mg and represents the magnesium based glass and suanite (Fig. 5; Mg). The bright white particles with a varied particle size refer to the UO_{2+x}/U_3O_8 identified by XRD (Fig. 4). Uranium does not appear to have reacted with the MBS components, even in the MBS-U high sample (Fig. 5a) where the uranium loading was high (42.22 wt.%; Table 1). It is postulated that the unreacted quartz resulted in a lower overall vitreous content and minimal uranium incorporation into the glass network. There was no evidence of Mg metal in the processed wasteforms by XRD or SEM/EDX analysis, signifying that the metal was successfully thermally passivated by HIPing. For reactive metal encapsulated in cementitious wasteforms, the volume expansion on oxidation (i.e. Mg to $Mg(OH)_2$), with concomitant H_2 production, could lead to the formation of stress-induced cracking [7]. This oxidation process was completed during HIP processing and the reaction product incorporated into the bulk glass matrix, avoiding any expansion issues.

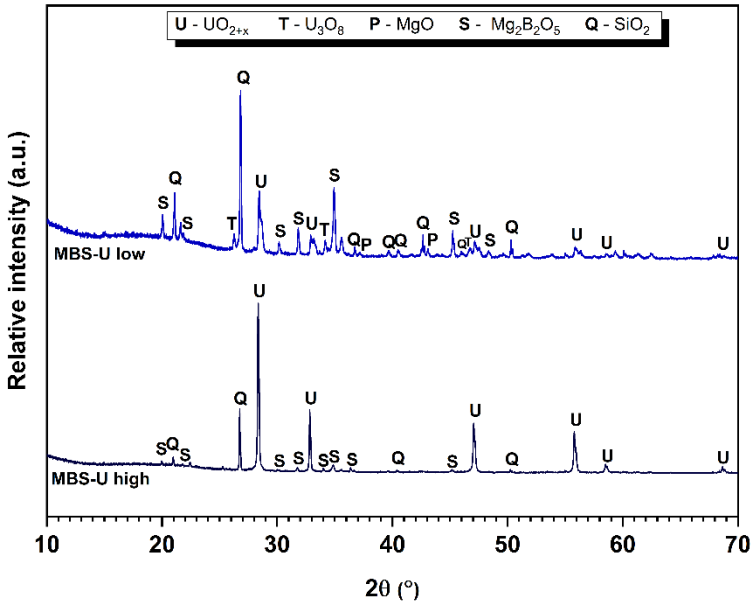

Figure 4. XRD patterns of wasteforms MBS-U high and MBS-U low

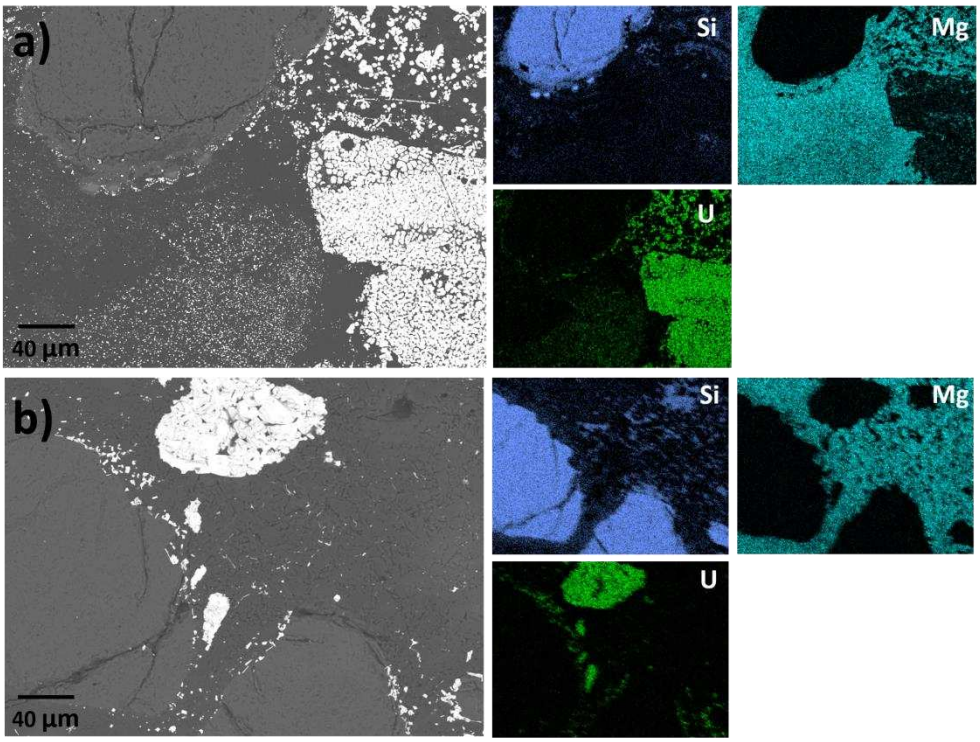

Figure 5. SEM/EDX of wasteforms a) MBS-U high and b) MBS-U low

4. Conclusions

Conceptual wasteforms were prepared and HIPed at The University of Sheffield using radioactive (U_3O_8) waste surrogates for magnesium-rich UK intermediate level wastes. The wasteforms were processed at 1250 °C, ≥ 70 MPa with a 2-hour dwell; all HIPed products exhibited volume reduction and remained hermetically sealed within the stainless steel canister. The processed wasteform was

observed to form dense, monolithic glass/ceramics with little visible porosity and good mechanical strength (no fractures formed during sectioning). The magnesium waste ($Mg(OH)_2$, Mg) was fully converted and immobilised in the bulk wasteform, however, U_3O_8 remained undigested (i.e. encapsulated) throughout the encapsulating glass matrix. The wasteform chemistries were not fully optimized during this study but further investigation could improve actinide waste incorporation. HIPing with radioactive waste simulants was successfully demonstrated using the active furnace isolation chamber (AFIC), which permitted the passively safe handling and processing of uranium wasteforms. The experience gained was invaluable to The University of Sheffield and collaborators, leading to greater confidence in the AFIC operational behaviour and contributing towards a technical safety case of hot isostatic pressing as a viable thermal treatment method of nuclear wastes.

5. References

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